DocCode - SCORE

SCORE Placeholder Sheet for IFW Content

Application Number: 18066105 Document Date: 12/14/2022

The presence of this form in the IFW record indicates that the following document type was received in electronic format on the date identified above. This content is stored in the SCORE database.

Since this was an electronic submission, there is no physical artifact folder, no artifact folder is recorded in PALM, and no paper documents or physical media exist. The TIFF images in the IFW record were created from the original documents that are stored in SCORE.

- Drawing

At the time of document entry (noted above):

- USPTO employees may access SCORE content via DAV or via the SCORE web page.
- External customers may access SCORE content via PAIR using the Supplemental Content tab.

Form Revision Date: March 1, 2019

Momentive EX1002
U.S. Patent No. 12,337,057

Title: Bio-Based and Biodegradable Elastomer for Cosmetic and Personal Care

Cross-Reference to Related Applications:

This application is a divisional of U.S. Application No. 16/992,831 filed on August 13, 2020, which claims the benefit of priority from U.S. Provisional Patent Application Serial No. 62/893,968 filed August 30, 2019 and U.S. Provisional Patent Application Serial No. 62/976,015 filed February 13, 2020, the contents of each of which are incorporated herein by reference.

Field of the Invention

This invention includes compositions and processing/method for preparing polyester and polyurethane type feedstocks for use in cosmetics. The compositions include elastomer systems based on greater than 85% or higher renewable, bio-based feedstocks, which are inherently biodegradable. The compositions can be incorporated into gels and are capable of forming stable mixtures in medium chain esters and less polar hydrocarbons.

Background

Silicone elastomers are a broad class of three dimensional cross-linked dimethicone polymers that form three-dimensional polymeric structures and provide a beneficial texture and appearance to cosmetics. They are generally formulated into products to enhance consumer appeal by yielding a preferred sensory aesthetic profile, while functioning as that of a line filler or soft focus particle. Additionally, they can act as sebum absorbers to reduce excess oil on the surface of the skin and act as mattifying agents, which is defined as making the skin less shiny. Further, these cross-linked dimethicone polymers are capable of delivering actives by acting as controlled release polymers and can also reduce the oily texture of high oil content formulas. Silicone elastomers may be co-formulated with common ingredients such as sun protection actives and pigments in order to provide elegant daily wear for skincare and cosmetics. Silicone elastomers are quite safe ingredients but suffer from the perception of being synthetic in origin and not being readily biodegradable, even though they are degradable in the environment.

Polyesters can be synthetic or naturally derived and can vary from rigid thermoplastic solids to low-viscosity oils. From Spiratex literature, Thermoplastic Polyester Elastomers, or TPE, combine the properties of high-performance elastomers and flexible polymers. Sometimes referred to as thermoplastic rubbers, these are high strength materials known for their ability to take repeated flex cycles and their resistance to many chemicals and oils. An important parameter in the

characterization of elastomers is measurement of hardness and resilience There are different methods of measuring hardness or stiffness and resilience, i.e. Durometer Hardness as described by ASTM D-2240. The test method describes twelve types of rubber hardness measurement devices known as durometers: Types A, B, C, D, DO, E, M, O, OO, OOO, OOO-S, and R. It is necessary to be within proper scale and adapt based on the behavior of the material. While elastomeric polymers have varying hardness, it was found that the hardness of the present invention was consistent to gel-like materials. The ASTM D2240 is an empirical test method and has been modified and adapted as it is a commonly used procedure for evaluating soft gels, i.e. biopolymer gelatins composed of polypeptides. Briefly, the method uses a texture analyzer to evaluate both hardness and elasticity (resilience) of the present invention and is based on the compression and decompression force profiles of an indenter into a specified depth into the present invention.

Silicone elastomers as generally used in cosmetics are micronized particles (from about 1 -100 microns) of silicone rubber, dispersed and semi-swollen into a carrier phase like isododecane, cyclomethicone or light silicone oils. Silicone elastomers for cosmetics require extensive milling and diluting into a carrier phase to obtain the correct balance of cosmetically acceptable properties. In this highly processed form, when the refractive index is matched between the silicone elastomer and the carrier phase, the final mixture can give the appearance of a gelled homogenous system, only further revealing the presence of the elastomer in sensorial testing. For instance, if the carrier phase is volatile, the act of spreading the silicone elastomer mixture on the skin results in the carrier phase vaporizing and leaving a micronized “ball bearing” particle of elastomer on the skin that exhibits a desirable texture and provides a mattifying property for sebum absorption on the skin. The state of the art of silicone elastomer dispersions as used in cosmetics includes almost all premium leave-on skin care product forms that yield a texture and function exceedingly well regarded by formulators and consumers alike.

While performance of dispersed silicone elastomers is unparalleled, there is a demand for alternatives to silicone elastomers since silicones, in part, come from non-renewable feedstocks of petroleum origin. Therefore, a primary goal is to create a high performing dispersed elastomer based primarily on feedstocks of renewable bio-sourced origins. Secondly, while they can be chemically degraded in the environment over time, silicones are not inherently biodegradable by microbial action. Therefore, a second criteria is an inherently biodegradable elastomer dispersion. Thirdly, the inherent nature of silicone elastomers exhibits functional compatibility with branched

chain hydrocarbons like isododecane and good compatibility with silicone fluids. They are therefore medium polar, semi-hydrophobic in nature and as a consequence will phase separate from more polar esters without the addition of other compatibilizing ingredients or emulsifiers. Therefore, an additional goal is to create a dispersed gelling or thickening high performing elastomer that meets the first two criteria but also providing compatibility with more polar cosmetic ingredients, such as esters and medium chain triglycerides (MCT), in order to formulate with ingredients not directly attainable with silicone elastomers. Fourth, the alternative to silicone gel should have comparable sensory aesthetic profiles.

Options for alternatives to petroleum-based polymers are of increasing importance for application in the personal care industry. Bio-based and biodegradable elastomeric polymers are an essential class of materials for the enhancement of textural attributes in cosmetic compositions. Elastomeric polymers swollen and dispersed in various cosmetic fluids may provide new formulation opportunities that are not achieved with current elastomeric polymers, i.e. hydrogels, silicone gels, oil-based thickeners, etc. Consequently, there is a need to develop new elastomeric polymers with enhanced textural attributes similar to those of silicone gels, hydrogels, oil-based thickeners, etc. The bio-based and biodegradable gel presented in this invention has good compatibility with cosmetic and natural oils and can be used as a gelling agent for these oils.

Prior art related to the leave on cosmetic industry includes numerous classes of polyesters and polyurethanes performing a variety of functions. Thousands of polyesters and polyurethanes are listed for commerce in the COSING (EU public cosmetic ingredients database). Many of these ingredients are common fully synthetically manufactured film forming polymers that act as hair sprays or binders when combined with other solvents, including water. Often these are dispersed as lattices or dispersions in water, often made from prepolymers that are crosslinked with di- or tri-amino chain extenders to form carbamates. Amine-based building blocks are not desirable for cosmetic raw material development due to the prevalence of high odor profiles and the common phenomenon of yellowing the final product formulation. Another class of urethanes are sold as solid, predominantly non-swellable micronized powders based on synthetic feedstocks from petroleum sources. For example, Grant Industries sells Granpowder USQ, a product containing 30-40% of a micronized non-swellable urethane powder with the INCI name HDI/Trimethylol Hexyllactone Crosspolymer. While exhibiting excellent tactile and soft focus (optical) properties, it does not have elastic properties analogous to silicone elastomers. It is a free-flowing powder with little to no elastic properties when dispersed in medium polar carrier fluids like MCTs.

Summary of the Invention

In view of the foregoing, the invention includes a bio-based and biodegradable swellable, elastic non-ionic, non-aqueous material using a polyester linked between a multifunctional, e.g. a tri-functional, polyurethane crosslinker in a natural origin reaction solvent, which is also referred to herein as a cosmetic emollient, using a urethanation catalyst such as a bismuth catalyst. The preferred catalysts are generally considered to be those which are non-toxic / safe alternatives to amine-based, organo-mercury or organo-tin based urethane catalysts. This solvent class can include MCT.

The invention also includes a process for preparing a gel. The process includes a milling process of the MCT based rubber elastomer with simultaneous or subsequent diluting with a solvent, which can be the same or different from the reaction solvent. A volatile cosmetic alkane of renewable feedstock is preferred to achieve a desired sensory aesthetic profile.

In one aspect of the invention there are provided cross-linked polyurethane elastomer rubber compositions which include

(a) a cross-linked polyurethane elastomer rubber;

(b) a cosmetic emollient; and

(c) a urethanation catalyst,

wherein the cosmetic emollient forms a solvent matrix which substantially surrounds the cross-linked polyurethane elastomer rubber. For purposes of the present invention, “substantially surrounds” shall be understood to mean that the solvent matrix is in intimate contact on the surface of the rubber and covers a substantial portion of the rubber surface. The emollient may but does not always completely envelop the rubber.

In another aspect of the invention there are provided processes for preparing the cross-linked polyurethane elastomer rubber compositions described herein. The processes include reacting a polyisocyanate with a prepolymer having at least two free hydroxyl groups in the presence of a urethanation catalyst and a cosmetic emollient under conditions sufficient to form a cross-linked polyurethane rubber.

Further aspects of the invention include gel compositions which contain a mixture of a cross-linked polyurethane elastomer rubber composition as described herein, in a milled form and at least one cosmetic emollient as well as methods of making the gel compositions. The said gel composition is a rubber dispersion, refined via one or more milling and diluting steps whereby each step yields a targeted equilibrium particle size range leading to a final product in the 1 to 100 micron range, preferable 1 to 60 microns. Still further aspects of the invention include cosmetics, emulsions, lotions, creams, etc., and products which contain the inventive compositions and gels.

As a result of the invention, there is provided a silicone alternative elastomeric gel of at least 85 or even >98% bio-based material. This bio-based elastomer was submitted to testing that resulted in achieving "Ultimate Biodegradable / Inherent Biodegradable" and is unknown in the prior art in relation to the body of performance attributes otherwise achieved. The main invention is an elastomer that is not silicone-based but approaches the high value texture previously only achievable via silicone chemistry. The invention disclosed is trademarked as Gransense™ and will be commercially available as a cosmetic material from Grant Industries (Elmwood Park, New Jersey, USA).

Brief Description of the Drawing

Figure 1 is biodegradation graph corresponding to Example 21.

Detailed Description of the Invention

In one aspect, the present invention relates to a polyurethane elastomeric rubber composition which comprises a bio-based polyol cross-linked with a bio-based isocyanate using a urethanation catalyst such as a bismuth catalyst in the presence of a cosmetic emollient. Isocyanates are compounds containing the isocyanate group (-NCO). They react with compounds containing alcohol (hydroxyl) groups to produce polyurethane polymers. The cross-linked polyurethane elastomer rubber is in further aspect of the invention included in a gel after being milled in the presence of a bio-based emollient or mixture of bio-based emollients. The polyurethane elastomeric gel has good compatibility with cosmetic and natural oils and can be used as a gelling agent for these oils among other desirable cosmetic formulary roles. The increased polarity of the polyurethane elastomer gel versus silicone elastomer counterparts allows for its incorporation into

increasingly polar formulation media in which silicone elastomers would otherwise not be compatible.

The cross-linked polyurethane elastomer rubber compositions of the invention preferably are those in which the prepolymer, the polyisocyanate, and the cosmetic emollient are bio-based and biodegradable. In some preferred aspects of the invention, the cross-linked polyurethane elastomer rubber composition is comprised of greater than about 85%, preferably greater than about 95% and in some alternative embodiments, greater than about 99% renewable, bio-based feedstocks or, stated alternatively, plant-derived (non-petroleum based) feedstocks. In an alternative embodiment, the rubber composition can be made using a polyester pre-polymer which is derived from entirely synthetic or petroleum-based feedstocks rather than bio-based feedstocks. Similarly, the emollient or mixture of emollients and/or the isocyanate can, in alternative embodiments, be derived from synthetic or petroleum based feedstocks rather than bio-based feedstocks.

Through a milling and dilution process, the polyurethane rubber composition is converted into an elastomeric gel that provides a smooth, non-tacky, non-oily, moisturizing skin-feel with enhanced playtime on the skin. The elastomeric gel of this invention is an elegant addition to the cosmetic formulator's toolbox for creating stable cosmetic formulas with improved compatibility toward more polar cosmetic emollients, actives, and additives that are commonly incorporated into the oil phase of oil-based cosmetics.

In this invention, a generalized process for preparing the polyurethane rubber composition and its subsequent conversion to a polyurethane elastomeric gel follows these steps:

First, a bio-based prepolymer is reacted with a bio-based isocyanate using a urethanation catalyst such as a bismuth catalyst at a suitable, controlled temperature, e.g. from about 20° C to about 100° C in a reaction medium of bio-based emollient or a mixture of bio-based emollients which act as solvent(s) to form an elastomeric polyurethane rubber composition. Alternatively, the process can include forming the rubber composition without stirring at room temperature over about 24 hours.

As a result of the reaction conditions, the emollient forms a solvent matrix which substantially surrounds and/or swells the polyurethane rubber.

Second, the formed rubber is converted to a dispersion via high shear milling whereby an optional additional charge of the same or different bio-based emollient is added to the rubber composition before or after milling. The mixture is preferably milled into a polyurethane gel concentrate, using a suitable device known to those of ordinary skill, for example, a high-shear disperser mixer. The milling preferably reduces the particle size of the rubber composition to preferably less than about 100 microns, and more preferably to a range of from about 1 to about 60 microns in cross-sectional diameter.

Third, the elastomer concentrate is finished to a cosmetically appropriate viscosity by further dilution with a secondary solvent which can be a bio-based emollient having either volatile or non-volatile properties depending on the targeted application and desired skin-feel properties of the finished elastomer gel. Thus, the gels may include a bio-based emollient or mixture of emollients which enhances aesthetic skin feel and/or enhance cosmetic formulation compatibility.

In some aspects, the rubber composition is comprised of a pre-polymer, in amounts of from about 5 to about 25 weight percent. The pre-polymer contains at least 2 hydroxyl groups. The preferably bio-based isocyanate can be present in amounts of from about 1 to about 20 weight percent and optionally the isocyanate contains from about 15 to about 38% or, alternatively, from about 15 to about 28% -NCO group. The overall molar ratio of -NCO of the isocyanate to -OH of the polyol can be from about 2:1 to about 1:2. The polyol can optionally have a hydroxyl value between 50-200, or alternatively 90-200 mg KOH/g.

The rubber composition also can include from about 0.1 to about 2.5 weight percent of the catalyst.

Other preferred aspects of the inventive rubber include that it has a hardness force greater than 200 g or, alternatively greater than 500 g, and less than 4000 g as measured by a texture analyzer prior to any milling or dilution and that it has a resilience greater than or equal to 70%, or alternatively 90%.

The rubber of the invention can in some aspects be classified as Ultimate Biodegradable / Inherent Biodegradable according to OECD 301-B and it can be made to contain as high as >97.0% Bio-based Carbon in accordance with ASTM D6866-18.

Formation of a millable elastomeric rubber than can be converted into a cosmetically elegant and stable gel requires consideration of several physical parameters inherent to the rubber formation. The hardness of the polyurethane rubber is an important factor that determines if it can be readily processed into a gel. If the polyurethane rubber is too hard, the rubber granules will not swell properly or grind into a smooth gel upon processing with an emollient. On the other hand, if the polyurethane rubber is too soft it will not easily process into a gel due to stickiness and lack of swellable granules. Three important factors determine the hardness of the polyurethane rubber:

First, the ratio of polymer content to carrier fluid is essential to consider to synthesize an optimal polyurethane rubber. The total weight percent of biobased emollients should range between 70-95%, or alternatively between 70-90% in the polyurethane rubber. If too much carrier fluid is used, the density of the elastomeric network will be too low to maintain viscosity. If too little carrier fluid is used, the polymer content may be too dense to properly disperse when milled.

Second, the ratios of bio-based hydroxyl functionality of the bio-based pre-polymer to the NCO functionality of the polyisocyanate can be between 2:1 to 1:2, and preferably 1:1.

Third, the amount of catalyst used in the synthesis of the polyurethane rubber is another factor that determines its ability to be processed into a gel. If too much catalyst is used the rubber will over-cure and will be too hard for processing into a gel. If too little catalyst is used the rubber will not form. In practice, the amount of catalyst can be about 0.1-2.5% by weight.

The gel composition of the invention can have a viscosity ranging from about 15,000 to about 1,000,000 cP in many embodiments of the invention and from about 40,000 to about 1,000,000 cP in alternative embodiments. The gels are optionally those which can be classified as Ultimate Biodegradable/Inherent Biodegradable according to OECD 301-B and/or contain up to 97% Bio-based Carbon in accordance with ASTM D6866-18. Optionally, a finisher containing an alcohol or optionally an amine may be added to quench unreacted isocyanate groups to the compositions of the invention. The gels of the invention can be a non-Newtonian fluid or a thixotropic fluid. The gels of the invention can include an optional personal or healthcare active, such as without limitation a vitamin such as vitamin C, and Vitamin A, sunscreen, plant extract, and/or fragrance.

Definitions

Thixotropic Gel Properties

The preferred polyester and/or polyurethane linkages in the elastomeric gel allow for the ability for hydrogen bonding to form over time. This behavior of the gel allows for a thixotropic property. A thixotropic fluid displays non-Newtonian pseudoplastic behavioral change as a dependence on time. Under static conditions these types of gels (within the scope of this invention) will appear as a "pseudo-plastic" but will begin to flow and have a reduction in viscosity when a constant force (agitation, mixing, shaking, shear) is applied. When there is no force applied and after a period of time the gel will recover to its initial steady state. Common examples of thixotropic fluids are yogurt and polyvinyl alcohol adhesive glue gel. There are many formulation advantages when incorporating a thixotropic gel into a formula compared to conventional oils, waxes, rubbers, or powders. Examples include but are not limited to maintaining film thickness upon application and improving spreadability of the cosmetic product during application and usage to impart a soft and elegant feel.

Thixotropic gels offer many advantages for formulators, such behaving as a suspending and thickening agent in sprays as well as memory type applications in both skin care and personal care. Additionally, thixotropic materials are considered process aids, and can offer enhanced stability, and controlled spreadability of the personal care product. Compared to silicone elastomers the shear thinning behavior may enhance the ease of mixing when incorporating other ingredients into the formula. The reduced viscosity would require less strain on mixing and shear dispersing processing equipment and a more rapid incorporation of personal care actives, thereby leading to a reduction in cost and timesaving in production. Another benefit of the thixotropic gel is to stabilize the formula and minimize phase separation and potentially stabilize particle suspensions, i.e. pigments.

Ultimate Biodegradability - The level of degradation achieved when the test compound is totally utilized by microorganisms resulting in the production of carbon dioxide, water, and mineral salts, and new microbial cellular constituents (biomass).

Inherent Biodegradability - A classification of chemicals for which there is unequivocal evidence of biodegradation (primary or ultimate) in any test of biodegradability.

Elastic - able to encompass variety and change; flexible and adaptable.

Elastomer – a natural or synthetic polymer / macromolecular material having elastic properties which can return to shape when distorted by physical stress, e.g. rubber.

Polymer - a substance that has a molecular structure consisting chiefly or entirely of a large number of similar units bonded together, e.g., many synthetic organic materials used as plastics and resins; Proteins have polypeptide molecules, which are natural polymers made from various amino acid monomer units. Nucleic acids are huge natural polymers made up of millions of nucleotide units.

Appropriate polymers and prepolymers include but are not limited to:

Azelate Polyols
Butanediol/adipic acid copolymer
Butanediol/azelaic acid copolymer
Butanediol/sebacic acid copolymer
Capryloyl Glycerin/sebacic acid copolymer
Capryloyl glycerin/sebacic acid copolymer
Capryloyl Glycerin/Sebacic Acid Copolymer
Castor oil derived Polyhydroxystearic acid
Cellulose
Collagen
Diheptyl succinate (and) capryloyl glycerin/sebacic acid copolymer
Dilinoleic acid/propanediol copolymer
Dimer acid diol
Lecithin
Poly(polyol sebacate)
Polybutylene succinate
Polybutylene succinate
Polycaprolactone
Polyester
Polyethylene Glycol
Polyglycerol
Polyglycolides
Polyhydroxyalkanoates
Polyhydroxybutyrates
Polylactic acid and Polylactides
Polylactide-co-glycolides
Polysaccharides
Propanediol/adipic acid copolymer

Propanediol/azelaic acid copolymer
Propanediol/sebacic acid copolymer
Propylene glycol/adipic acid copolymer
Propylene glycol/azelaic acid copolymer
Propylene glycol/sebacic acid copolymer
Pullulan
Starch
Trimethylpentanediol/adipic acid copolymer,
and mixtures thereof.

The preferred polyol for the synthesis of the elastomeric rubber is a diol- or polyol-functionalized polyester with an effective molecular weight between 280-3000 g/mol and alternatively between 500 -3,000 g/mol. The polyol should have an acid value <2 (mg KOH/g), a hydroxyl value between 50-200 or 90-200 (mg KOH/g), and water content <0.1 (K.F., w/w%).- A preferred prepolymer is dilinoleic acid/propanediol copolymer is derived from 100% bio-based sources and has good compatibility with cosmetic oils. Preferably the copolymer should be terminated in hydroxyl groups and have a low acid value, as hydroxyl groups react more readily with isocyanates than carboxylic acids. Castor oil can also be used as polyol for the synthesis of polyurethane rubbers because it naturally contains multiple hydroxyl groups. In addition, there are many polyols available that can be used in the synthesis of polyurethane elastomer gels.

Appropriate polyols include but are not limited to:
1,2-ethanediol
1,2-propanediol
1,3-propanediol
caprylyl glycol
castor oil
corn oil
diethylene glycol
ethylene glycol
ethylene oxide
glycerol
heptanediols
Hexanediols
hydrogenated or epoxidized vegetable oil
Isomeric butanediols
isosorbide
linseed oil
olive oil
other hydroxy containing compounds
pentaerythritol

Pentanediols
polytetramethylene ether glycol
propylene glycol
propylene oxide
silanol
sugar alcohols
Triethylene glycolether gylcol,
and mixtures thereof.

Appropriate Carboxylic Acids include but are not limited to
Azelaic acid
Citric acid
Dilinoleic acid
Dimer acid
Itaconic Acid
Lactic acid
Polylactic acid
Sebacic acid
Trilinoleic acid,
and mixtures thereof.

The emollients used in the synthesis of the polyurethane rubber can be esters, ethers, alkanes, or mixtures thereof. The emollients used in the processing of this rubber into a gel can be esters, ethers, alkanes, or mixtures thereof. The emollients preferably have a viscosity between 1-65 at 20°C (mPas). The spreading value (mm^{2}/10 min) of the emollient is preferably between 500-2500.

Appropriate emollients or solvents include but are not limited to:
Butyl Lactate
Butylene glycol
C12-15 Alkyl Lactate
C12-C15 Alkyl benzoate
C13-C15 alkanes
C16-18 alkanes
C18-C22 alkanes
Caprylic/Capric Triglyceride
Caprylic/Capric/Succinic
Triglyceride
Caprylyl-Caprylate/Caprate
Castor oil
Cetyl Ethylhexanoate
Coco-Caprylate/Caprate
Cocoglycerides
Decyl oleate
Dibutyl adipate

Dicaprylyl Carbonate
Dicaprylyl Ether
Diheptyl Succinate
Dodecane
Ethyl lactate
Ethylhexyl Isononanoate
Glycerin
Glyceryl trihexanoate
Glyceryl triheptanoate
Glyceryl trioctanoate.
Hemisqualane
Heptyl Undecylenate
Isododecane
Isononyl Isononanoate
Isopropyl Myristate
Isopropyl palmitate
Jojoba oil
Mirystyl Myristate
Neopentyl Glycol Diheptanoate
Octyl palmitate
Oleyl Eurcate
Olive squalane
Polybutene
Propylene carbonate
Propylene glycol
Propylene glycol
dicaprylate/dicaprate
Shea butter ethyl esters
Squalane
Tridecane
Triethylhexanoin
Triheptanoin
Undecane,
and mixtures thereof.

A 1,5-pentamethylene diisocyanate trimer was used as the preferred isocyanate for the synthesis of the polyurethane elastomer. This isocyanate, derived from bio-based feedstocks, readily reacts with polyols in the presence of a polyurethane catalyst and emollient to form polyurethane rubbers. In addition, a plethora of di-functional isocyanates are available that are widely utilized in industry.

Appropriate functionalized isocyanates include but are not limited to:

1,1'-Methylenebis(4-isocyanatocyclohexane)

1,3,3-Trimethyl-1-(isocyanatomethyl)-5-isocyanatocyclohexane

1,3,5-Triazine-2,4,6(1H,3H,5H)-trione, 1,3,5-tris[(5-isocyanato- 1,3,3-trimethylcyclohexyl)methyl]

1,3-Bis(isocyanatomethyl)cyclohexane

1,3-Diazetidine-2,4-dione, 1,3-bis[4-[(2-isocyanatophenyl)methyl]phenyl]

1,3-Diazetidine-2,4-dione, 1,3-bis[4-[(4-isocyanatophenyl)methyl]phenyl]

1,3-Phenylene diisocyanate

1,3-Propanediol, 2-ethyl-2-(hydroxymethyl)-, reaction products 5-isocyanato-1-(isocyanatomethyl)- 1,3,3-trimethylcyclohexane

1,4-Phenylene diisocyanate

1,5-Diisocyanato-2-methylpentane

1,5-Pentamethylene diisocyanate

1,5-Pentamethylene diisocyanate dimer

1,5-Pentamethylene diisocyanate trimer

1,6-Hexamethylene diisocyanate

1,8-Diisocyanato-2,4-dimethyloctane

2,2,4-Trimethylhexane 1,6-diisocyanate

2,2'-Diisocyanatodiphenylmethane

2,4,4-Trimethylhexane 1,6-diisocyanate

2,4,6-triisopropyl-m-phenylene diisocyanate

2,4'-Methylenediphenyl diisocyanate

2,4-Toluene diisocyanate

2,4-Toluene diisocyanate trimer

2,4-Toluenediisocyanate dimer

2,5(6)-Bis(isocyanatomethyl)bicyclo[2.2.1]heptane

2,6-Toluene diisocyanate

3,3'-Dimethoxy-4,4'-biphenylene diisocyanate

3,3'-Dimethyl-4,4'-biphenylene isocyanate

4,4',4''-Triisocyanatotriphenylmethane

4,4-MDI uretidinone

4,4'-Methylenediphenyl diisocyanate

80% 2,4-TDI; 20% 2,6-TDI, blend of isomers

Benzene, 1-[(2,4-diisocyanatophenyl)methyl]- 3-isocyanato-2-methyl

Bis(isocyanatomethyl)cyclohexane

Diphenyl oxide 4,4'-diisocyanate

Diphenylmethanediisocyanate

Hexamethylene diisocyanate biuret

Hexamethylene diisocyanate dimer

Hexamethylene diisocyanate isocyanurate

Methyl 2,6-diisocyanatohexanoate

Naphthalene, 1,5-diisocyanato

Octahydro-4,7-methano-1H-indenedimethyl diisocyanate
Polymethylenepolyphenyl polyisocyanate
Tris(4-isocyanatophenyl) thiophosphate,
and mixtures thereof.

Bismuth or zinc based polyurethane catalysts are preferred for the synthesis of the polyurethane rubber due to their relatively low-toxicity. However, organometallic and amine based polyurethane catalysts can also be used. Bismuth based catalysts are preferred for cosmetic applications due to low toxicity relative to amine, mercury, or tin-based catalyst.

Possible urethanation catalysts include but not limited to:
Lead compounds
Mercury compounds (i.e. mercury salts, mercury hydroxide, mercury decanoate, bis(phenyl mercury) dodecenyl succinate), and
Stannous compounds (i.e. stannous octoate, stannous chloride).

Preferred urethanation catalysts with reduced toxicity relative to tin, mercury and lead include but are not limited to:
Acid Phosphate complex
Aluminum
Bis-(2-dimethylaminoethyl)-ether
Bismuth carboxylate
Bismuth esters
Bismuth Citrate
Bismuth alkanoates
Bismuth neodecanoate
Dimethylaminopropylamine
DABCO (1,4-diazabicyclo[2.2.2]octane and DABCO derivative
Metal complex
Mixed carboxylate
N-methylimidazole
N-methylmorpholine
Tertiary amines
Triethylamine
Zinc acetate
Zinc acetylacetonate
Zinc complex
Zinc esters and alkanoates
Zinc neodecanoate
Zinc neodecanoate

Zinc octoate
Zinc oxalate
Zirconium,
and mixtures thereof.

Cosmetic powders may be combined with the invented elastomer to enhance the performance of the gel by altering its texture, absorbency, formula stability, and soft-focus features desirable in finished cosmetic products. The powders may be used to provide structural support or behave as fillers or alter the final appearance of the gel to have a more “mattifying, soft focus” appearance. The powders can be used to provide a good slip and smoothness to the final formulation of the product, but not limited to, press powders, lotions, creams, hair gels, hair creams, mascaras, body creams, serums, lip care etc. The powders can also be used to modify the viscosity of the final formula due to its inherent nature to absorb a finite amount of liquid from the formula.

Appropriate powders include but are not limited to (synthetic and natural) and blends thereof:
Acrylate copolymer
Alumina
Aluminum Oxide
Aluminum Silicate
Boron Nitride
Butter coated powders (where the Butter can be, but are not limited to, Shea, Mango, Cocoa, Almond, where the powders are but not limited to, Mica, Talc, Aluminum, Cellulose, Polyhydroxyalkanoate)
Calcium Starch Octenylsuccinate
Cellulose
Cellulose Acetate
Dimethicone/Vinyl dimethicone crosspolymer
Glass beads
Kaolin Clay
Mica
Natural waxes (such as but not limited to, Carnauba Wax, Beeswax, Castor oil etc.)
Nylon
Polybutylene Succinate
Polyester
Polyethylene
Polyhydroxyalkanoate
Polylactic acid
Polymethylsilsequioxane
Polypropylene
Polytetrafluoroethylene

Polyurethane powder (such as the powder of a copolymer of hexamethylene diisocyanate and of trimethylol hexyl lactone)
Polyvinylalcohol
Polyvinylchrloride
Sericite
Silica
Starch
Synthetic waxes
Paraffin wax
Talc
Trimethoxysilicate
Zeolite
Zinc Stearate
Zinc oxide and
Titanium dioxide.

When processing the polyurethane elastomer rubber into a gel, a compatible emollient must be used in order for the newly forming polymeric microparticles to react. Triglycerides, esters, and ethers with high polarity can be used to swell the particles during the reaction and milling process. Preferable emollients include plant origin medium chain triglycerides (MCT) such as glyceryl trihexanoate, glyceryl triheptanoate, and glyceryl trioctanoate, or mixtures thereof. Once the elastomer rubber is processed into a concentrated gel, volatile emollients with a dry skin feel can be added to the gel until the desired viscosity is achieved. Triglycerides, esters, ethers, and alkanes can be used during this process.

The stability of polyurethane elastomer gel is dependent on the emollient or mixture of emollients used in the synthesis of the rubber and the processed gel. If the polarity of the emollient/s is too low, the gel may initially form but will separate over time. Generally, triglycerides, esters, ethers, and alkanes can be used in various combinations. Preferably a mixture of plant origin emollients such as medium chain triglycerides, C9-C12 alkanes, and esters derived from short-chain fatty acids and alcohols such as caprylate/caprate. In some aspects, the emollients can be considered secondary solvents and be selected from among for example, triheptanoin; undecane; tridecane. Alternatively, the secondary solvents are naturally derived alkanes or naturally derived esters.

The gel compositions can include a mixture of the cross-linked polyurethane elastomer compositions described herein, preferably in micronized form and a cosmetic emollient. For example, some gel compositions can include from about 5 to about 30 weight % or from about 5 to about 17 weight % of the micronized cross-linked polyurethane elastomer rubber composition.

The gel compositions can also include one or more cosmetically acceptable ingredients or emollients in amount from about 70 to about 95 weight % or from about 83 to about 95 weight %.

Examples

In the following examples, we describe a bio-based and biodegradable cross-linked polyurethane elastomer rubber and a bio-based and biodegradable cross-linked polyurethane elastomer gel. The elastomer rubber is processed into the elastomer gel which can be further processed for optimal performance as a cosmetic ingredient.

As outlined in the description of the invention, the formation of a polyurethane rubber involves the cross-linking of a bio-sourced pre-polymer containing at least two hydroxyl groups with a polyisocyanate in the presence of a catalyst and sufficient amounts of bio-based cosmetic emollients. The pre-polymer selected for the examples was a copolymer of C18-unsaturated fatty acid dimers and 1,3-propanediol (DAPD) with a hydroxyl value within the range of 60-80 mg KOH/g and a bio-based aliphatic polyisocyanate, pentylene diisocyanate trimer (PDT) containing around 20% NCO content. The bismuth catalyst was bismuth neodecanoate. The cosmetic emollient was a mixture of coco-caprylate/caprate and glyceryl triheptanoate.

Example 1: Synthesis of polyurethane rubber

To an 8 oz glass jar was added 11.25 g (12.5 wt%) DAPD polyol, 3.15 g (3.5 wt%) PDT, 18.81 g (20.9 wt%) of glyceryl triheptanoate and 56.34 g (62.6 wt%) of coco-caprylate/caprate. The mixture was stirred by a propeller mixer for 10 minutes and 0.45 g (0.5 wt%) of a bismuth catalyst was added. After stirring the mixture for an additional 5 minutes, stirring was stopped and the reactor was placed in an oil bath and heated to 60 °C. The mixture was heated until a cured rubber is formed whereupon the reactor is removed from heat. Typical gelling times range between 5 minutes and 2 hours.

Example 2: Synthesis of high-density polyurethane rubber

To an 8 oz glass jar was added 17.05 g (18.9 wt%) DAPD polyol, 4.77 g (5.3 wt%) PDT, 16.9 g (18.78 wt%) of glyceryl triheptanoate and 50.6 g (56.2 wt%) of coco-caprylate/caprate. The mixture was stirred by a propeller mixer for 10 minutes and 0.68 g (0.76 wt%) of a bismuth

neodecanoate was added. After stirring the mixture for an additional 5 minutes, stirring was stopped and the reactor was placed in an oil bath and heated to 60 °C. The mixture was heated until a cured rubber is formed whereupon the reactor is removed from heat. Typical gelling times range between 5 minutes and 2 hours.

Example 3: Synthesis of low-density polyurethane rubber

To an 8 oz glass jar was added 6.82 g (7.58 wt%) DAPD polyol, 1.91 g (2.12 wt%) PDT, 20.27g (22.5 wt%) of glyceryl triheptanoate and 60.73 g (67.5 wt%) of coco-caprylate/caprate. The mixture was stirred by a propeller mixer for 10 minutes and 0.27 g (0.3 wt%) of a bismuth neodecanoate. After stirring the mixture for an additional 5 minutes, stirring was stopped and the reactor was placed in an oil bath and heated to 60 °C. The mixture was heated until a cured rubber is formed whereupon the reactor is removed from heat. Typical gelling times range between 5 minutes and 2 hours.

Example 4: Synthesis of polyurethane rubber in glyceryl triheptanoate

To an 8 oz glass jar was added 11.25g (12.5 wt%) DAPD polyol, 3.15 g (3.5 wt%) PDT, and 75.15 g (83.5 wt%) of glyceryl triheptanoate. The mixture was stirred by a propeller mixer for 10 minutes and 0.45g (0.5 wt%) of bismuth neodecanoate was added. After stirring the mixture for an additional 5 minutes, stirring was stopped and the reactor was placed in an oil bath and heated to 60 °C. The mixture was heated until a cured rubber is formed whereupon the reactor is removed from heat. Typical gelling times range between 5 minutes and 2 hours.

Example 5: Synthesis of polyurethane rubber in coco-caprylate/caprate

To an 8 oz glass jar was added 11.25 g (12.5 wt%) DAPD polyol, 3.15g (3.5 wt%) PDT, and 75.15 g (83.5 wt%) of coco-caprylate/caprate. The mixture was stirred by a propeller mixer for 10 minutes and 0.45g (0.5 wt%) of bismuth neodecanoate catalyst was added. After stirring the mixture for an additional 5 minutes, stirring was stopped and the reactor was placed in an oil bath and heated to 60 °C. The mixture was heated for 24 hours during which time no elastomeric gel was formed.

Material	Example 1 Rubber		Example 2 Rubber		Example 3 Rubber		Example 4 Rubber		Example 5 Rubber	
	wt %	Mass	wt %	Mass	wt %	Mass	Wt %	Mass	Wt %	Mass
DAPD	12.5	11.25	18.94	17.05	7.58	6.82	12.5	11.25	12.5	11.25
PDT	3.5	3.15	5.3	4.77	2.12	1.91	3.5	3.15	3.5	3.15
Bismuth neodecano-ate	0.5	0.45	0.76	0.68	0.3	0.27	0.5	0.45	0.5	0.45
Coco-Caprylate/Caprate	20.9	18.81	18.78	16.9	22.52	20.27	0	0	83.5	75.1
Glyceryl Triheptanoate	62.6	56.34	56.22	50.6	67.48	60.73	83.5	75.15	0	0
Total	100	90	100	90	100	90	100	90	100	90
Appearance	Moderately firm, hazy rubber		Firm, hazy rubber		Soft, hazy rubber		Moderately firm, clear rubber		Clear solution, no gelation	
Texture Analyzer, Force, (Grams (g))	1269.8		3234.2		230.82		1176.9		No Rubber Formed	
Texture Analyzer, Force, (Newtons (N))	12.45		31.72		2.26		11.54		No Rubber Formed	
Resilience, %	96.4		95.3		82.3		96.3		No Rubber Formed	

Table 1. Experimental parameters and characterization data for the formation of rubbers described in Examples 1-5.

Example 6: Process for preparing an elastomer gel containing a volatile cosmetic emollient

A mixing vessel is charged with 100 g of Example 1 rubber and 11.1 g of glyceryl triheptanoate. The mixture is milled by applying high shear mixing to generate a viscous paste to generate a viscous paste containing generally sub-100 micron particles. The mixture is further diluted with 12.3 g of glyceryl triheptanoate to form a soft, concentrated pre-elastomer by high shear mixing which is then dispersed through a high shear mill to render the polyurethane particles to less than about 60 microns. The particle concentrate is further diluted with mixing by adding 18 g of C9-C12 alkanes (Vegelight 1214, Grant Industries, USA) to produce a smooth cosmetic elastomer with a slightly volatile texture profile and a viscosity of 102,440 cP (Brookfield DV-I+, Spindle TD, 1.5 RPM). This elastomer gel will be commercially available as a part of the Gransense™ product line from Grant Industries (Elmwood Park, NJ, USA).

Example 7. Process for preparing an elastomer gel containing a non-volatile cosmetic emollient

A mixing vessel is charged with 100 g of /Example 1 rubber and 11.1 g of glyceryl triheptanoate. The mixture is milled as described in the preceding example. The mixture is diluted with 12.3 g of glyceryl triheptanoate to form a soft, concentrated pre-elastomer by high shear mixing to reduce the polyurethane particles to less than about 60 microns. The particle concentrate is further diluted with mixing by adding 30g of glyceryl triheptanoate to produce a bouncy cosmetic elastomer with a moisturizing skin feel and a viscosity of 416,667 cP (Brookfield DV-I+, Spindle TE, 0.6 RPM). This elastomer gel will be commercially available as a part of the Gransense™ product line from Grant Industries (Elmwood Park, NJ, USA).

Example 8. Process for preparing a low-viscosity elastomer containing a non-volatile cosmetic emollient

A mixing vessel is charged with 100 g of /Example 1 rubber and 11.1 g of glyceryl triheptanoate. The mixture is milled as described in the preceding example. The mixture is diluted with 12.3 g of glyceryl triheptanoate to form a soft, concentrated pre-elastomer by high shear mixing to reduce the polyurethane particles to less than about 60 microns. The particle concentrate is further diluted with mixing by adding 58.4g of glyceryl triheptanoate to produce a pourable cosmetic elastomer with a moisturizing and velvety skin feel and a viscosity of 37,500 cP (Brookfield DV-I+, Spindle

TC, 3.0RPM). This elastomer gel will be commercially available as a part of the Gransense™ product line from Grant Industries (Elmwood Park, NJ, USA).

As outlined in the description of the invention, the formation of a polyurethane rubber is not limited to the components provided in Examples 1-5. For Example 9, the prepolymer was a copolymer of C18 unsaturated fatty acid dimers and bio-derived 1,4-butanediol (DABD) with a hydroxyl value within the range of 80-100 mg KOH/g. For Example 10, the cosmetic emollient was a mixture of isododecane and coco-caprylate/caprate. For Example 11, the selected pre-polymer was castor oil (CO). For Example 12, the catalyst selected was zinc neodecanoate. For Example 13, the polyisocyanate used was hexamethylene diisocyanate trimer (HDT). Rubbers were prepared from the reaction equivalents provided in Table 2 by following the protocol described for Examples 1-5.

		Example 9	**Example 10**	**Example 11**	**Example 12**	**Example 13**
Material		**wt %**	**wt%**	**wt%**	**wt%**	**wt%**
Pre-Polymer	**DAPD**	0	12.5	0	11.25	12.35
	DABD	11.88	0	0	0	0
	CO	0	0	10.8	0	0
Polyisocyanate	**PDT**	4.04	3.5	7	3.15	0
	HDT	0	0	0	0	3.6
Catalyst	**Bismuth Neodecanoate**	0.58	0.5	0.5	0	0.52
	Zinc Neodecanoate	0	0	0	1.8	0
Emollient	**Coco-Caprylate/Caprate**	62.62	41.75	0	61.48	62.63

	Glyceryl Triheptanoate	20.88	0	81.7	20.52	20.86
	Isododecane	0	41.75	0	0	0
Total		100	100	100	100	100
Appearance		Moderately firm hazy rubber	Soft hazy rubber	Firm clear rubber	Hazy soft rubber	Moderately firm hazy rubber
Texture Analyzer, Force, (Grams (g))		830.44	226.59	2993.06	300.81	926.33
Texture Analyzer, Force, (Newtons, (N))		8.14	2.22	29.35	2.95	9.08

Table 2. Experimental parameters and characterization data for the formation of rubbers described in Examples 9-13.

Example 14. Process for preparing an elastomer gel containing a personal care active

A mixing vessel equipped with side-sweep is charged with 90 g of Example 6 and stirred at 120 RPM. To this is added 20 g of finely milled ascorbic acid in portions over 1 hour. The mixture is stirred until homogenous to generate a viscous, opaque white paste.

Example 15. SPF-50 Sunscreen

To prepare an SPF-50 sunscreen, the ingredients in Phase A, including the elastomer from Example 6, were combined in the main kettle with homogenizer and mixed until uniform. Then Phase B was added to the main kettle while mixing with a side sweep agitator blade until uniform. The SPF was measured *in vitro* based on the usage recommendations for zinc oxide and titanium dioxide products from Grant Industries.

Phase	Ingredient Trade Name	Description (Manufacturer)	Weight %
A	Purolan IDD	Isododecane (Lanxess)	13.50
	Cetiol LC	Coco-caprylate/caprate (BASF)	2.00
	Bentone Gel ISD V	Isododecane & Disteardimonium Hectorite & Propylene carbonate (Elementis)	12.50
	Granpowder EDC-600	Divinyldimethicone/Dimethicone/phenylsilsesquioxane crosspolymer (Grant Industries)	4.00
	UV Cut TIO2-55-CG	Titanium dioxide & caprylic/capric triglyceride & stearic acid & alumina & polyhydroxystearic acid (Grant Industries)	20.00
	UV Cut ZNO-68-CG	Zinc oxide & caprylic/capric triglyceride & polyhydroxystearic acid (Grant Industries)	25.00
	Granresin PMSQ-ID	Polymethylsilsesquioxane & Isododecane (Grant Industries)	5.00
	EXAMPLE 6	Gransense™ Elastomer Gel	15.00
	Pelemol PHS-8	Polyhydroxystearic acid (Phoenix Chemical)	2.00
B	Aerosil 200	Silica (Evonik)	1.00
		Formula Total	100.00

Table 3. Formula for the preparation of an SPF-50 sunscreen containing the Gransense™ elastomer gel from Example 6.

Example 16. W/O Emulsion Cream

Incorporation of the elastomer from this invention allows for the stabilization of a W/O emulsion cream with a viscosity ranging between 5,000-50,000 cPs. The presence of the invented elastomer provided higher compatibility with the polar oil phase of this formula as well as the natural polyglyceryl-based emulsifier while achieving the desirable cushion/cloud-like feel that is usually only attainable with silicone elastomer formulations. There is a market demand for higher natural content in cosmetic formulas with formulators opting for naturally derived surfactants, emollients, and thickening aids. As demonstrated by this formulation, the elastomer of this invention provides broader formulating possibilities in the natural and bio-derived formulation landscapes and will also enable the development of products with desirable textural and performance profiles.

To prepare the W/O emulsion cream containing the Gransense™ elastomer from Example 6, first combine the Phase A ingredients from Table 4 in a vessel and mix with a homogenizer at room temperature until a uniform consistency is obtained. In a side vessel, combine the Phase B ingredients. Add the Phase B ingredients to Phase A while homogenizing and mix until uniform.

Phase	Ingredient Trade name	Description (Manufacturer)	Weight %
A	Cetiol LC	Coco-Caprylate/caprate (BASF)	12.40
	Naturesoft 800	Cellulose (Micropowders Inc)	2.00
	Zea Mays (Corn) Starch	Agenaflo 9050 (Agrana)	2.00
	EXAMPLE 6	Gransense™ Elastomer gel	15.00
	Gransurf PG-14	Polyglyceryl-6 polyricinoleate & polyglyceryl-10 dioleate (Grant Industries)	7.00
	Aerosil 200	Silica (Evonik)	0.20

B	Deionized Water		50.20
	Glycerin	Glycerin	5.00
	Butylene Glycol	Butylene Glycol	3.00
	Sodium Chloride	Sodium Chloride	0.70
	Nipaguard SCM	Methylisothiazolinone & propylene glycol & sorbitan caprylate	1.00
		Formula Total	100.00

Table 4. Formula for the preparation of a W/O emulsion cream containing the Gransense™ elastomer gel from Example 6.

Example 17. Cream-to-Powder Foundation

Incorporation of the elastomer from this invention allows for the stabilization of a W/O emulsion cream with a viscosity ranging between 500,000 – 1,000,000 cPs. Presence of the invented elastomer from Example 6 allowed the use and stabilization of Amino Acid treated inorganic pigments. Amino acid treated pigments are commonly used in color cosmetics however a high percentage and myriad combinations of difference emulsifiers and wetting agents are generally required for their stabilization. Combination of the invented elastomer gel from Example 6 with natural polyglyceryl and phospholipid-based emulsifiers in the presence of a polar oil phase allowed a stable W/O, while achieving known silicone elastomer cushion/cloud-like feel.

To prepare the cream-to-powder foundation containing the Gransense™ elastomer from Example 6, combine ingredients from Phase A listed in Table 5 in the main vessel and mix with a homogenizer until uniform. In a separate container, combine Phase B ingredients and micro-pulverize until the color is fully blended and uniform. Add Phase B to Phase A while homogenizing until uniform. In a side vessel, combine Phase C ingredients and mix with a homogenizer. Add Phase C to Phase AB while homogenizing until a uniform foundation cream is obtained.

Phase	Ingredient Trade Name	Description (Manufacturer)	Weight %
A	Cetiol LC	Coco-caprylate/caprate (BASF)	10.00
	Vegelight 1214	Coconut alkanes & coco-caprylate/caprate (Grant Industries)	1.00
	EXAMPLE 6	Gransense™ Elastomer Gel	15.00
	Gransurf PG-14	Polyglyceryl-6 polyricinoleate & polyglyceryl-10 dioleate (Grant Industries)	8.00
	Lecithin	Lecithin	1.50
B	NAI-TR-10	Titanium dioxide & disodium stearoyl glutamate & aluminum hydroxides (Miyoshi)	7.2
	NAID-Y-77492	Iron oxides (CI 77492) & disodium stearoyl glutamate & aluminum hydroxides (Miyoshi America)	2.10
	NAID-R-77491	Iron oxides (CI 77492) & disodium stearoyl glutamate & aluminum hydroxides (Miyoshi America)	0.47
	NAID-B-77499	Iron oxides (CI 77499) & disodium stearoyl glutamate & aluminum hydroxides (Miyoshi America)	0.19
	Sericite DNN	Mica (Ikeda)	6.00
	Silica	Silica	0.70
C	Deionized Water		34.87
	Bentone Hydroclay 2000	Hectorite (Elementis)	2.00

	Glycerin	Glycerin	5.00
	Butylene Glycol	Butylene Glycol	1.00
	Solagum AX	Acacia Senegal gum & xanthan gum (Seppic)	0.07
	Lexgard Natural	Glyceryl caprylate & glyceryl undecylenate (Inolex)	1.00
	Sodium chloride	Sodium chloride	0.70
		Formula total	100.00

Table 5. Formula for the preparation of a cream-to-powder foundation containing the Gransense™ elastomer gel from Example 6.

Example 18. Luminous Lipstick

The invented elastomer is ideal for lip-care applications due to its good compatibility with common cosmetic waxes and pigments. When added to a lip care formulation, the invented elastomer provides moisturization, cushiony feel, and improved compatibility between the varyingly polar and apolar ingredients.

To prepare a luminous lipstick containing the Gransense™ Elastomer from Example 6, the ingredients from Table 6 were weighed into the main kettle, which was equipped with a 3-prong blade. The vessel was heated to 90-95 °C and mixed until uniform. The lipstick is poured into a lipstick applicator package at 75-80 °C.

Phase	Ingredient Trade Name	Description (Manufacturer)	Weight %
A	Refined Candelilla Wax MD-21	Euphoria Cerifera (Candelilla) Wax (Ikeda)	13

	Carnauba Wax	Copernica Cerifera (Carnauba) Wax (Koster Keunen)	3
	NF Yellow Beeswax 423 G	Beeswax (Koster Keunen)	2
	Rita SAO	Prunus Amygdalus Dulcis (Sweet Almond) Oil (Rita Corporation)	18
	Eutanol G	Octyldodecanol (BASF)	5
	Coconut Oil	Cocos Nucifera (Coconut) oil (Jeen)	1.5
	EXAMPLE 6	Gransense™ Elastomer gel (Grant Industries)	15
	D&C Red No. 7, 40% in Castor Oil	Ricinus Communis Seed Oil & Red 7 (Miyoshi)	30
	TIO2, 50% in Castor Oil	Titanium dioxide (and) Castor Oil (Miyoshi)	8
	Aerosil 200	Silica (Evonik)	0.4
	Sucralose	Sucralose	0.1
	Covi-OX T-90 EU C	Tocopherol (BASF)	1
	Kester Wax K-60P	Polyhydroxystearic Acid (Koster Keunen)	3
		Formula Total	100

Table 6. Formula for the preparation of a luminous lipstick containing the Gransense™ elastomer gel from Example 6.

Example 19. Repairing Shampoo

To prepare a repairing shampoo containing the Gransense™ Elastomer from Example 8, the ingredients from Table 7 were weighed into the main kettle and homogenized. Phase B was sprinkled into Phase A with mixing. Phase C was weighed in a side kettle and heated to a proper temperature whereupon it was added to Phase AB and mixed for 10-15 minutes. Then Phase D was added and mixed for 5-10 minutes. To finish, Phase E was added and mixed into the formula.

Phase	Ingredient Trade Name	Description (Manufacturer)	Weight %
A	Deionized Water	Water	47.7
	Carbopol Aqua SF-1 Polymer	Acrylates Copolymer (Lubrizol)	5
B	Jaguar C-14S	Guar Hydroxypropyltrimonium Chloride (Solvay)	0.3
C	Iselux Ultra Mild	Water (and) Sodium Methyl Isethionate (and) Cocamidopropyl Betaine (and) Sodium Methyl Oleyl Taurate (and) Lauryl Glucoside (and) Coco-Glucoside (Innospec)	37
	Chembetaine C	Cocamidopropyl Betaine (Lubrizol)	2
	Jeemide HCA-RC3	Cocamide DEA (Jeen)	3
D	**EXAMPLE 8**	Gransense™ Elastomer Gel (Grant Industries)	2
	Euperlan PK 771	Glycol Distearate (and) Sodium Laureth Sulfate (and) Cocamide MEA (and) Laureth-10 (BASF)	3
E	Lexguard Natural	Glyceryl Caprylate (and) Glyceryl Undecylenate (Inolex)	1

	Orchidia Gras Ocean Waves Fragrance ORC1500049	Fragrance	0.5
		Formula Total	100

Table 7. Formula for the preparation of a repairing shampoo containing the Gransense™ elastomer gel from Example 8.

Example 20. Anhydrous Formulation

The invented elastomer gel can be used in anhydrous cosmetic and personal care formulations when advantageous. To prepare an anhydrous formula containing the Gransense™ elastomer gel from Example 6, the ingredients from Table 8 were combined together by mixing until homogenous. The anhydrous formulation described below can serve as a carrier for cosmetic active ingredients in other anhydrous formulations.

Phase	Ingredient Trade Name	Description (Manufacturer)	Weight %
A	**EXAMPLE 6**	Gransense ™ Elastomer gel	70.0
	Cetiol B	Dibutyl Adipate (BASF)	30.0
		Formula Total	100.0

Table 8. Formula for the preparation of an anhydrous formula containing the Gransense™ elastomer gel from Example 6.

Compatibility with common personal care ingredients

To demonstrate the unique compatibility of the polyurethane elastomer of this invention with common personal care ingredients and emollients, the elastomer from Example 6 was mixed with the selected personal care ingredients in ratios of 1:9, 1:1, and 9:1. When a solid or wax is used,

the elastomer and wax were heated to the melting point of the wax and then combined and allowed to cool. The mixtures are evaluated and ranked according to the keys in the footnote of the following table. A commercial silicone elastomer blend from Grant Industries was used as reference. The results are shown below. Compared to a conventional silicone elastomer gel, the polyurethane elastomer gel of this invention can be dispersed in cosmetic esters as well as common cosmetic waxes. Interestingly, the polyurethane elastomer gel is more compatible with sunscreen actives than the silicone elastomer.

Raw Material	Gransense™ Elastomer (Example 6)			Gransil DMCM-5		
	9:1	1:1	1:9	9:1	1:1	1:9
Dimethicone, 5 cst	I	I	OD	T	HD	C/T
Isododecane	I	I	OD	C	C	C
Ethylhexyl methoxycinnamate	T	HD	OD	I	I	OD
Castor Oil	HD	HD	HD	I	I	OD
C12-15 Alkyl Benzoate	T	OD	OD	I	OD	C
Coco-Caprylate/Caprate	HD	HD	HD	I	OD	C
Beeswax*	D*	C*	C*	I*	C*	C*
Carnauba Wax*	D*	D*	C*	I*	C*	I*
Avobenzone*	D*	D*	C*	I*	I*	I*

C= clear, T = translucent, HD = Hazy/Dispersible, OD= Opaque/Dispersible, I = Incompatible

= wax (heated to melting point then mixed), C = Compatible (homogenous), D* = dispersible (some crystallization), I*= incompatible (separation)

Table 9. Summary of compatibility results of various cosmetic raw materials with Gransense™ elastomer gel from Example 6 as compared to a common silicone elastomer.

Evaluation of Rubber Hardness

Elastomeric rubbers and the gelled compositions prepared from the rubbers can be characterized by their hardness or firmness. The Gelatin Manufacturers Institute of America employs equipment such as a "texture analyzer" (Model TA.XT Plus, Stable Micro Systems Inc., Godalming, England) to quantify the hardness or firmness of materials with similar properties to the compositions of rubbers and gels described in this invention. By using a texture analyzer, the surface of the rubbers and gels are subjected to compression by a probe with a 5.0 kg weight as the load cell, at a determined speed of 1.0 mm/s, and to a programmed depth of 10 mm into the rubber or gel, followed by retreat at the same speed. The resistance force detected by the probe of the Texture Analyzer during the compression of the gel or rubber defines the "hardness" as taught by Lin et al. (US 8,222,363 B2). The hardness value measured by the Texture Analyzer is recorded by Gram (g) force and can be converted to Newton (N) by dividing by 101.97.

In this invention, the hardness of the rubber, measured by the Texture Analyzer as the force in grams applied by the rubber when compressed, is a determining factor in the successful formation of elastomeric gels from the respective elastomeric rubber precursor. By varying the concentration of the polyurethane-forming components of rubber composition (i.e. pre-polymer and polyisocyanate moieties), rubbers of varying hardnesses were formed. Additionally, the identity of the cosmetic emollient chosen as a matrix had an effect on the rubber hardness. It was determined that suitably hard gels were formed when mixtures of the required components were combined to form a gel with a minimum hardness of 200.0 g, preferably 500.0 g, to maximally 4000 g, as determined by Texture analysis prior to milling or diluting the formed rubber When the rubber hardness was below 200.0 g, or above 4000 g hardness, a suitable elastomeric rubber could not be yielded through the above described milling procedures.

An additional parameter provided by the texture analyzer was the resilience of the rubber. We defined the resilience as the area of the force curve after release of compression (Force-Time area 2-3), divided by the area of the force curve during the compression (Force-Time area 1-2), multiplied by 100%. A resilience value of 100% would represent an idealized elastic material. Through experimentation, it was determined that a suitable polyurethane rubber, as described by this invention, requires a resilience value of at least 70%, preferably at least 90%.

Example 21 - Testing the Ultimate Biodegradability/Inherent Biodegradability of the Gransense™ elastomer gel

The elastomer gel of Example 6 was submitted for biodegradation testing in accordance with OECD 301 B: CO_2 Evolution (Modified Sturm Test) at Situ Biosciences (Wheeling, IL).

A sample was submitted, and the results data and graph were analyzed by curve fit to establish a plateau for the rate of biodegradation. Referring now to Figure 1,the OECD 301B-Biodegradation graph shows the test chamber carbon dioxide (CO2) measurements as the percent of theoretical maximum (% ThCO2). Curve fit is applied to calculate the predicted fit (solid curve line). The shading below the curve fit applies to the biodegradation requirement (10 to 60% ThCO2) for the determination of Biodegradability and shows that the required degradation amount has been met. See WO 2014/167518A, the contents of which are incorporated herein by reference.

In conclusion, the sample achieved the requirements for Ultimate Degradation / Inherent Biodegradation by exceeding the 60% threshold before the end of the 28-day test time frame.

Example 22: Testing for the % bio-based carbon content of the Gransense ™ Elastomer Gel

The elastomer gel of Example 6 was submitted for % Biobased Carbon in accordance with ASTM D6866-18 Method B using Radiocarbon Isotope Analysis at Beta Analytic Inc (Miami, FL). A naturally occurring isotope of carbon that is radioactive and decays in such a way that there is none left after about 45,000 years following the death of a plant or animal. Interpretation and application of the results is straightforward. A value of 100% biobased or biogenic carbon would indicate that 100% of the carbon came from plants or animal by-products (biomass) living in the natural environment and a value of 0% would mean that all of the carbon was derived from petrochemicals, coal, and other fossil sources. A value between 0-100% would indicate a mixture. The higher the value, the greater the proportion of naturally sourced components in the material.

A sample was submitted, and the results data concluded that the sample contained 100% Biobased Carbon Content (as a fraction of total organic carbon).

WE CLAIM:

1. A method of preparing a non-aqueous gel composition, comprising:

a) micronizing a cross-linked polyurethane elastomer rubber composition, comprising a cross-linked polyurethane elastomer rubber and a urethanation catalyst in the presence of a cosmetic emollient wherein the cosmetic emollient forms a solvent matrix substantially surrounding the cross-linked polyurethane elastomer rubber; and optionally,

b) combining the mixture resulting from step a) with a secondary solvent whereby a non-aqueous gel composition is formed.

2. The process of claim 1, wherein the secondary solvent is the secondary solvent is selected from the group consisting of triheptanoin; undecane; tridecane; or wherein the secondary solvents are naturally derived alkanes or naturally derived esters.

3. The process of claim 1, wherein the amount of the micronized cross-linked polyurethane elastomer rubber composition in the non-aqueous gel composition is from about 30 to about 5 weight %.

4. The process of claim 1, wherein the amount of the cosmetic emollient in the non-aqueous gel composition is from about 70 to about 95 weight %.

5. The process of claim 1, further comprising combining the non-aqueous gel composition with an active composition, optionally selected from the group consisting of selected from vitamins, sunscreens, plant extracts, fragrances and mixtures thereof.

6. The process of claim 1, further comprising combining the non-aqueous gel composition with a member of the group consisting of fragrances, colorants, preservatives, active compositions, and mixtures thereof.

7. The process of claim 1, wherein the micronized cross-linked polyurethane elastomer rubber composition has a cross-sectional diameter of from about 1 to about 61 microns.

8. The process of claim 1, wherein non-aqueous gel composition has a viscosity ranging from about 15,000 cP to about 1,000,000 cP.

9. The process of claim 1, wherein the cross-linked polyurethane elastomer rubber composition has a hardness force greater than 200 g, as measured by a texture analyzer prior to any milling or dilution and the cross-linked polyurethane elastomer rubber composition has a resilience greater than or equal to 70%.

10. The process of claim 1, wherein the cross-linked polyurethane rubber composition is formed with a prepolymer having at least two free hydroxyl groups.

11. The process of claim 1, wherein the solvent matrix comprises a second cosmetic emollient.

12. The process of claim 10, wherein the polyurethane elastomer rubber is formed with from about 5 to about 25 weight percent of a prepolymer having at least two free hydroxyl groups.

13. The process of claim 1, wherein the polyurethane elastomer rubber composition is formed with from about 1 to about 20 weight percent of an isocyanate functionalized molecule and a prepolymer having OH-groups.

14. The process of claim 10, wherein the prepolymer is a polyester reaction product of a diol and a dimer acid.

15. The process of claim 1, wherein the polyurethane elastomer rubber composition is formed with a polyisocyanate, optionally containing from about 15 to about 38 weight% NCO.

16. The process of claim 15, wherein the overall molar ratio between the NCO in the polyisocyanate and the OH groups in the prepolymer is from 2:1 to 1:2.

17. The process of claim 1, wherein the amount of urethanation catalyst in the cross-linked polyurethane elastomer rubber composition is from about 0.1 to about 2.5 weight%.

18. The process of claim 1, wherein the urethanation catalyst is a bismuth, zinc, or amine catalyst.

19. The process of claim 1, wherein the cross-linked polyurethane elastomer rubber composition includes an amount of a finisher containing an alcohol or an amine sufficient to quench unreacted isocyanate groups.

20. The process of claim 1, wherein the cross-linked polyurethane elastomer rubber composition is formed with a bio-based and biodegradable prepolymer.

21. The process of claim 15, wherein the prepolymer, the polyisocyanate, and the cosmetic emollient are bio-based and biodegradable.

22. The process of claim 1, wherein the cross-linked polyurethane elastomer rubber composition is comprised of greater than about 85% renewable, bio-based feedstocks.

23. The process of claim 21, wherein the bio-based and biodegradable polyisocyanate is 1,5-pentamethylene diisocyanate trimer.

Abstract

A polyurethane elastomeric rubber composition containing a bio-based polyol cross-linked with a bio-based isocyanate using a urethanation catalyst such as a bismuth catalyst in the presence of a cosmetic emollient is disclosed. The cross-linked polyurethane elastomer rubber is in further aspect of the invention included in a gel after being milled in the presence of a bio-based emollient or mixture of bio-based emollients. The polyurethane elastomeric gel has good compatibility with cosmetic and natural oils and can be used as a gelling agent for these oils among other desirable cosmetic formulary roles.

Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82A (07-13)
Approved for use through 01/31/2018. OMB 0651-0035
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

TRANSMITTAL FOR POWER OF ATTORNEY TO ONE OR MORE REGISTERED PRACTITIONERS

NOTE: This form is to be submitted with the Power of Attorney by Applicant form (PTO/AIA/82B) to identify the application to which the Power of Attorney is directed, in accordance with 37 CFR 1.5, unless the application number and filing date are identified in the Power of Attorney by Applicant form. If neither form PTO/AIA/82A nor form PTO/AIA82B identifies the application to which the Power of Attorney is directed, the Power of Attorney will not be recognized in the application.

Application Number	
Filing Date	Herewith
First Named Inventor	Anna K. CROOM, et al.
Title	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE
Art Unit	
Examiner Name	
Attorney Docket Number	GRAN-1012-U-D

SIGNATURE of Applicant or Patent Practitioner

Signature	/Michael N. Mercanti/	Date (Optional)	
Name	Michael N. Mercanti	Registration Number	33966
Title (if Applicant is a juristic entity)			
Applicant Name (if Applicant is a juristic entity)			

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4(d) for signature requirements and certifications. If more than one applicant, use multiple forms.

☑ *Total of 1 forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82B (07-13)
Approved for use through 01/31/2018. OMB 0651-0035
U.S. Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number

POWER OF ATTORNEY BY APPLICANT

I hereby revoke all previous powers of attorney given in the application identified in either the attached transmittal letter or the boxes below.

Application Number	Filing Date

(Note: The boxes above may be left blank if information is provided on form PTO/AIA/82A.)

☑ I hereby appoint the Patent Practitioner(s) associated with the following Customer Number as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above: 20311

OR

☐ I hereby appoint Practitioner(s) named in the attached list (form PTO/AIA/82C) as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the patent application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above. (Note: Complete form PTO/AIA/82C.)

Please recognize or change the correspondence address for the application identified in the attached transmittal letter or the boxes above to:

☑ The address associated with the above-mentioned Customer Number

OR

☐ The address associated with Customer Number:

OR

☐ Firm or Individual Name					
Address					
City		State		Zip	
Country					
Telephone		Email			

I am the Applicant (if the Applicant is a juristic entity, list the Applicant name in the box):

GRANT INDUSTRIES, INC.

☐ Inventor or Joint Inventor (title not required below)

☐ Legal Representative of a Deceased or Legally Incapacitated Inventor (title not required below)

☑ Assignee or Person to Whom the Inventor is Under an Obligation to Assign (provide signer's title if applicant is a juristic entity)

☐ Person Who Otherwise Shows Sufficient Proprietary Interest (e.g., a petition under 37 CFR 1.46(b)(2) was granted in the application or is concurrently being filed with this document) (provide signer's title if applicant is a juristic entity)

/ / SIGNATURE of Applicant for Patent

The undersigned (whose title is supplied below) is authorized to act on behalf of the applicant (e.g., where the applicant is a juristic entity).

Signature	/Daniel Grant/	Date (Optional)	7/28/2015
Name	Daniel Grantholt		
Title	General Counsel		

NOTE: Signature - This form must be signed by the applicant in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications. If more than one applicant, use multiple forms.

☑ Total of 1 forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Docket No. GRAN-1012-U-D

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

	Examiner:	Unknown Art Unit: Unknown
Re:	Application of:	Anna K. CROOM, et al.
	Serial No.:	To be assigned
	Filed:	Herewith
	For:	**BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE**
	Confirmation No.:	Unknown

INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

December 14, 2022

Sir:

Applicants respectfully submit this Information Disclosure Statement pursuant to 37 C.F.R. §§ 1.97 and 1.98 in order to comply with the duty of disclosure under 37 C.F.R. § 1.56. These referenced are listed on the attached form PTO/SB/08a.

The subject application is a divisional of U.S. Patent Application No. 16/992,831 filed August 13, 2020. All of the references listed on the attached form PTO/SB/08a have been previously submitted to, considered or received by the Examiner in U.S. Patent Application No. 16/992,831 and provided herein.

This submission does not represent that a search has been made or that no better art exists. While the term "references" is used in citing the documents called to the Examiner's attention herein, Applicants do not make any admission that each or all of them are "prior art" references within the meaning of the statutory and case law.

Applicants reserve the right to contend, where appropriate, that a reference asserted against any claim of the present application is not prior art under the facts and the law.

Applicants also reserve the right to present appropriate arguments and/or evidence to establish patentability over the references, should one or more of the references be applied against the claims of the present application.

Applicants request that the Examiner independently determine those items which the Examiner would consider the most pertinent of all the references cited herein.

This Information Disclosure Statement is filed with the application and is therefore within three (3) months of the filing date of this application. Accordingly, this document complies with the requirements of 37 C.F.R. § 1.97(b). It is respectfully requested that the references cited in the accompanying PTO/SB/08a form be considered and made of record.

Respectfully submitted,
LUCAS & MERCANTI, LLP

By: /Michael N. Mercanti/
Michael N. Mercanti
Reg. No. 33,966

LUCAS & MERCANTI, LLP
30 Broad Street, 21st Floor
New York, New York 10004
Phone: 212-661-8000
Fax: 212-661-8002

CERTIFICATE OF ELECTRONIC FILING
I hereby certify that this document is being electronically transmitted to the Commissioner for Patents via EFS-Web on December 14, 2022.

LUCAS & MERCANTI, LLP

BY: /Carla Curado/
Carla Curado

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To: MINXI RAO
MEDLER FERRO WOODHOUSE & MILLS PLLC
8201 GREENSBORO DR., STE. 1060
MCLEAN, VA 22102

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing *(day/month/year)*	16 OCT 2020
Applicant's or agent's file reference 0113-0006WO1	**FOR FURTHER ACTION** See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US 20/41540	10 July 2020 (10.07.2020)	10 July 2019 (10.07.2019)

International Patent Classification (IPC) or both national classification and IPC

IPC - A61K 8/87; A61Q 19/00; C08G 18/72 (2020.01)

CPC - A61K 8/87; A61Q 19/00; C08G 18/72; C08G 18/32; C08G 2220/00

Applicant NANOMETICS LLC (D.B.A. PHD BIOSCIENCES)

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA/US	Date of completion of this opinion	Authorized officer
Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	25 September 2020	Lee Young PCT Help Desk Telephone No. 571-272-4300

Form PCT/ISA/237 (cover sheet) (revised January 2019)

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/41540

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed.

   ☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(b)).

3. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing:

   a. ☐ forming part of the international application as filed:

      ☐ in the form of an Annex C/ST.25 text file.

      ☐ on paper or in the form of an image file.

   b. ☐ furnished together with the international application under PCT Rule 13*ter*.1(a) for the purposes of international search only in the form of an Annex C/ST.25 text file.

   c. ☐ furnished subsequent to the international filing date for the purposes of international search only:

      ☐ in the form of an Annex C/ST.25 text file (Rule 13*ter*.1(a)).

      ☐ on paper or in the form of an image file (Rule 13*ter*.1(b) and Administrative Instructions, Section 713).

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that forming part of the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/41540

Box No. V **Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Claims	2-4, 6-21, 23-26, 29-32, 33/(6), 34-35, 36/(6), 37/(6)	YES
	Claims	1, 5, 22, 27-28, 33/(1), 36/(1), 37/(1)	NO
Inventive step (IS)	Claims	None	YES
	Claims	1-37	NO
Industrial applicability (IA)	Claims	1-37	YES
	Claims	None	NO

2. Citations and explanations:
Claims 1, 5, 22, 27, 33/(1), 36/(1), and 37/(1) lack novelty under PCT Article 33(2) as being anticipated by US 4,661,099 A to von Bittera et al. (hereinafter von Bittera).

Regarding claim 1, von Bittera discloses of a gel composition comprising a polyurethane elastomer gel (col 1 lines 7-12: "The present invention relates to novel self-adhesive sheet-like structures comprising... adhesive layer based on polyurethane gel... [obtained by] a reaction mixture...") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (col 1 lines 11-13: "...[obtained by] a reaction mixture which comprises diisocyanates and/or polyisocyanates..."; example 1: "...6.1 parts of polyisocyanate 4..."; col 7 lines 39-41: "Polyisocyanate 4: 4,4'-Diisocyanatodiphenylmethane liquefied by prepolymerization with tripropylene glycol..."; has two isocyanate functional groups); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (col 1 lines 11-14: "...[obtained by] a reaction mixture which comprises diisocyanates and/or polyisocyanates and an excess amount of high molecular weight polyols..."; example 1: "100 parts of polyether 1, 6.1 parts of polyisocyanate 4..."; see col 7 line 57, polyol 1 has 4 hydroxyl groups); (C) an optional polyurethane reaction catalyst (example 1: "100 parts of polyether 1, 6.1 parts of polyisocyanate 4 and 0.6 parts of dibutyltin dilaurate are, within one minute, thoroughly mixed and poured out onto silicone-treated paper... [a]fter 20 minutes, the mixture has congealed to form a gel"; see instant specification [068]: "Appropriate polyurethane catalysts include... Dibutyltin dilaurate...").

Regarding claim 5, von Bittera further discloses the gel composition of claim 1 wherein the polyisocyanate or mixture of polyisocyanates is a low molecular weight polyisocyanate or mixture of polyisocyanates (example 1: "...6.1 parts of polyisocyanate 4..."; col 7 lines 39-41: "Polyisocyanate 4: 4,4'-Diisocyanatodiphenylmethane liquefied by prepolymerization with tripropylene glycol...") and wherein the polyol or mixture of polyols contains two or more hydroxyl, amine, thiol, or carboxylic acid groups (example 1: "100 parts of polyether 1, 6.1 parts of polyisocyanate 4..."; see col 7 line 57, polyol 1 has 4 hydroxyl groups).

Regarding claim 22, von Bittera discloses of a method of making a polyurethane elastomer (col 1 lines 7-12: "The present invention relates to novel self-adhesive sheet-like structures comprising... adhesive layer based on polyurethane gel... [obtained by] a reaction mixture...") comprising: I) mixing a polyisocyanate reactant and a polyol reactant (col 1 lines 11-14: "...[obtained by] a reaction mixture which comprises diisocyanates and/or polyisocyanates and an excess amount of high molecular weight polyols..."; example 1: "100 parts of polyether 1, 6.1 parts of polyisocyanate 4..."), wherein the polycisocyanate reactant comprises two or more isocyanate functional groups (example 1: "...6.1 parts of polyisocyanate 4..."; col 7 lines 39-41: "Polyisocyanate 4: 4,4'-Diisocyanatodiphenylmethane liquefied by prepolymerization with tripropylene glycol..."; has two isocyanate functional groups) and the polyol reactant comprises two or hydroxyl groups (example 1: "100 parts of polyether 1, 6.1 parts of polyisocyanate 4..."; see col 7 line 57, polyol 1 has 4 hydroxyl groups); and II) optionally adding a polyurethane reaction catalyst (example 1: "100 parts of polyether 1, 6.1 parts of polyisocyanate 4 and 0.6 parts of dibutyltin dilaurate are, within one minute, thoroughly mixed and poured out onto silicone-treated paper... [a]fter 20 minutes, the mixture has congealed to form a gel"; see instant specification [068]: "Appropriate polyurethane catalysts include... Dibutyltin dilaurate...").

Regarding claim 27, von Bittera further discloses of the method of claim 22, further comprising preparing the polyisocyanate reactant from hexamethylene diisocyanate (example 5: "A mixture of 100 parts of polyether 1, 3.6 parts of polyisocyanate 5 and 3.parts of dibutyltin dilaurate..."; col 7 lines 44-45: "Polyisocyanate 5: 1,6-Hexamethylene diisocyanate modified by trimerization, average NCO functionality...").

Regarding claim 33/(1), von Bittera discloses of a topical formulation comprising: the gel composition of claim 1; and a pharmaceutically active ingredient, wherein the pharmaceutically active ingredient is a personal care active ingredient or a healthcare active ingredient (col 1 lines 7-16: "The present invention relates to novel self-adhesive sheet-like structures comprising... [a] polyurethane gel... [obtained by] a reaction mixture which comprises diisocyanates and/or polyisocyanates and an excess amount of high molecular weight polyols... they can be used, for example, for medical purposes as an adhesive plaster tolerated by the skin..."; col 6 lines 42-44: "An embodiment of a skin plaster containing an active compound which is suitable for transdermal administration of the active compound...").

---Continued in Supplemental Box---

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/41540

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claims 12 and 13 lack antecedent basis. Claim 12 depends on claim 1, and states "wherein greater than 50% of the carbon content of the topically acceptable solvent is derived from plant sources". However, claim 1 does not disclose of a topically acceptable solvent. Claim 13 depends on claim 6, and similarly states "wherein greater than 50% of the carbon content of the topically acceptable solvent is derived from plant sources". However, claim 6 does not disclose of a topically acceptable solvent. In the interest of completing the international search, the term "solvent" in claims 12 and 13 has been interpreted to be a typo for "carrier".

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/41540

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:
Box V.2 Citations and Explanations

Regarding claim 36/(1), von Bittera discloses of a medical medically acceptable gel comprising the gel composition of claim 1 (col 1 lines 7 -16: "The present invention relates to novel self-adhesive sheet-like structures comprising... [a] polyurethane gel... [obtained by] a reaction mixture which comprises diisocyanates and/or polyisocyanates and an excess amount of high molecular weight polyols... they can be used, for example, for medical purposes as an adhesive plaster tolerated by the skin...").

Regarding claim 37/(1), von Bittera discloses of a topical formulation comprising the gel composition of claim 1 (col 1 lines 7-16: "The present invention relates to novel self-adhesive sheet-like structures comprising... [a] polyurethane gel... [obtained by] a reaction mixture which comprises diisocyanates and/or polyisocyanates and an excess amount of high molecular weight polyols... they can be used, for example, for medical purposes as an adhesive plaster tolerated by the skin...").

Claims 1, 22, and 28 lack novelty under PCT Article 33(2) as being anticipated by US 2018/0208720 A1 to Mitsui Chemicals, Inc. (hereinafter Mitsui).

Regarding claim 1, Mitsui discloses of a gel composition comprising a polyurethane elastomer gel (para [0013]: "The present invention includes"; para [0014]: "...a polyurethane gel including a gel layer... wherein the gel layer is produced by...") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0014]: "...by allowing at least aliphatic polyisocyanate having an average functionality of more than 2.0 to react with..."; see table 1, example 6: "Aliphatic Polyisocyanate(B)L 0.61"; production example 3: "Aliphatic Polyisocyanate (B): Alcohol-Modified Isocyanurate Derivative of PDI"; PDI is pentamethylene diisocyanate); and (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0014]: "...react with polyol having an average functionality of 3.0 or less..."; see table 1, example 6: "Trifunctional polyoxyalkylene polyol... EP-505S... 0.05"; para [0353]: "EP-550S: ethylene oxide-propylene oxide copolymer trifunctional polyoxyalkylene polyol, trade name ACTCOL EP-505S, manufactured by Mitsui Chemicals, Inc., average functionality 3").

Regarding claim 22, Mitsui discloses of a method of making a polyurethane elastomer (para [0013]: "The present invention includes"; para [0014]: "...a polyurethane gel including a gel layer... wherein the gel layer is produced by...") comprising: I) mixing a polyisocyanate reactant and a polyol reactant (para [0014]: "...by allowing at least aliphatic polyisocyanate having an average functionality of more than 2.0 to react with polyol having an average functionality of 3.0 or less..."), wherein the polycisocyanate reactant comprises two or more isocyanate functional groups (see table 1, example 6: "Aliphatic Polyisocyanate(B)L 0.61"; production example 3: "Aliphatic Polyisocyanate (B): Alcohol-Modified Isocyanurate Derivative of PDI"; PDI is pentamethylene diisocyanate) and the polyol reactant comprises two or hydroxyl groups (s see table 1, example 6: "Trifunctional polyoxyalkylene polyol... EP-505S... 0.05"; para [0353]: "EP-550S: ethylene oxide -propylene oxide copolymer trifunctional polyoxyalkylene polyol, trade name ACTCOL EP-505S, manufactured by Mitsui Chemicals, Inc., average functionality 3").

Regarding claim 28, Mitsui further discloses of the method of claim 22, further comprising preparing the polyisocyanate reactant from pentamethylene diisocyanate (see table 1, example 6: "Aliphatic Polyisocyanate(B)L 0.61"; Production Example 3: "Aliphatic Polyisocyanate (B): Alcohol-Modified Isocyanurate Derivative of PDI"; PDI is pentamethylene diisocyanate, see para [0255]- para [0259]).

Claims 1, 5, and 22 lack novelty under PCT Article 33(2) as being anticipated by EP 1 142 959 A1 to Dai-Ichi Kogyo Seiyaku Co., Ltd. (hereinafter Dai-Ichi '959).

Regarding claim 1, Dai-Ichi '959 discloses of a gel composition comprising a polyurethane elastomer gel (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0023]: "The polyurethane resin suited for use as the gelling drug is obtained by...") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0023]: "...is obtained by using the following polyisocyanates as a raw material... [a]mong these polyisocyanates, hexamethylene diisocyanate..."; see table 1, polyisocyanate used is hexamethylene diisocyanate); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0024]: "Similarly, examples of the polyol as a raw material of the polyurethane resin... castor oil is preferably used in view of the reactivity"; see table 1, castor oil is used as the polyol); and (C) an optional polyurethane reaction catalyst (table 1: "Dibutyltin dilaurate"; see instant specification [068]: "Appropriate polyurethane catalysts include... Dibutyltin dilaurate...").

Regarding claim 5, Dai-Ichi '959 further discloses of the gel composition of claim 1 wherein the polyisocyanate or mixture of polyisocyanates is a low molecular weight polyisocyanate or mixture of polyisocyanates (para [0023]: "...is obtained by using the following polyisocyanates as a raw material... [a]mong these polyisocyanates, hexamethylene diisocyanate..."; see table 1, polyisocyanate used is hexamethylene diisocyanate) and wherein the polyol or mixture of polyols contains two or more hydroxyl, amine, thiol, or carboxylic acid groups (para [0024]: "Similarly, examples of the polyol as a raw material of the polyurethane resin... castor oil is preferably used in view of the reactivity"; see table 1, castor oil (glyceryl triricinoleate) is used as the polyol).

---Continued in Supplemental Box---

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/41540

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of:
Box V.2 Citations and Explanations

Regarding claim 22, Dai-Ichi '959 discloses of the method of making a polyurethane elastomer (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0023]: "The polyurethane resin suited for use as the gelling drug is obtained by...") comprising: I) mixing a polyisocyanate reactant and a polyol reactant (para [0023]: "In the present invention, the polyurethane resin can be preferably used as the resin base. The polyurethane resin suited for use as the gelling drug is obtained by using the following polyisocyanates as a raw material... [a]mong these polyisocyanates, hexamethylene diisocyanate..."; para [0024]: "Similarly, examples of the polyol as a raw material of the polyurethane resin... castor oil is preferably used in view of the reactivity"), wherein the polycisocyanate reactant comprises two or more isocyanate functional groups and the polyol reactant comprises two or hydroxyl groups (see table 1, polyisocyanate used is hexamethylene diisocyanate and castor oil is used as the polyol); and II) optionally adding a polyurethane reaction catalyst (table 1: "Dibutyltin dilaurate"; see instant specification [068]: "Appropriate polyurethane catalysts include... Dibutyltin dilaurate...").

Claims 6, 14-17, 33/(6), and 37/(6) lack inventive step under PCT Article 33(3) as being obvious over Dai-Ichi '959.

Regarding claim 6, Dai-Ichi '959 discloses of a gel composition comprising a polyurethane elastomer (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0023]: "The polyurethane resin suited for use as the gelling drug is obtained by...") from the reaction of: (A) castor oil (para [0024]: "Similarly, examples of the polyol as a raw material of the polyurethane resin... castor oil is preferably used in view of the reactivity"; see table 1, castor oil is used as the polyol); (B) isophorone diisocyanate (para [0023]: "In the present invention, the polyurethane resin can be preferably used as the resin base. The polyurethane resin suited for use as the gelling drug is obtained by using the following polyisocyanates as a raw material... [a]mong these polyisocyanates... isophorone diisocyanate..."), wherein the molar ratio of isocyanate groups to hydroxyl groups is between 1:1 and 1:2 (para [0026]: "As is apparent from the results of Tables 1 to 3... gelling occurs only in case where the ratio of the polyisocyanate to the polyol is close to 1:1..."); and (C) an optional polyurethane reaction catalyst (table 1: "Dibutyltin dilaurate"; see instant specification [068]: "Appropriate polyurethane catalysts include... Dibutyltin dilaurate..."); and wherein a personal care or healthcare active ingredient is optionally incorporated into the polyurethane elastomer gel by dissolving the personal care or healthcare active ingredient in the topically acceptable solvent during the formation of the polyurethane elastomer gel, or by admixing the personal care or healthcare active ingredient with a formed polyurethane elastomer gel (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0017]: "Drugs such as allyl isothiocyanate..."). However, Dai-Ichi '959 does not disclose of a specific example or embodiment of a gel composition comprising a polyurethane elastomer wherein the polyurethane is formed from isophorone diisocyanate and castor oil. However, it would have been obvious to one of ordinary skill in the art to use isophorone diisocyanate and castor oil as the reactants for forming the polyurethane, based on the teachings of Dai-Ichi '959, since Dai-Ichi '959 discloses that these reactants can be used.

Regarding claim 14, Dai-Ichi '959 discloses of a process for preparing the gel composition of claim 1 (para [0023]: "In the present invention, the polyurethane resin can be preferably used as the resin base. The polyurethane resin suited for use as the gelling drug is obtained by using the following..."), comprising reacting: (A) a polyol (para [0024]: "Similarly, examples of the polyol as a raw material of the polyurethane resin... castor oil is preferably used in view of the reactivity"); (B) isophorone diisocyanate (para [0023: "The polyurethane resin suited for use as the gelling drug is obtained by using the following polyisocyanates as a raw material... [a]mong these polyisocyanates... isophorone diisocyanate..."); and (C) an optional polyurethane reaction catalyst (table 1: "Dibutyltin dilaurate"; see instant specification [068]: "Appropriate polyurethane catalysts include... Dibutyltin dilaurate..."),

Regarding claim 15, Dai-Ichi '959 discloses of a process for preparing the gel composition of claim 6 (para [0023]: "In the present invention, the polyurethane resin can be preferably used as the resin base. The polyurethane resin suited for use as the gelling drug is obtained by using the following..."), comprising reacting: (A) castor oil (para [0024]: "Similarly, examples of the polyol as a raw material of the polyurethane resin... castor oil is preferably used in view of the reactivity"); (B) isophorone diisocyanate (para [0023: "The polyurethane resin suited for use as the gelling drug is obtained by using the following polyisocyanates as a raw material... [a]mong these polyisocyanates... isophorone diisocyanate..."); and (C) an optional polyurethane reaction catalyst (table 1: "Dibutyltin dilaurate"; see instant specification [068]: "Appropriate polyurethane catalysts include... Dibutyltin dilaurate...").

Regarding claim 16, Dai-Ichi '959 discloses of a gel composition prepared according to the process of claim 14 (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0023]: "In the present invention, the polyurethane resin can be preferably used as the resin base. The polyurethane resin suited for use as the gelling drug is obtained by using the following polyisocyanates as a raw material..."; para [0024]: "Similarly, examples of the polyol as a raw material of the polyurethane resin... castor oil is preferably used in view of the reactivity"; see table 1).

Regarding claim 17, Dai-Ichi '959 discloses of a gel composition prepared according to the process of claim 15 (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0023]: "In the present invention, the polyurethane resin can be preferably used as the resin base. The polyurethane resin suited for use as the gelling drug is obtained by using the following polyisocyanates as a raw material..."; para [0024]: "Similarly, examples of the polyol as a raw material of the polyurethane resin... castor oil is preferably used in view of the reactivity"; see table 1).

---Continued in Supplemental Box---

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/41540

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of:
Box V.2 Citations and Explanations

Regarding claim 33/(6), Dai-Ichi '959 discloses of a formulation comprising: the gel composition of claim 6; and a pharmaceutically active ingredient, wherein the pharmaceutically active ingredient is a personal care active ingredient or a healthcare active ingredient (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0002]: "Allyl isothiocyanate... has been suggested to utilize it as an active ingredient of antimicrobial drugs, antifungal drugs, preservatives, and repellents..."). However, Dai-Ichi '959 does not specifically disclose that the formulation is a topical formulation. However, it would have been obvious to one of ordinary skill in the art to use the formulation comprising the gel composition of claim 6 and a pharmaceutically active ingredient which is a healthcare active agent, as disclosed by Dai-Ichi '959, in order to form a gel composition which imparts the healthcare properties to the skin.

Regarding claim 37/(6), Dai-Ichi '959 discloses of a formulation comprising the gel composition of claim 6 comprising a pharmaceutically active ingredient (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0002]: "Allyl isothiocyanate... has been suggested to utilize it as an active ingredient of antimicrobial drugs, antifungal drugs, preservatives, and repellents..."). However, Dai-Ichi '959 does not specifically disclose that the formulation is a topical formulation. However, it would have been obvious to one of ordinary skill in the art to use the formulation comprising the gel composition of claim 6 and a pharmaceutically active ingredient which is a healthcare active agent, as disclosed by Dai-Ichi '959, in order to form a gel composition which imparts the healthcare properties to the skin.

Claims 6, 10-11, 26, and 35 lack inventive step under PCT Article 33(3) as being obvious over Mitsui.

Regarding claim 6, Mitsui discloses of a gel composition comprising a polyurethane elastomer (para [0013]: "The present invention includes"; para [0014]: "...a polyurethane gel including a gel layer... wherein the gel layer is produced by...") from the reaction of: (A) castor oil (para [0014]: "...by allowing at least aliphatic polyisocyanate having an average functionality of more than 2.0 to react with polyol having an average functionality of 3.0 or less..."; para [0084]: "Examples of the polyester polyol include vegetable oil polyester polyols... e.g., castor oil fatty acid containing ricinoleic acid, hydrogenated castor oil fatty acid containing 12-hydroxystearic acid..."); and (B) isophorone diisocyanate (para [0014]: "...by allowing at least aliphatic polyisocyanate having an average functionality of more than 2.0 to react with..."; para [0129]: "Examples of the alicyclic diisocyanate include... 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (isophoronediisocyanate) [sic] (IPDI)..."), wherein the molar ratio of isocyanate groups to hydroxyl groups is between 1:1 and 1:2 (para [0111]: "In one shot process, for example, aliphatic polyisocyanate having an average functionality of more than 2.0 and polyol having an average functionality of 3.0 or less are formulated (mixed) so that the equivalent ratio (NCO/active hydrogen group) of the isocyanate group in the aliphatic polyisocyanate relative to the active hydrogen group (hydroxyl group) in polyol is, for example, 0.2 or more, preferably 0.4 or more, and for example, 0.8 or less, preferably 0.7 or less..."). However, Mitsui does not disclose of a specific example or embodiment, wherein the gel composition comprising polyurethane elastomer is made from castor oil and isophorone diisocyanate. However, it would have been obvious to one of ordinary skill in the art to use castor oil and isophorone diisocyanate the reactants in forming the polyurethane gel, based on the teachings of Mitsui, since Mitsui discloses that each are suitable reactants.

Regarding claim 10, Mitsui further discloses gel composition of claim 1, wherein the polyurethane catalyst is a bismuth group containing catalyst (para [0112]: "In the above-described reaction, as necessary, for example, a known urethane-formation catalyst such as amines and organic metal compounds can be added"; para [0114]: "Examples of the organic metal compound include... organic bismuth compounds such as bismuth octylate and bismuth neodecanoate").

Regarding claim 11, Mitsui further discloses gel composition of claim 6, wherein the polyurethane catalyst is a bismuth group containing catalyst (para [0112]: "In the above-described reaction, as necessary, for example, a known urethane-formation catalyst such as amines and organic metal compounds can be added"; para [0114]: "Examples of the organic metal compound include... organic bismuth compounds such as bismuth octylate and bismuth neodecanoate").

Regarding claim 26, Mitsui further discloses of the method of claim 22, wherein the polyisocyanate reactant is derived from the polymerization of a polyisocyanate (see table 1, example 6: "Aliphatic Polyisocyanate(B). 0.61"; production example 3: "Aliphatic Polyisocyanate (B): Alcohol-Modified Isocyanurate Derivative of PDI"; para [0255]: "A four-neck flask... was charged with 500 parts by mass of pentamethylene diisocyanate (a) produced in Production Example 1, 0.5 parts by mass of isobutylalcohol, 0.3 parts by mass of 2,6-di(tert-butyl)-4-methylphenol, and 0.3 parts by mass of tris(tridecyl) phosphite, and the mixture was allowed to react at 80 degrees centigrade for 2 hours"; production example 1: "Production of Pentamethylene Diisocyanate (a)"; see para [0246] to para [0248], pentamethylene diisocyanate is derived from pentamethylenediamine and dichlorobenzene). However, Mitsui does not disclose that the polyisocyanate reactant is derived from the polymerization of another polyisocyanate. However, it would have been obvious to one of ordinary skill in the art through routine experimentation to form a polyisocyanate reactant from the polymerization of another polyisocyanate, in order to form a polyisocyanate reactant with specific reactivity to form the polyurethane elastomer.

Regarding claim 35, Mitsui discloses of a foot conforming shoe insert or shoe sole comprising the gel composition of claim 1 or claim 6 (para [0204]: "The polyurethane gel 1 can be suitably used as a... shoe sole...").

---Continued in Supplemental Box---

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/41540

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of:
Box V.2 Citations and Explanations

Claims 2-4, 7, 9, 12-13, 23, and 25 lack inventive step under PCT Article 33(3) as being obvious over Dai-Ichi '959 in view of JP 3631542 B2 to Dai-Ichi Kogyo Seiyaku Co., Ltd. (hereinafter Dai-Ichi '542).

Regarding claim 2, Dai-Ichi '959 discloses of the gel composition of claim 1, wherein the gel composition comprises a pharmaceutically active agent, allyl thioisocyanate (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0017]: "Drugs such as allyl isothiocyanate..."). However, Dai-Ichi '959 does not disclose that the gel composition comprises a topically acceptable carrier. However, in a similar invention, Dai-Ichi '542 discloses of a composition comprising a polyurethane elastomer (para [0001]: "The present invention, over time bactericidal, relates Preparation of the polyurethane resin molded Body having antimicrobial properties"; para [0006]: "By gelling reaction film form or a process for preparing polyurethane resin molding for manufacturing a sheet-form polyurethane resin molded product") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0006]: "(B) a polyfunctional isocyanate"); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0006]: "(C) Castor Oil"); C) an optional polyurethane reaction catalyst (para [0006]: "(D) catalyst"); and (D) an optional topically acceptable carrier fluid, wherein a pharmaceutically active agent, allyl thioisocyanate, is dissolved (para [0006]: "(A) allyl isothiocyanate alone or hydrophobic medium containing the allyl isothiocyanate"), wherein the topically acceptable carrier is to prevent volatilization of allyl thioisocyanate and is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, oils, and combinations thereof (para [0014]: "As the hydrophobic medium to be those used as a volatile inhibitor of allyl isothiocyanate, for example benzyl benzoate, esters such as dioctyl phthalate, mineral oils, vegetable oils such as cottonseed oil acids and the like"). Therefore, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959 and Dai-Ichi '542 and form the gel composition of claim 1 comprising a pharmaceutically active agent allyl thioisocyanate, as disclosed by Dai-Ichi '959, wherein the gel composition further comprises a topically acceptable carrier selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, oils, and combinations thereof, as disclosed by Dai-Ichi '542, in order to prevent volatilization of allyl thioisocyanate, as disclosed by Dai-Ichi '542, as discussed above.

Regarding claim 3, Dai-Ichi '959 discloses of the gel composition of claim 1, wherein the gel composition comprises a pharmaceutically active agent, allyl thioisocyanate (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0017]: "Drugs such as allyl isothiocyanate..."). However, Dai-Ichi '959 does not disclose that the gel composition comprises a topically acceptable carrier. However, in a similar invention, Dai-Ichi '542 discloses of a composition comprising a polyurethane elastomer (para [0001]: "The present invention, over time bactericidal, relates Preparation of the polyurethane resin molded Body having antimicrobial properties"; para [0006]: "By gelling reaction film form or a process for preparing polyurethane resin molding for manufacturing a sheet-form polyurethane resin molded product") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0006]: "(B) a polyfunctional isocyanate"); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0006]: "(C) Castor Oil"); C) an optional polyurethane reaction catalyst (para [0006]: "(D) catalyst"); and (D) an optional topically acceptable carrier fluid, wherein a pharmaceutically active agent, allyl thioisocyanate, is dissolved (para [0006]: "(A) allyl isothiocyanate alone or hydrophobic medium containing the allyl isothiocyanate"), wherein the topically acceptable carrier is to prevent volatilization of allyl thioisocyanate and wherein the topically acceptable carrier fluid is selected from vegetable oil (para [0014]: "As the hydrophobic medium to be those used as a volatile inhibitor of allyl isothiocyanate, for example... vegetable oils such as cottonseed oil acids and the like"). However, Dai-Ichi '542 does not disclose that the topically acceptable carrier fluid is selected from the group consisting of diisooctyl succinate, heptyl undecylenate, neopentyl glycol diheptanoate, coco-caprylate/caprate, triheptanoin, caprylic/capric triglyceride, dodecane, tridecane, C13-15 alkane, squalene, squalene, isoamyl laurate, isopentyl laurate, caprylic/capric/myristic/stearic triglyceride, caprylic/capric/succinic triglyceride, isopropyl myristate, jojoba esters, tricaprylin, and palm oil. However, it would have been obvious to one of ordinary skill in the art to use palm oil as the topically acceptable carrier fluid, based on the teachings of Dai-Ichi '542, since Dai-Ichi '542 discloses that vegetable oils can be used as the topically acceptable carrier fluid, and palm oil is a type of vegetable oil. Therefore, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959 and Dai-Ichi '542 and form the gel composition of claim 1 comprising a pharmaceutically active agent allyl thioisocyanate, as disclosed by Dai-Ichi '959, wherein the gel composition further comprises a topically acceptable carrier selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, oils, and combinations thereof, as disclosed by Dai-Ichi '542, in order to prevent volatilization of allyl thioisocyanate, as disclosed by Dai-Ichi '542, as discussed above.

---Continued in Supplemental Box---

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/41540

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:
Box V.2 Citations and Explanations

Regarding claim 4, Dai-Ichi '959 discloses of the gel composition of claim 1, wherein the gel composition further comprises a pharmaceutically active agent, allyl thioisocyanate (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0017]: "Drugs such as allyl isothiocyanate..."). However, Dai-Ichi '959 does not disclose that pharmaceutically active ingredient is dissolved in a topically acceptable carrier fluid. However, in a similar invention, Dai-Ichi '542 discloses of a composition comprising a polyurethane elastomer (para [0001]: "The present invention, over time bactericidal, relates Preparation of the polyurethane resin molded Body having antimicrobial properties"; para [0006]: "By gelling reaction film form or a process for preparing polyurethane resin molding for manufacturing a sheet-form polyurethane resin molded product") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0006]: "(B) a polyfunctional isocyanate"); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0006]: "(C) Castor Oil"); C) an optional polyurethane reaction catalyst (para [0006]: "(D) catalyst"); and (D) an optional topically acceptable carrier fluid, wherein a pharmaceutically active agent, allyl thioisocyanate, is dissolved (para [0006]: "(A) allyl isothiocyanate alone or hydrophobic medium containing the allyl isothiocyanate"), wherein the topically acceptable carrier is to prevent volatilization of allyl thioisocyanate and is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, oils, and combinations thereof (para [0014]: "As the hydrophobic medium to be those used as a volatile inhibitor of allyl isothiocyanate, for example benzyl benzoate, esters such as dioctyl phthalate, mineral oils, vegetable oils such as cottonseed oil acids and the like"). Therefore, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959 and Dai-Ichi '542 and form the gel composition of claim 1 comprising a pharmaceutically active agent allyl thioisocyanate, as disclosed by Dai-Ichi '959, wherein the allyl thioisocyanate is dissolved in a topically acceptable carrier, as disclosed by Dai-Ichi '542, in order to prevent volatilization of allyl thioisocyanate, as disclosed by Dai-Ichi '542, as discussed above.

Regarding claim 7, Dai-Ichi '959 discloses of the gel composition of claim 6, wherein the gel composition comprises a pharmaceutically active agent, allyl thioisocyanate (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0017]: "Drugs such as allyl isothiocyanate..."). However, Dai-Ichi '959 does not disclose that the gel composition comprises a topically acceptable carrier. However, in a similar invention, Dai-Ichi '542 discloses of a composition comprising a polyurethane elastomer (para [0001]: "The present invention, over time bactericidal, relates Preparation of the polyurethane resin molded Body having antimicrobial properties"; para [0006]: "By gelling reaction film form or a process for preparing polyurethane resin molding for manufacturing a sheet-form polyurethane resin molded product") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0006]: "(B) a polyfunctional isocyanate"); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0006]: "(C) Castor Oil"); C) an optional polyurethane reaction catalyst (para [0006]: "(D) catalyst"); and (D) an optional topically acceptable carrier fluid, wherein a pharmaceutically active agent, allyl thioisocyanate, is dissolved (para [0006]: "(A) allyl isothiocyanate alone or hydrophobic medium containing the allyl isothiocyanate"), wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof (para [0014]: "As the hydrophobic medium to be those used as a volatile inhibitor of allyl isothiocyanate, for example benzyl benzoate, esters such as dioctyl phthalate, mineral oils, vegetable oils such as cottonseed oil acids and the like"; mineral oil comprises hydrocarbons). Therefore, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959 and Dai-Ichi '542 and form the gel composition of claim 6 comprising a pharmaceutically active agent allyl thioisocyanate, as disclosed by Dai-Ichi '959, wherein the gel composition further comprises a topically acceptable carrier selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof, as disclosed by Dai-Ichi '542, in order to prevent volatilization of allyl thioisocyanate, as disclosed by Dai-Ichi '542, as discussed above.

Regarding claim 9, Dai-Ichi '959 discloses of the gel composition of claim 6, wherein the gel composition further comprises a pharmaceutically active agent, allyl thioisocyanate (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0017]: "Drugs such as allyl isothiocyanate..."). However, Dai-Ichi '959 does not disclose that pharmaceutically active ingredient is dissolved in a topically acceptable carrier fluid. However, in a similar invention, Dai-Ichi '542 discloses of a composition comprising a polyurethane elastomer (para [0001]: "The present invention, over time bactericidal, relates Preparation of the polyurethane resin molded Body having antimicrobial properties"; para [0006]: "By gelling reaction film form or a process for preparing polyurethane resin molding for manufacturing a sheet-form polyurethane resin molded product") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0006]: "(B) a polyfunctional isocyanate"); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0006]: "(C) Castor Oil"); C) an optional polyurethane reaction catalyst (para [0006]: "(D) catalyst"); and (D) an optional topically acceptable carrier fluid, wherein a pharmaceutically active agent, allyl thioisocyanate, is dissolved (para [0006]: "(A) allyl isothiocyanate alone or hydrophobic medium containing the allyl isothiocyanate"), wherein the topically acceptable carrier is to prevent volatilization of allyl thioisocyanate (para [0014]: "As the hydrophobic medium to be those used as a volatile inhibitor of allyl isothiocyanate, for example benzyl benzoate, esters such as dioctyl phthalate, mineral oils, vegetable oils such as cottonseed oil acids and the like"). Therefore, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959 and Dai-Ichi '542 and form the gel composition of claim 6 comprising a pharmaceutically active agent allyl thioisocyanate, as disclosed by Dai-Ichi '959, wherein the allyl thioisocyanate is dissolved in a topically acceptable carrier, as disclosed by Dai-Ichi '542, in order to prevent volatilization of allyl thioisocyanate, as disclosed by Dai-Ichi '542, as discussed above.

---Continued in Supplemental Box---

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/41540

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of:
Box V.2 Citations and Explanations

Regarding claim 12, Dai-Ichi '959 discloses of the gel composition of claim 1, wherein the gel composition further comprises a pharmaceutically active agent, allyl thioisocyanate (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0017]: "Drugs such as allyl isothiocyanate..."). However, Dai-Ichi '959 does not disclose that pharmaceutically active ingredient is dissolved in a topically acceptable carrier fluid. However, in a similar invention, Dai-Ichi '542 discloses of a composition comprising a polyurethane elastomer (para [0001]: "The present invention, over time bactericidal, relates Preparation of the polyurethane resin molded Body having antimicrobial properties"; para [0006]: "By gelling reaction film form or a process for preparing polyurethane resin molding for manufacturing a sheet-form polyurethane resin molded product") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0006]: "(B) a polyfunctional isocyanate"); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0006]: "(C) Castor Oil"); C) an optional polyurethane reaction catalyst (para [0006]: "(D) catalyst"); and (D) an optional topically acceptable carrier fluid, wherein a pharmaceutically active agent, allyl thioisocyanate, is dissolved (para [0006]: "(A) allyl isothiocyanate alone or hydrophobic medium containing the allyl isothiocyanate"), wherein the topically acceptable carrier is to prevent volatilization of allyl thioisocyanate and greater than 50% of the carbon content of the topically acceptable carrier is derived from plant sources (para [0014]: "As the hydrophobic medium to be those used as a volatile inhibitor of allyl isothiocyanate, for example... vegetable oils such as cottonseed oil acids [sic] and the like"). Therefore, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959 and Dai-Ichi '542 and form the gel composition of claim 1 comprising a pharmaceutically active agent allyl thioisocyanate, as disclosed by Dai-Ichi '959, wherein the allyl thioisocyanate is dissolved in a topically acceptable carrier wherein greater than 50% of the carbon content of the topically acceptable carrier is derived from plant sources, as disclosed by Dai-Ichi '542, in order to prevent volatilization of allyl thioisocyanate, as disclosed by Dai-Ichi '542, as discussed above.

Regarding claim 13, Dai-Ichi '959 discloses of the gel composition of claim 6, wherein the gel composition further comprises a pharmaceutically active agent, allyl thioisocyanate (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0017]: "Drugs such as allyl isothiocyanate..."). However, Dai-Ichi '959 does not disclose that pharmaceutically active ingredient is dissolved in a topically acceptable carrier fluid. However, in a similar invention, Dai-Ichi '542 discloses of a composition comprising a polyurethane elastomer (para [0001]: "The present invention, over time bactericidal, relates Preparation of the polyurethane resin molded Body having antimicrobial properties"; para [0006]: "By gelling reaction film form or a process for preparing polyurethane resin molding for manufacturing a sheet-form polyurethane resin molded product") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0006]: "(B) a polyfunctional isocyanate"); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0006]: "(C) Castor Oil"); C) an optional polyurethane reaction catalyst (para [0006]: "(D) catalyst"); and (D) an optional topically acceptable carrier fluid, wherein a pharmaceutically active agent, allyl thioisocyanate, is dissolved (para [0006]: "(A) allyl isothiocyanate alone or hydrophobic medium containing the allyl isothiocyanate"), wherein the topically acceptable carrier is to prevent volatilization of allyl thioisocyanate and greater than 50% of the carbon content of the topically acceptable carrier is derived from plant sources (para [0014]: "As the hydrophobic medium to be those used as a volatile inhibitor of allyl isothiocyanate, for example... vegetable oils such as cottonseed oil acids [sic] and the like"). Therefore, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959 and Dai-Ichi '542 and form the gel composition of claim 1 comprising a pharmaceutically active agent allyl thioisocyanate, as disclosed by Dai-Ichi '959, wherein the allyl thioisocyanate is dissolved in a topically acceptable carrier wherein greater than 50% of the carbon content of the topically acceptable carrier is derived from plant sources, as disclosed by Dai-Ichi '542, in order to prevent volatilization of allyl thioisocyanate, as disclosed by Dai-Ichi '542, as discussed above.

Regarding claim 23, Dai-Ichi '959 discloses of the method of claim 22, wherein the gel composition comprises a pharmaceutically active agent, allyl thioisocyanate (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0017]: "Drugs such as allyl isothiocyanate..."). However, Dai-Ichi '959 does not disclose that the polyisocyanate and polyol reactant are in a topically acceptable carrier fluid in a reactant concentration of 80%. However, in a similar invention, Dai-Ichi '542 discloses of a composition comprising a polyurethane elastomer (para [0001]: "The present invention, over time bactericidal, relates Preparation of the polyurethane resin molded Body having antimicrobial properties"; para [0006]: "By gelling reaction film form or a process for preparing polyurethane resin molding for manufacturing a sheet-form polyurethane resin molded product") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0006]: "(B) a polyfunctional isocyanate"); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0006]: "(C) Castor Oil"); C) an optional polyurethane reaction catalyst (para [0006]: "(D) catalyst"); and (D) an optional topically acceptable carrier fluid, wherein a pharmaceutically active agent, allyl thioisocyanate, is dissolved (para [0006]: "(A) allyl isothiocyanate alone or hydrophobic medium containing the allyl isothiocyanate"), wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof (para [0014]: "As the hydrophobic medium to be those used as a volatile inhibitor of allyl isothiocyanate, for example benzyl benzoate, esters such as dioctyl phthalate, mineral oils, vegetable oils such as cottonseed oil acids and the like"; mineral oil comprises hydrocarbons). However, Dai-Ichi '542 does not disclose that the reactants are dispersed in the topically acceptable carrier at a concentration of 80 wt%.

---Discussion of claim 23 continued in Supplemental Box---

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/41540

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of:
Box V.2 Citations and Explanations

Continuation of discussion of claim 23

However, it would have been obvious to one of ordinary skill in the art through routine experimentation to adjust the amount of reactants in the carrier composition, such that it is at a concentration of 80 wt%, in order to ensure that there is a sufficient amount of reactants to actually form the polyurethane elastomer. Therefore, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959 and Dai-Ichi '542 and form the method of claim 22 comprising a pharmaceutically active agent allyl thioisocyanate, as disclosed by Dai-Ichi '959, wherein the reactants are dispersed in a topically acceptable carrier selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof in a concentration of 80 wt%, as disclosed by Dai-Ichi '542, in order to prevent volatilization of allyl thioisocyanate, as disclosed by Dai-Ichi '542, as discussed above.

Regarding claim 25, Dai-Ichi '959 discloses of the method of claim 22, wherein the gel composition comprises a pharmaceutically active agent, allyl thioisocyanate (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0017]: "Drugs such as allyl isothiocyanate..."). However, Dai-Ichi '959 does not disclose that the polyisocyanate and polyol reactant are in a topically acceptable carrier fluid in a reactant concentration of 80% or that the pharmaceutically active ingredient is dissolved in the topically acceptable carrier fluid. However, in a similar invention, Dai-Ichi '542 discloses of a composition comprising a polyurethane elastomer (para [0001]: "The present invention, over time bactericidal, relates Preparation of the polyurethane resin molded Body having antimicrobial properties"; para [0006]: "By gelling reaction film form or a process for preparing polyurethane resin molding for manufacturing a sheet-form polyurethane resin molded product") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0006]: "(B) a polyfunctional isocyanate"); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0006]: "(C) Castor Oil"); C) an optional polyurethane reaction catalyst (para [0006]: "(D) catalyst"); and (D) an optional topically acceptable carrier fluid, wherein a pharmaceutically active agent, allyl thioisocyanate, is dissolved (para [0006]: "(A) allyl isothiocyanate alone or hydrophobic medium containing the allyl isothiocyanate"), wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof (para [0014]: "As the hydrophobic medium to be those used as a volatile inhibitor of allyl isothiocyanate, for example benzyl benzoate, esters such as dioctyl phthalate, mineral oils, vegetable oils such as cottonseed oil acids and the like"; mineral oil comprises hydrocarbons). However, Dai-Ichi '542 does not disclose that the reactants are dispersed in the topically acceptable carrier at a concentration of 80 wt%. However, it would have been obvious to one of ordinary skill in the art through routine experimentation to adjust the amount of reactants in the carrier composition, such that it is at a concentration of 80 wt%, in order to ensure that there is a sufficient amount of reactants to actually form the polyurethane elastomer. Therefore, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959 and Dai-Ichi '542 and form the method of claim 22 comprising a pharmaceutically active agent allyl thioisocyanate, as disclosed by Dai-Ichi '959, wherein the pharmaceutically active ingredient is dispersed in a topically acceptable carrier selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof in a concentration of 80 wt%, as disclosed by Dai-Ichi '542, in order to prevent volatilization of allyl thioisocyanate, as disclosed by Dai-Ichi '542, as discussed above.

Claims 18-21, 29-32, and 34 lack inventive step under PCT Article 33(3) as being obvious over Dai-Ichi '959 in view of US 2011/0014139 A1 to Viala et al. (hereinafter Viala).

Regarding claim 18, Dai-Ichi '959 discloses of the gel composition of claim 1, as discussed above. However, Dai-Ichi '959 does not disclose of a process for preparing a gel paste composition using the gel composition of claim 1. In a similar invention, Viala discloses of a composition comprising a polyurethane elastomer (para [0032]: "Preferred polyurethanes or polyurethane dispersions to be used according to the invention are obtainable by"; para [0033]: "A) preparing isocyanate-functional prepolymers of") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0034]: "A1) organic polyisocyanates"; para [0047]: "Suitable polyisocyanates of component A1) are in particular the aliphatic, aromatic or cycloaliphatic polyisocyanates with an NCO functionality of greater than or equal to 2..."); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0035]: "A2) polymeric polyols... [having] OH functionalities of preferably 1.5 to 6..."); and (C) an optional polyurethane reaction catalyst (para [0113]: "To increase the rate of the isocyanate addition reaction, the catalysts known in polyurethane chemistry can be used"). Viala discloses that the composition comprising the polyurethane elastomer is in the form of an aqueous dispersion (para [0031]: "The polyurethanes present in the sun protection compositions according to the invention are... in particular in the form of aqueous dispersions"), which is dispersed by shearing the polyurethane (para [0133]: "The dispersion preferably takes place after the chain extension. For this, the dissolved and chain-extended polyurethane polymer is optionally either introduced into the dispersion water with strong shear, such as, for example, with vigorous stirring..."). Viala discloses that the viscosity of the dispersion can be adjusted to form a composition in a particular form for application (para [0140]: "Within the context of the present invention, the sun protection compositions are differentiated in particular by their consistency: cream (viscous), lotion and milk (flowable), gels (semisolid), oils, and also liquid formulations such as, for example, spray, balm and aqueous solutions"). However, Viala does not disclose of a process for preparing a gel paste composition, comprising shearing a polyurethane gel composition and combining the sheared polyurethane elastomer gel with an additional quantity of the carrier fluid to form a gel paste composition. However, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959 and Viala and form a gel composition comprising a polyurethane elastomer gel, as disclosed by Dai-Ichi '959, wherein a gel paste is formed by shearing the gel composition and adding an additional quantity of the carrier fluid, based on the teachings of Viala, since Viala discloses that an aqueous dispersion of a polyurethane elastomer is formed by shearing the polyurethane elastomer in water (the carrier fluid), and that the aqueous dispersion can be in different forms based on the viscosity of the dispersion, such as a cream (a viscous formulation similar to a paste), as discussed above.

---Continued in Supplemental Box---

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/41540

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:
Box V.2 Citations and Explanations

Regarding claim 19, Dai-Ichi '959 further discloses of the gel composition of claim 1, which comprises an antimicrobial agent (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0002]: "Allyl isothiocyanate... has been suggested to utilize it as an active ingredient of antimicrobial drugs..."). However, Dai-Ichi '959 does not disclose of a process for preparing a gel paste composition using the gel composition of claim 1. In a similar invention, Viala discloses of a composition comprising a polyurethane elastomer (para [0032]: "Preferred polyurethanes or polyurethane dispersions to be used according to the invention are obtainable by"; para [0033]: "A) preparing isocyanate-functional prepolymers of") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0034]: "A1) organic polyisocyanates"; para [0047]: "Suitable polyisocyanates of component A1) are in particular the aliphatic, aromatic or cycloaliphatic polyisocyanates with an NCO functionality of greater than or equal to 2..."); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0035]: "A2) polymeric polyols... [having] OH functionalities of preferably 1.5 to 6..."); and (C) an optional polyurethane reaction catalyst (para [0113]: "To increase the rate of the isocyanate addition reaction, the catalysts known in polyurethane chemistry can be used"). Viala discloses that the composition comprising the polyurethane elastomer is in the form of an aqueous dispersion (para [0031]: "The polyurethanes present in the sun protection compositions according to the invention are... in particular in the form of aqueous dispersions"), which is dispersed by shearing the polyurethane (para [0133]: "The dispersion preferably takes place after the chain extension. For this, the dissolved and chain-extended polyurethane polymer is optionally either introduced into the dispersion water with strong shear, such as, for example, with vigorous stirring..."). Viala discloses that the viscosity of the dispersion can be adjusted to form a composition in a particular form for application (para [0140]: "Within the context of the present invention, the sun protection compositions are differentiated in particular by their consistency: cream (viscous), lotion and milk (flowable), gels (semisolid), oils, and also liquid formulations such as, for example, spray, balm and aqueous solutions"). Viala discloses that the aqueous dispersion can be combined with a sunscreen agent (para [0227]: "The sun protection composition according to the invention comprises one or more sun protection filters and/or sun protection filter substances and/or substances conferring sun protection"). However, Viala does not disclose of a process for preparing a gel paste composition, comprising shearing a polyurethane gel composition and combining the sheared polyurethane elastomer gel with an active agent. However, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959 and Viala and form a gel composition comprising a polyurethane elastomer gel and an active composition, as disclosed by Dai-Ichi '959, wherein a gel paste is formed by shearing the gel composition and adding an active agent, based on the teachings of Viala, since Viala discloses that an aqueous dispersion of a polyurethane elastomer is formed by shearing the polyurethane elastomer in water (the carrier fluid) and combining it with an active agent (sun screen agent), and that the aqueous dispersion can be in different forms based on the viscosity of the dispersion, such as a cream (a viscous formulation similar to a paste), as discussed above.

Regarding claim 20, Dai-Ichi '959 discloses of the gel composition of claim 6, as discussed above. However, Dai-Ichi '959 does not disclose of a process for preparing a gel paste composition using the gel composition of claim 6. In a similar invention, Viala discloses of a composition comprising a polyurethane elastomer (para [0032]: "Preferred polyurethanes or polyurethane dispersions to be used according to the invention are obtainable by"; para [0033]: "A) preparing isocyanate-functional prepolymers of") prepared from the reaction of: (A) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0035]: "A2) polymeric polyols... [having] OH functionalities of preferably 1.5 to 6..."); (B) isophorone diisocyanate (para [0034]: "A1) organic polyisocyanates"; para [0048]: "Examples of such suitable polyisocyanates are... isophorone diisocyanate (IPDI)..."); and (C) an optional polyurethane reaction catalyst (para [0113]: "To increase the rate of the isocyanate addition reaction, the catalysts known in polyurethane chemistry can be used"). Viala discloses that the composition comprising the polyurethane elastomer is in the form of an aqueous dispersion (para [0031]: "The polyurethanes present in the sun protection compositions according to the invention are... in particular in the form of aqueous dispersions"), which is dispersed by shearing the polyurethane (para [0133]: "The dispersion preferably takes place after the chain extension. For this, the dissolved and chain-extended polyurethane polymer is optionally either introduced into the dispersion water with strong shear, such as, for example, with vigorous stirring..."). Viala discloses that the viscosity of the dispersion can be adjusted to form a composition in a particular form for application (para [0140]: "Within the context of the present invention, the sun protection compositions are differentiated in particular by their consistency: cream (viscous), lotion and milk (flowable), gels (semisolid), oils, and also liquid formulations such as, for example, spray, balm and aqueous solutions"). However, Viala does not disclose of a process for preparing a gel paste composition, comprising shearing a polyurethane gel composition and combining the sheared polyurethane elastomer gel with an additional quantity of the carrier fluid to form a gel paste composition. However, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959 and Viala and form a gel composition comprising a polyurethane elastomer gel, as disclosed by Dai-Ichi '959, wherein a gel paste is formed by shearing the gel composition and adding an additional quantity of the carrier fluid, based on the teachings of Viala, since Viala discloses that an aqueous dispersion of a polyurethane elastomer is formed by shearing the polyurethane elastomer in water (the carrier fluid), and that the aqueous dispersion can be in different forms based on the viscosity of the dispersion, such as a cream (a viscous formulation similar to a paste), as discussed above.

Regarding claim 21, Dai-Ichi '959 further discloses of the gel composition of claim 6, which comprises an antimicrobial agent (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0002]: "Allyl isothiocyanate... has been suggested to utilize it as an active ingredient of antimicrobial drugs..."). However, Dai-Ichi '959 does not disclose of a process for preparing a gel paste composition using the gel composition of claim 6. In a similar invention, Viala discloses of a composition comprising a polyurethane elastomer (para [0032]: "Preferred polyurethanes or polyurethane dispersions to be used according to the invention are obtainable by"; para [0033]: "A) preparing isocyanate-functional prepolymers of") prepared from the reaction of: (A) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0035]: "A2) polymeric polyols... [having] OH functionalities of preferably 1.5 to 6..."); (B) isophorone diisocyanate (para [0034]: "A1) organic polyisocyanates"; para [0048]: "Examples of such suitable polyisocyanates are... isophorone diisocyanate (IPDI)..."); and (C) an optional polyurethane reaction catalyst (para [0113]: "To increase the rate of the isocyanate addition reaction, the catalysts known in polyurethane chemistry can be used").

---Discussion of claim 21 continued in Supplemental Box---

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/41540

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of:
Box V.2 Citations and Explanations

Continuation of discussion of claim 21

Viala discloses that the composition comprising the polyurethane elastomer is in the form of an aqueous dispersion (para [0031]: "The polyurethanes present in the sun protection compositions according to the invention are... in particular in the form of aqueous dispersions"), which is dispersed by shearing the polyurethane (para [0133]: "The dispersion preferably takes place after the chain extension. For this, the dissolved and chain-extended polyurethane polymer is optionally either introduced into the dispersion water with strong shear, such as, for example, with vigorous stirring..."). Viala discloses that the viscosity of the dispersion can be adjusted to form a composition in a particular form for application (para [0140]: "Within the context of the present invention, the sun protection compositions are differentiated in particular by their consistency: cream (viscous), lotion and milk (flowable), gels (semisolid), oils, and also liquid formulations such as, for example, spray, balm and aqueous solutions"). Viala discloses that the aqueous dispersion can be combined with a sunscreen agent (para [0227]: "The sun protection composition according to the invention comprises one or more sun protection filters and/or sun protection filter substances and/or substances conferring sun protection"). However, Viala does not disclose of a process for preparing a gel paste composition, comprising shearing a polyurethane gel composition and combining the sheared polyurethane elastomer gel with an active agent. However, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959 and Viala and form a gel composition comprising a polyurethane elastomer gel and an active composition, as disclosed by Dai-Ichi '959, wherein a gel paste is formed by shearing the gel composition and adding an active agent, based on the teachings of Viala, since Viala discloses that an aqueous dispersion of a polyurethane elastomer is formed by shearing the polyurethane elastomer in water (the carrier fluid) and combining it with an active agent (sun screen agent), and that the aqueous dispersion can be in different forms based on the viscosity of the dispersion, such as a cream (a viscous formulation similar to a paste), as discussed above.

Regarding claim 29, Dai-Ichi '959 and Viala disclose of a polyurethane elastomer gel paste prepared by the method of claim 18 (Dai-Ichi '959 and Viala disclose of the method of claim 18 forming a gel paste, Dai-Ichi '959 and Viala then must disclose of a gel paste made by the method of claim 18).

Regarding claim 30, Dai-Ichi '959 and Viala disclose of a polyurethane elastomer gel paste prepared by the method of claim 19 (Dai-Ichi '959 and Viala disclose of the method of claim 19 forming a gel paste, Dai-Ichi '959 and Viala then must disclose of a gel paste made by the method of claim 19).

Regarding claim 31, Dai-Ichi '959 and Viala disclose of a polyurethane elastomer gel paste prepared by the method of claim 20 (Dai-Ichi '959 and Viala disclose of the method of claim 20 forming a gel paste, Dai-Ichi '959 and Viala then must disclose of a gel paste made by the method of claim 20).

Regarding claim 32, Dai-Ichi '959 and Viala disclose of a polyurethane elastomer gel paste prepared by the method of claim 21 (Dai-Ichi '959 and Viala disclose of the method of claim 21 forming a gel paste, Dai-Ichi '959 and Viala then must disclose of a gel paste made by the method of claim 21).

Regarding claim 34, Dai-Ichi '959 and Viala disclose of the polyurethane elastomer gel paste of any of claims 29 to 32, and Viala discloses of a topical formulation comprising the polyurethane elastomer and a pharmaceutically active ingredient, wherein the pharmaceutically active ingredient is a personal care active ingredient or a healthcare active ingredient (para [0001]: "The present invention relates to sun protection compositions for application to the skin, comprising special polyurethanes, and also to the use of said polyurethanes for the preparation of sun protection products"; para [0031]: "The polyurethanes present in the sun protection compositions according to the invention are... in particular in the form of aqueous dispersions"; para [0227]: "The sun protection composition according to the invention comprises one or more sun protection filters and/or sun protection filter substances and/or substances conferring sun protection").

Claims 8 and 24 lack inventive step under PCT Article 33(3) as being obvious over Dai-Ichi '959 in view of Dai-Ichi '542 and in further view of US 2012/0046358 A1 to Cheng et al. (hereinafter Cheng).

Regarding claim 8, Dai-Ichi '959 discloses of the gel composition of claim 6, wherein the gel composition comprises a pharmaceutically active agent, allyl thioisocyanate (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0017]: "Drugs such as allyl isothiocyanate..."). However, Dai-Ichi '959 does not disclose that the gel composition comprises a topically acceptable carrier. Dai-Ichi '959 discloses of the method of claim 22, wherein the gel composition comprises a pharmaceutically active agent, allyl thioisocyanate (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0017]: "Drugs such as allyl isothiocyanate..."). However, Dai-Ichi '959 does not disclose that the polyisocyanate and polyol reactant are in a topically acceptable carrier fluid in a reactant concentration of 80%.

---Discussion of claim 8 continued in Supplemental Box---

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/41540

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of:
Box V.2 Citations and Explanations

Continuation of discussion of claim 8

However, in a similar invention, Dai-Ichi '542 discloses of a composition comprising a polyurethane elastomer (para [0001]: "The present invention, over time bactericidal, relates Preparation of the polyurethane resin molded Body having antimicrobial properties"; para [0006]: "By gelling reaction film form or a process for preparing polyurethane resin molding for manufacturing a sheet-form polyurethane resin molded product") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0006]: "(B) a polyfunctional isocyanate"); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0006]: "(C) Castor Oil"); C) an optional polyurethane reaction catalyst (para [0006]: "(D) catalyst"); and (D) an optional topically acceptable carrier fluid, wherein a pharmaceutically active agent, allyl thioisocyanate, is dissolved (para [0006]: "(A) allyl isothiocyanate alone or hydrophobic medium containing the allyl isothiocyanate"), wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof (para [0014]: "As the hydrophobic medium to be those used as a volatile inhibitor of allyl isothiocyanate, for example benzyl benzoate, esters such as dioctyl phthalate, mineral oils, vegetable oils such as cottonseed oil acids and the like"; mineral oil comprises hydrocarbons). However, Dai-Ichi '542 does not disclose that the reactants are dispersed in the topically acceptable carrier at a concentration of 80 wt%, or, that the topically acceptable carrier fluid is selected from the group consisting of diisooctyl succinate, heptyl undecylenate, neopentyl glycol diheptanoate, and coco-caprylate/caprate. However, it would have been obvious to one of ordinary skill in the art through routine experimentation to adjust the amount of reactants in the carrier composition, such that it is at a concentration of 80 wt%, in order to ensure that there is a sufficient amount of reactants to acrtually form the polyurethane elastomer. However, in a similar invention, Cheng discloses of a composition comprising allyl thioisocyanate dispersed in a topically acceptable carrier, coco-caprylate/caprate (para [0034]: "The formulations of the pharmaceutical products and dietary supplements described in this invention can be administered... topically"; para [0020]: "Compositions described in this invention contain one or more of the isothiocyanates or their derivatives or their metabolites as API together with other ingredients listed below"; para [0021]: "(a) 0.5-50 portion (w/w) of API, which includes isothiocyanates... isothiocyanates include... allyl isothiocyanate (AITC)..."; para [0024]: "(b2) 0 to 500 portions (w/w) of oil components, were selected from fatty acids or triglyceride, monoglyceride or diglyceride, which include... coconut oil..."; coconut oil contains coco-caprylate/caprate, see the article entitled "What Is Coco-Caprylate Doing In My Natural Skin Care Products?" by Charla Jones, page 2: "Coco-caprylate/caprate is a skin-conditioning agent naturally derived from coconut oil to provide high hydration, superb spreadability and elegant slip"). Therefore, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959, Dai-Ichi '542, and Cheng and form the gel composition of claim 6 comprising a pharmaceutically active agent allyl thioisocyanate, as disclosed by Dai-Ichi '959, wherein the gel composition further comprises a topically acceptable carrier selected from vegetable oils, as disclosed by Dai-Ichi '542, wherein the topically acceptable carrier is coconut oil comprising coco-caprylate/caprate, as disclosed by Cheng, in order to prevent volatilization of allyl thioisocyanate, as disclosed by Dai-Ichi '542, as discussed above.

Regarding claim 24, Dai-Ichi '959 discloses of the method of claim 22, wherein the gel composition comprises a pharmaceutically active agent, allyl thioisocyanate (para [0013]: "The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel"; para [0017]: "Drugs such as allyl isothiocyanate..."). However, Dai-Ichi '959 does not disclose that the gel composition comprises a topically acceptable carrier. However, in a similar invention, Dai-Ichi '542 discloses of a composition comprising a polyurethane elastomer (para [0001]: "The present invention, over time bactericidal, relates Preparation of the polyurethane resin molded Body having antimicrobial properties"; para [0006]: "By gelling reaction film form or a process for preparing polyurethane resin molding for manufacturing a sheet-form polyurethane resin molded product") prepared from the reaction of: (A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups (para [0006]: "(B) a polyfunctional isocyanate"); (B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups (para [0006]: "(C) Castor Oil"); C) an optional polyurethane reaction catalyst (para [0006]: "(D) catalyst"); and (D) an optional topically acceptable carrier fluid, wherein a pharmaceutically active agent, allyl thioisocyanate, is dissolved (para [0006]: "(A) allyl isothiocyanate alone or hydrophobic medium containing the allyl isothiocyanate"), wherein the topically acceptable carrier fluid is selected from vegetable oils, which comprise triglycerides (para [0014]: "As the hydrophobic medium to be those used as a volatile inhibitor of allyl isothiocyanate, for example... vegetable oils such as cottonseed oil acids [sic] and the like"). However, Dai-Ichi '542 does not disclose that the topically acceptable carrier fluid is selected from the group consisting of diisooctyl succinate, heptyl undecylenate, neopentyl glycol diheptanoate, and coco-caprylate/caprate. However, in a similar invention, Cheng discloses of a composition comprising allyl thioisocyanate dispersed in a topically acceptable carrier, coco-caprylate/caprate (para [0034]: "The formulations of the pharmaceutical products and dietary supplements described in this invention can be administered... topically"; para [0020]: "Compositions described in this invention contain one or more of the isothiocyanates or their derivatives or their metabolites as API together with other ingredients listed below"; para [0021]: "(a) 0.5-50 portion (w/w) of API, which includes isothiocyanates... isothiocyanates include... allyl isothiocyanate (AITC)..."; para [0024]: "(b2) 0 to 500 portions (w/w) of oil components, were selected from fatty acids or triglyceride, monoglyceride or diglyceride, which include... coconut oil..."; coconut oil contains coco-caprylate/caprate, see the article entitled "What Is Coco-Caprylate Doing In My Natural Skin Care Products?" by Charla Jones, page 2: "Coco-caprylate/caprate is a skin-conditioning agent naturally derived from coconut oil to provide high hydration, superb spreadability and elegant slip"). Therefore, it would have been obvious to one of ordinary skill in the art to combine the teachings of Dai-Ichi '959, Dai-Ichi '542, and Cheng and form the gel composition of claim 6 comprising a pharmaceutically active agent allyl thioisocyanate, as disclosed by Dai-Ichi '959, wherein the gel composition further comprises a topically acceptable carrier selected from vegetable oils, as disclosed by Dai-Ichi '542, wherein the topically acceptable carrier is coconut oil comprising coco-caprylate/caprate, as disclosed by Cheng, in order to prevent volatilization of allyl thioisocyanate, as disclosed by Dai-Ichi '542, as discussed above.

Claims 1-37 have industrial applicability as defined by PCT Article 33(4) because the subject matter can be made or used in industry.

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC PAYMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
18/066,105	12/14/2022 05:17:52 PM ET	GRAN-1012-U-D

Title of Invention

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	1563	FILED BY	Carla Curado
PATENT CENTER #	61300708	AUTHORIZED BY	Michael Mercanti
CUSTOMER #	20311	FILING DATE	-
CORRESPONDENCE ADDRESS	-	FIRST NAMED INVENTOR	Anna K. CROOM

Payment Information

PAYMENT METHOD	PAYMENT TRANSACTION ID	PAYMENT AUTHORIZED BY
CARD / 1054	E2022BDH19300220	Carla Curado

FEE CODE	DESCRIPTION	ITEM PRICE($)	QUANTITY	ITEM TOTAL($)
4011	BASIC FILING FEE- UTILITY	80.00	1	80.00
2311	EXAMINATION OF ORIGINAL PATENT APPLICATION	400.00	1	400.00
2111	UTILITY PATENT APPL. SEARCH FEE	350.00	1	350.00
			TOTAL AMOUNT:	$830.00

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/08a (01-22)
Approved for use through 05/31/2024. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	
Filing Date	
First Named Inventor	Anna K. CROOM, et al.
Art Unit	
Examiner Name	
Attorney Docket Number	GRAN-1012-U-D

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	10035871	B2	2018-07-31	LANGER, et al.	
	2	8222363	B2	2012-07-17	LIN, et al.	
	3	9376404	B2	2016-06-28	NAKAGAWA, et al.	
	4	9610237	B2	2017-04-04	BURGO, et al.	
	5	5284897	A	1994-02-08	COLUMBUS, et al.	
	6	4661099	A	1987-04-28	VON BITTERA, et al.	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	
	First Named Inventor	Anna K. CROOM, et al.
	Art Unit	
	Examiner Name	
	Attorney Docket Number	GRAN-1012-U-D

	1	20180079852	A1	2018-03-22	HECKING, et al.	
	2	20150128335	A1	2015-05-14	DEHNI	
	3	20030092932	A1	2003-05-15	TONG, et al.	
	4	20180371149	A1	2018-12-27	LANGER, et al.	
	5	20130079486	A1	2013-03-28	HIDESAKI, et al.	
	6	20110045983	A1	2011-02-24	HEALY, et al.	
	7	20180208720	A1	2018-07-26	HASEGAWA, et al.	
	8	20110014139	A1	2011-01-20	VIALA, et al.	
	9	20120046358	A1	2012-02-23	CHENG, et al.	
	10	20090232752	A1	2009-09-17	CARSON, et al.	
	11	20190169390	A1	2019-06-06	PETERSON, et al.	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	
	First Named Inventor	Anna K. CROOM, et al.
	Art Unit	
	Examiner Name	
	Attorney Docket Number	GRAN-1012-U-D

	12	20160067153	A1	2016-03-10	CHEN, et al.	
	13	20180311140	A1	2018-11-01	PERNER, et al.	
	14	20180369125	A1	2018-12-27	WOODLAND, et al.	

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	2013074655	WO	A1	2013-05-23	INOLEX INVESTMENT CORPORATION		
	2	2018183440	WO	A1	2018-10-04	FORD GLOBAL TECHNOLOGIES, LLC		
	3	2014167518	WO	A1	2014-10-16	STERIPAK PTY LTD		
	4	6892253	JP	B2	2021-06-23	MITSUI CHEMICALS INC	English Abstract	
	5	2021007489	WO	A1	2021-01-14	NANOMETICS LLC		
	6	2021231527	WO	A1	2021-11-18	NANOMETICS LLC		

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	
	First Named Inventor	Anna K. CROOM, et al.
	Art Unit	
	Examiner Name	
	Attorney Docket Number	GRAN-1012-U-D

	7	2021257937	WO	A1	2021-12-23	NANOMETICS LLC		
	8	1142959	EP	A1	2001-10-10	DAI ICHI KOGYO SEIYAKU CO LTD		
	9	3631542	JP	B2	2005-03-23	DAI ICHI KOGYO SEIYAKU CO LTD	English Abstract	

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T5
	1	International Search Report and Written Opinion for International Application No. PCT/US2020/046170 (10 Pages) (November 18, 2020).	
	2	International Preliminary Report on Patentability for International Application No. PCT/US2020/046170 (9 Pages) (March 10, 2022).	
	3	Written Opinion corresponding to PCT/US2020/041540 (14 Pages) (October 16, 2020).	
	4	Becker et al., "Safety Assessment of Polyurethanes as Used in Cosmetics,", Cosmetic Ingredient Review, pages 1-96., 2017.	

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	
	First Named Inventor	Anna K. CROOM, et al.
	Art Unit	
	Examiner Name	
	Attorney Docket Number	GRAN-1012-U-D

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	
	First Named Inventor	Anna K. CROOM, et al.
	Art Unit	
	Examiner Name	
	Attorney Docket Number	GRAN-1012-U-D

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Michael N. Mercanti/	Date (YYYY-MM-DD)	2022-12-14
Name/Print	Michael N. Mercanti	Registration Number	33966

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
04 October 2018 (04.10.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/183440 A1

(51) International Patent Classification:
B29C 64/00 (2017.01)

(21) International Application Number:
PCT/US2018/024754

(22) International Filing Date:
28 March 2018 (28.03.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/477,863 28 March 2017 (28.03.2017) US

(71) Applicant: **FORD GLOBAL TECHNOLOGIES, LLC** [US/US]; 330 Town Center Drive, Suite 800, Dearborn, MI 48126 (US).

(72) Inventors: **RYAN, Emily**; 15973 Oceana, Allen Park, MI 48101 (US). **LANGHORST, Amy**; 113 1/2 E. Ann St #3, Ann Arbor, MI 48104 (US). **LEE, Ellen**; 1540 Meadowside Drive, Ann Arbor, MI 48104 (US). **MIELEWSKI, Deborah, Frances**; 1499 Maywood Avenue, Ann Arbor, MI 48103 (US).

(74) Agent: **BURRIS, Kelly, K.**; Burris Law, PLLC, 300 River Place, Suite 1775, Detroit, MI 48207 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

WO 2018/183440 A1

(54) Title: BIO-BASED POLYURETHANE RESIN FOR ADDITIVE MANUFACTURING

(57) Abstract: A bio-based polyurethane and method of forming an article using an additive manufacturing process is provided by the present disclosure. The bio-based polyurethane includes an isocyanate, a bio-based polyol, at least one functional blocking unit, a catalyst, a reactive diluent, at least one chain extender, and at least one photoinitiator. The bio-based polyurethane is placed into a bath, and the additive manufacturing process is initiated. The bath is exposed to UV light, and then at least one or more portions of the bath is polymerized, forming the article layer-by-layer. Further the formed articles are exposed to an additional UV cure and/or thermal cure.

BIO-BASED POLYURETHANE RESIN FOR ADDITIVE MANUFACTURING

FIELD

[0001] The present disclosure relates to 3D printing, or additive manufacturing, and more specifically to environmentally friendly materials for use with stereolithography and other processes that photopolymerize a part from a bath of liquid resin.

BACKGROUND

[0002] The statements in this section merely provide background information related to the present disclosure and may not constitute prior art.

[0003] There are many conflicting pressures for automotive manufacturers to build safer, yet lighter and more efficient vehicles. New technologies are constantly being developed in an effort to reduce vehicle mass through a variety of means such as raw materials, processing methods, and their integration into vehicle structures. These new technologies enable more efficiently designed and manufactured structures that are able to meet structural performance requirements, while still reducing vehicle mass and therefore improving fuel economy.

[0004] One area of advancement is the proliferation of additive manufacturing of plastics. New additive manufacturing processes have the potential to dramatically disrupt traditional part production methods. Additive manufacturing techniques provide significant opportunities to inexpensively prototype, customize, and generate parts with highly complex geometries. One additive manufacturing process, stereolithography (SLA), uses ultraviolet light to photopolymerize a part from a bath of liquid resin. An SLA machine builds each part by shining a pattern of UV light into a bath of liquid resin corresponding to cross-sections of each layer of the part, causing each layer to cure.

[0005] However, as additive manufacturing processes (including SLA processes) become faster, less expensive, and closer to being production ready, the use of petroleum-based polymers will continue to have a negative impact on the environment with an increased carbon footprint of automotive vehicles.

[0006] These issues with petroleum-based polymers and other materials that are not readily biodegradable or recyclable are addressed by the present disclosure.

SUMMARY

[0007] A composition including a bio-based and/or renewable polyol for production of a polyurethane (PU) article by an additive manufacturing method is provided by the present disclosure. The compositions and processes disclosed herein enable sustainable prototyping and part production by virtue of the bio-based and/or renewable polyols. Generally, the composition forms a bath for the additive manufacturing processes. The components may be mixed prior to being placed in a container for the bath, or alternatively, some of the components may be pre-mixed and placed in a container before other components. The composition forms a bath which may be cured by UV light, utilizing free radical polymerization.

[0008] In one form, a photo-curable composition for use in additive manufacturing is provided that comprises an isocyanate, a bio-based polyol, at least one functional blocking unit, a catalyst, a reactive diluent, at least one chain extender; and at least one photoinitiator. In a variation of the composition, at least one solvent and/or a filler may also be employed. The filler may be, by way of example, talc, fibers, and calcium carbonate.

[0009] The bio-based polyol is selected from the group consisting of vegetable oil, soy bean oil, rapeseed oil, canola oil, peanut oil, cashew oil, walnut oil, almond oil, cotton seed oil, neem seed oil, sunflower oil, safflower oil, olive oil, canola oil, grape seed oil, coconut oil, palm oil, linseed oil, castor oil, fish oil, algae oil, and from animal fat oil, among others as set forth herein. Further, the bio-based polyol in one form has average molecular weight from about 200 to 10,000 and may include about 50 to 80% primary hydroxyl groups, and more specifically, about 67% primary hydroxyl content.

[0010] In a variation of the composition, the bio-based polyol is a mixture of at least one bio-based polyol and at least one petroleum-based polyol.

[0011] In one form, the composition in weight percentage includes isocyanate of about 50 to 80 wt.%, the catalyst is about 0.01-0.5 wt.%, the reactive diluent is greater than zero and up to about 20 wt.%, the photoinitiator is about 0.1 to 2 wt.%, with a balance of the isocyanate, the functional blocking unit, and the chain

extender. In one form, the isocyanate is about 0.5 to 5 mol equivalent to polyol functionality, the at least one functional blocking unit is about 0.5 to 5 mol equivalent to polyol functionality, and the chain extender is about 0.1 to 1 mol equivalent to polyol functionality.

[0012] In another form of the present disclosure, a method of forming an article using an additive manufacturing process is provided that comprises mixing a photo-curable composition comprising an isocyanate, a bio-based polyol, at least one functional blocking unit, a catalyst, a reactive diluent, at least one chain extender, and at least one photoinitiator. The composition is then placed into a bath, and the additive manufacturing process is initiated. The bath is exposed to UV light, at least one or more portions of the bath are polymerized to form the article layer-by-layer, and then the formed article is exposed to an additional UV cure and/or thermal cure.

[0013] The additive manufacturing process is one of stereolithography (SLA) or digital light processing (DLP).

[0014] In one form of the method, the reactive diluent is added to the composition during the polymerizing step. Further, an additional component selected from the group consisting of at least one solvent and at least one filler may be added to the composition.

[0015] It should be understood that these various part configurations, scanning technologies, and methods of manufacture and assembly may be implemented individually or in any combination while remaining within the scope of the present disclosure.

[0016] Further areas of applicability will become apparent from the description provided herein. It should be understood that the description and specific examples are intended for purposes of illustration only and are not intended to limit the scope of the present disclosure.

DRAWINGS

[0017] In order that the disclosure may be well understood, there will now be described various forms thereof, given by way of example, reference being made to the accompanying drawings, in which:

[0018] FIG. 1 is a schematic view of a multifunctional polyol reacting with a catalyst to form a functionalized pre-polymer according to the teachings of the present disclosure;

[0019] FIG. 2 is a schematic view of the functionalized pre-polymer of FIG. 1 reacting with a catalyst to form an acrylated blocked polyurethane (PU) according to the teachings of the present disclosure;

[0020] FIG. 3 is a schematic view of the acrylated blocked PU of FIG. 2 being exposed to UV light and forming a crosslinked blocked prepolymer with unreacted chain extenders according to the teachings of the present disclosure;

[0021] FIG. 4 is a schematic view of the crosslinked blocked prepolymer of FIG. 3 forming segmented PU with a partially substituted network according to the teachings of the present disclosure; and

[0022] FIG. 5 is a flow diagram of a method of forming an article according to the teachings of the present disclosure.

[0023] The drawings described herein are for illustration purposes only and are not intended to limit the scope of the present disclosure in any way.

DETAILED DESCRIPTION

[0024] The following description is merely exemplary in nature and is not intended to limit the present disclosure, application, or uses. It should be understood that throughout the drawings, corresponding reference numerals indicate like or corresponding parts and features.

[0025] Various environmentally-friendly polymeric compositions are provided herein, which utilize a bio-based and/or renewable polyol(s). The composition is formed by free radical polymerization, which is a method of polymerization by which a polymer forms by the successive addition of free radical building blocks. Free radicals can be formed via a number of different mechanisms usually involving separate initiator molecules. Following its generation, the initiating free radical adds nonradical monomer units, thereby growing the polymer chain. To initiate the polymerization, radicals are formed. This may be done, for example, by heating the initiator until a bond is homolytically cleaved. Alternatively, UV radiation may be used to cleave a bond, producing free radicals.

[0026] The composition includes the following components: (A) isocyanate component, (B) polyol component, (C) functional blocking unit

component, (D) catalyst component, (E) reactive diluent component, (F) chain extender component, and (G) photoinitiator component. Additional components such as a solvent component (H), filler component (I), or the like may be added. Some of the components such as component (E), (H), and (I) may be optional.

[0027] Isocyanate Component

[0028] The isocyanate component provides reactivity with component (B), the polyol component, with the secondary amine group of the blocking agent, component (C), and primary amine or hydroxyl group of component (F), the chain extender. Component (A) should be non-reactive with water to prevent foaming of the composition. The isocyanate component (A) may include one type of isocyanate or a mixture of isocyanates. Example isocyanates include aliphatic and non-aliphatic di-(poly-) isocyanates such as methyl diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), meta-tetramethylxylylene diisocyanate (TMXDI), 4,4′-diisocyanato-methylenedicyclohexane, aromatic diisocyanates, or a combination thereof.

[0029] Polyol Component

[0030] Generally, the polyol component includes bio-based and/or renewable polyol(s) with existing bonds or chemical structures capable of reacting with UV light. The polyol may be a single polyol or a mixture of polyols forming a polyol component. The polyol component (B) includes a subcomponent (a) a bio-based and/or renewable polyol or a mixture of bio-based and/or renewable polyols, and an optional subcomponent (b) a petroleum-based polyol or mixture of polyols.

[0031] The bio-based and/or renewable polyol in one form is a modified vegetable oil. Any suitable bio-based oils, particularly vegetable oils, through which air has been passed to remove impurities, functionalize the oil with hydroxyl(-OH) group(s), epoxy(C-O-C) group(s), and/or to thicken the oil may be used. The bio-based and/or renewable polyol may be a hydroxyl- or epoxy-group containing polyol. The bio-based and/or renewable polyol in one form includes an epoxidized oil. Examples of suitable bio-based oils which may be used after being blown include vegetable or seed oils such as soy bean oil, rapeseed oil, canola oil, peanut oil, cashew oil, walnut oil, almond oil, cotton seed oil, neem seed oil, sunflower oil, safflower oil, olive oil, canola oil, grape seed oil, coconut oil, palm oil, linseed oil, castor oil, fish oil, algae oil, an oil derived from animal fats such as lanolin, or a combination thereof.

[0032] Example blown oils are described in U.S. Pat. Nos. 6,180,686 and 6,624,244, the contents of which are incorporated herein by reference in their entirety, and are commercially available under Urethane Soy Systems Company (USSC) under the name SoyOyl®. In at least one form, the bio-based polyol is SoyOyl® P38N. In another form, the bio-based polyol is BioBased Technologies Agrol Prime™ A-56 or BioBased Technologies Agrol Prime™ A-110.

[0033] The bio-based and/or renewable polyol includes a polyol having an average molecular weight from about 400 to 10,000, 1000 to 5000, or 200 to 3000. The bio-based and/or renewable polyol may include primary hydroxyl groups, secondary hydroxyl groups, or both. In one form, the bio-based and/or renewable polyol includes about 50 to 80%, 55 to 75%, or 60 to 70% primary hydroxyl groups. In still another form, the bio-based and/or renewable polyol has about 67% primary hydroxyl content.

[0034] The bio-based and/or renewable polyol in one form is a carbon dioxide-based polyol. Utilizing carbon dioxide as carbon feedstock for component (B) could reduce greenhouse gas emissions and lower dependency on fossil fuels. Using waste carbon dioxide from various industrial processes may result in a bio-based and/or renewable polyol with a low carbon footprint. In addition, waste carbon dioxide is significantly cheaper than petroleum-based resources. The carbon dioxide-based polyols may be based on the co-polymerization of carbon dioxide with epoxides to yield a polyol having 5, 10, 20, 30, 40, 50% or more by weight carbon dioxide.

[0035] As set forth above, a subcomponent (b), a petroleum-based polyol may be added to the composition. For example, the bio-based and/or renewable polyol may form 100, 98, 96, 94, 92, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45%, or less of the entire polyol component (B). The bio-based and/or renewable polyol may include between 0.5 and 100 wt. %, 5 to 75 wt. %, or 30 to 45 wt. % of the polyol component (a), based on the total weight of the polyol component; the remainder may be formed by the petroleum-based polyol (b). In yet another form, the petroleum-based polyol is entirely absent such that component (B) includes only bio-based and/or renewable polyol(s).

[0036] The petroleum-based polyol may include compounds having a number average molecular weight of from about 400 to 10,000, 470 to 8,000, or 1,000 to 6,500 and contain amino groups, hydroxyl groups, thiol groups, or a

combination thereof. These isocyanate-reactive compounds generally contain from 1 to 8 isocyanate-reactive groups, and in one form from 2 to 6 isocyanate-reactive groups. Suitable compounds include polyethers, polyesters, polyacetals, polycarbonates, polyesterethers, polyester carbonates, polythioethers, polyamides, polyesteramides, polysiloxanes, polybutadienes, polyacetones, the like, or a combination thereof.

[0037] Suitable hydroxyl-containing polyethers are known and commercially available. Such polyether polyols can be prepared, for example, by the polymerization of epoxides such as ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, styrene oxide, or epichlorohydrin, optionally in the presence of BF_3, or by chemical addition of such epoxides, optionally as mixtures or successively, to starting components containing reactive hydrogen atoms such as water, alcohols, or amines. Example polyethers include polyoxyalkylene polyether polyols such as polyoxyethylene diol, polyoxypropylene diol, polyoxybutylene diol, polytetramethylene diol, or a combination thereof.

[0038] Hydroxyl-containing polyesters are also suitable for use in component (B). Suitable hydroxyl-containing polyesters include reaction products of polyhydric alcohols (preferably diols), optionally with the addition of trihydric alcohols, and polybasic (preferably dibasic) carboxylic acids. Instead of free polycarboxylic acids, the corresponding polycarboxylic acid anhydrides or corresponding polycarboxylic acid esters of lower alcohols or mixtures thereof may be used for preparing the polyesters. The polycarboxylic acids may be aliphatic, cycloaliphatic, aromatic, or heterocyclic and may be substituted, *e.g.*, by halogen atoms, and/or unsaturated.

[0039] Suitable polyacetals include compounds obtained from the condensation of glycols such as diethylene glycol, triethylene glycol, 4,4′-dihydroxydiphenylmethane, and hexanediol, with formaldehyde or by the polymerization of cyclic acetals such as trioxane.

[0040] Suitable polycarbonates include those prepared by the reaction of diols such as 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, tetraethylene glycol, or thiodiglycol, with phosgene or diaryl carbonates such as diphenyl carbonate.

[0041] Suitable polyester carbonates include those prepared by the reaction of polyester diols with or without other diols such as 1,3-propanediol, 1,4-

butanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, tetraethylene glycol, or thiodiglycol with phosgene, cyclic carbonates, or diaryl carbonates such as diphenyl carbonate. Suitable polyester carbonates more generally include compounds such as those disclosed in U.S. Pat. No. 4,430,484, which is incorporated herein by reference in its entirety.

[0042] Suitable polythioethers include the condensation products obtained by the reaction of thiodiglycol, either alone or with other glycols, formaldehyde, or amino alcohols. The products obtained are polythio-mixed ethers, polythioether esters, or polythioether ester amides, depending on the components used.

[0043] Suitable polyester amides and polyamides include, for example, the predominantly linear condensates prepared from polybasic saturated and unsaturated carboxylic acids or the anhydrides thereof and polyvalent saturated or unsaturated amino alcohols, diamines, polyamines, and mixtures thereof.

[0044] The polyol component (B) may contain primary polyol, secondary polyol, or a combination thereof. The polyol(s) according to the present disclosure include primary or secondary hydroxyl functionality, may be multi-functional (tris- or greater), and may include unsaturated linkages or be free from unsaturated linkages. The polyol component (B) may be any polyol or a mixture of polyols with hydroxy group(s), epoxy group(s), or both. The polyol component may include bio-based and/or renewable polyol(s) with existing bonds or chemical structures capable of reacting with UV light. Such polyols may have enhanced reactivity due to naturally occurring double bonds. Thus, the polyols may be used in the composition as component (B) without any modification. Yet, such polyols may result in a less-controlled polymerization process. Alternatively, the polyol component (B) may include polyol(s) modified to react with UV light, crosslink, and/or polymerize in a predetermined way. The modification may afford more control over the forming process. For example, polyol(s) having acrylate functionality may be modified to have hydroxy group(s), epoxy group(s), or both. The modification may include changing external linkages, altering chemical properties, modifying chain length, adjusting stiffness of bonds of the polyols, or a combination thereof.

[0045] Functional Blocking Unit

[0046] As set forth above, the composition according to the present disclosure further includes component (C), a functional blocking unit or a blocking

agent. Prior to polymerization, a prepolymer combines with the functional blocking unit (C) to form a blocked prepolymer. The blocking agent (C) then provides reversible reactivity with the isocyanate group during the application of heat in the thermal cure stage of the process. The blocking agent (C) in one form contains a free radical reactive group. The blocking agent (C) may include ε-caprolactam, methyl ether ketoxime (butanone oxime), secondary amines, triazole derivatives and pyrazole derivatives, or a combination thereof. The blocking unit may be, for example, 2-(tert-butylamino)ethyl methacrylate (TBAEMA). Further, the blocking agent (C) may include other chemistry capable of adjusting the polyol in a desirable way.

[0047] Catalyst Component

[0048] The isocyanate component (A) is reacted with the polyol component (B) in the presence of a catalyst component (D) to form a prepolymer. For component (D), any suitable catalyst capable of controlling reaction kinetics may be used. For example, an environmentally-friendly catalyst may be used. Alternatively, typically used catalysts such as organo-metallic tin compounds may be used. If an environmentally undesirable catalyst is used, it may be removed from the bath after the prepolymer is formed.

[0049] Example catalyst may include tributylamine, triethylenediamine, benzyldmethylamine, N-methylmorpholine, N-ethylmorpholine, N,N,N′,N′-tetramethylethylene diamine, pentamethyldiethylene triamine, and higher homologs, 1,4-diazabicyclo[2.2.2]octane, N-methyl-N′-(dimethylaminoethyl)piperazine, bis(dimethylaminoalkyl)piperazines, N,N-dimethylbenzylamine, N,N-dimethylcyclohexylamine, N,N-diethylbenzylamine, bis(N,N-diethylaminoethyl)adipate, N,N,N′,N′-tetramethyl-1,3-butanediamine, N,N-dimethyl-β-phenylethylamine, N,N,N',N",N"-pentamethyl-dipropylenetriamine, 1,2-dimethylimidazole, 2-methylimidazole, 1,3-propanediamine, N'-(3-(dimethylamino)propyl)-N,N-dimethyl, monocyclic and bicyclic amidines, bis(dialkylamino)alkyl ethers (U.S. Pat. No. 3,330,782), tertiary amines containing amide groups (preferably formamide groups), or a combination thereof.

[0050] Suitable catalysts include tertiary amines containing isocyanate reactive hydrogen atoms. Examples of such catalysts include triethanolamine, triisopropanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, N,N-dimethylethanolamine, their reaction products with alkylene oxides (such as

propylene oxide and/or ethylene oxide), secondary-tertiary amines, or a combination thereof.

[0051] Other suitable catalysts include organo-metallic compounds, especially organic tin, bismuth, and zinc compounds. Suitable organic tin compounds include those containing sulfur such as dioctyl tin mercaptide, tin(II) salts of carboxylic acids such as tin(II) acetate, tin(II) octoate, tin(II) ethylhexoate, and tin(II) laurate, as well as tin(IV) compounds such as dibutyltin dilaurate, dibutyltin dichloride, dibutyltin diacetate, dibutyltin maleate, and dioctyltin diacetate. Suitable bismuth compounds include bismuth neodecanoate, bismuth versalate, and various bismuth carboxylates. Suitable zinc compounds include zinc neodecanoate and zinc versalate. Mixed metal salts containing more than one metal such as carboxylic acid salts containing both zinc and bismuth are also suitable catalysts.

[0052] Reactive Diluent

[0053] The composition according to the present disclosure further includes component (E), the reactive diluent component. The additive manufacturing process requires the polyol component (B) to have reduced viscosity and enhanced sensitivity to UV light compared to polyols used in typical PU manufacturing. The printing process requires low viscosity of about 1 cps to 10,000 cps (centipoise), 500 cps to 8,000 cps, or 1,000 cps to 5,000 cps to enable proper 3D printing. Additionally, increased sensitivity to UV light is desired for UV-curing of the composition. Due to all of these factors, the composition includes one or more diluents (E). The diluents may be added to the composition prior to placement in the 3D printing bath or during the polymerization/3D printing process. Generally, the reactive diluents decrease viscosity of the composition to improve flow during processing, increase molecular weight of the composition, provide additional reactive sites for free radical polymerization, increase sensitivity to UV light of the composition, or a combination thereof.

[0054] Non-limiting examples of diluents include methyl methacrylates, acrylates, alkylene carbonates, methacrylics, the like, or a combination thereof. In another form, the reactive diluent may include methacrylate such as diethylene glycol methylacrylate, alkylene carbonates, isoborynyl methacrylate, di(ethylene glycol) methyl ether methacrylate, the like, or a combination thereof.

[0055] Chain Extender

[0056] The chain extender, component (F), is incorporated into the prepolymer during thermal cure and following polymerization. The amine or hydroxyl containing compounds of the chain extender rapidly react with free isocyanate groups to prevent melting during thermal post-processing. Any suitable chain extender may be used and generally has a selected stiffness to alter hard segment properties of the resultant poly-urethane/poly-urea network. Non-limiting example chain extenders include hydroxyl-containing chain extenders such as glycols and polyols, hydroxyl-containing polyethers having a molecular weight of less than 399 such as polyoxyalkylene polyether polyols and amine chain extenders such as those containing exclusively aromatically bound primary or secondary (preferably primary) amino groups and which may also contain alkyl substituents. The chain extender may further include diamines such as cyclic aliphatic diamines, low molecular weight, high functionality-containing polyols, epoxy curatives, the like, or a combination thereof. A non-limiting example of a chain extender may include 1,4-butanediol, ethylene glycol, triethanolamine, diaaminodicyclohyxyl methane, castor oil polyol, cycloaliphatic amine, modified cyclo-aliphatic amine adducts, isophorondiamine, or a combination thereof.

[0057] Photoinitiator

[0058] Because the additive manufacturing processes to which the teachings of the present disclosure are applied utilize photopolymerization, the photoinitiator component (G) includes one or more photoinitiators which convert absorbed UV light energy into chemical energy in the form of initiating species such as free radicals or cations. Photoinitiators are thus sensitive to UV light, undergo a photoreaction on absorption of light, and produce the reactive species. Photoinitiators initiate and/or catalyze the polymerization reaction of the composition upon exposure of the composition to UV light.

[0059] The type of initiator used depends on the wavelength range in which they will activate. A UV light source emits in the 200 to 400 nm wavelength range. Thus, a photoinitiator absorbing in the 200 to 400 nm wavelength range may be used. Examples of suitable photoinitiators absorbing in this area include those with free radical initiating function, cationic initiating function, or both. The photoinitiators may thus polymerize through double bonds, epoxy groups, or both.

[0060] The photoinitiator may include benzoylphosphine oxides, aryl ketones, benzophenones, hydroxylated ketones, 1-hydroxyphenyl ketones, α-

Aminoketone, α-Hydroxyketone, ketals, metallocenes, BAPO, MAPO, phosphine oxides, or a combination thereof. The photoinitiator may include benzoylphosphine oxides such as, for example, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, 2,4,6-trimethylbenzoyl phenyl, ethoxy phosphine oxide, bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1, 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone, 2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one, 4-benzoyl-4′-methyl diphenyl sulphide, 4,4′-bis(diethylamino) benzophenone, 4,4′-bis(N,N′-dimethylamino)benzophenone, bis (eta 5-2,4-cyclopentadien-1-yl) bis [2,6-difluoro-3-(1H-pyrrol-1-yl) phenyl]titaniumor, the like, or a combination thereof.

[0061] The photoinitiator may include onium salts, halonium salts, iodosyl salts, selenium salts, sulfonium salts, sulfoxonium salts, diazonium salts, metallocene salts, isoquinolinium salts, phosphonium salts, arsonium salts, tropylium salts, dialkylphenacylsulfonium salts, thiopyrilium salts, diaryl iodonium salts, triaryl sulfonium salts, sulfonium antimonate salts, ferrocenes, di(cyclopentadienyliron)arene salt compounds, pyridinium salts, or a combination thereof. The photoinitiator may include aromatic diazonium salts, aromatic sulfonium salts, aromatic iodonium salts, metallocene based compounds, aromatic phosphonium salts and silanol aluminum complexes.

[0062] The photoinitiator component (G) may further include one or more photosensitizers. Photosensitizers enhance the polymerization reaction by absorbing UV light and transferring the energy to the desired reactants. Examples of suitable photosensitizers include anthraquinones such as 2-methylanthraquinone, 2-ethylanthraquinone, 2-tertbutylanthraquinone, 1-chloroanthraquinone, and 2-amylanthraquinone, thioxanthones and xanthones such as isopropyl thioxanthone, 2-chlorothioxanthone, 2,4-diethylthioxanthone, and 1-chloro-4-propoxythioxanthone, methyl benzoyl formate, methyl-2-benzoyl benzoate, 4-benzoyl-4′-methyl diphenyl sulphide, 4,4′-bis(diethylamino)benzophenone, or a combination thereof.

[0063] Solvents

[0064] The composition may further include one or more solvents as component (H). The solvent should be as environmentally friendly as possible. Non-limiting examples of component (H) include alcohols, dichloromethane, chloroform, ethylene chloride, ethyl acetate, N-hexane, methanol, the like, or a combination thereof.

[0065] Fillers

[0066] The composition may also include one or more fillers (I). The fillers may be added to fine-tune properties of the resin, the formed article, or both. The fillers may modify one or more of the following properties of the formed article: dimensional stability over time, functionality, durability, good wear-resistance, fade-resistance, chemical-resistance, water-resistance, UV-resistance, good thermal resistance, memory retention, desired gloss, color, mechanical properties such as toughness, strength, dimensional stability, the like, or a combination thereof. Non-limiting examples of component (I) may be talc, fibers such as natural or synthetic fibers, $CaCO_3$, or other non-UV absorbing compounds that do not interfere with the cure.

[0067] Weight Percentages

[0068] Weight percentages of individual components may differ. Based on the total weight of the composition, the following components may have the following weight percentages: component (B) may form 50 to 80, 55 to 75, or 60 to 70 wt.%, component (D) may form about 0.01-0.5, 0.05 to 0.25, or 0.08 to 0.1 wt.%, component (E) may form about 0 to 20, 1 to 15, or 5 to 10 wt.%, component (G) may form about 0.1 to 2, 0.25 to 1.5, or 0.5 to 1 wt.%, and components (A), (C), (F), (H) and/or (I) may form the balance. The amount of components (A), (C), and (F) is determined based on the amount of polyol functionality in the following manner: the composition may include component (A) in the amount of about 0.5 to 5, 1 to 4, or 2.1 to 2.8 mol equivalent to polyol functionality, component (C) in the amount of about 0.5 to 5, 1 to 4, or 2.1 to 2.8 mol equivalent to polyol functionality, and component (F) in the amount of about 0.1 to 1, 0.2 to 0.8, or 0.3 to 0.5 mol equivalent to polyol functionality.

[0069] Referring to FIGS. 1-4, the composition including one or more components (A)-(I) named above undergoes polymerization upon exposure to UV light and a network re-arrangement during a thermal cure. A schematic reaction of the components forming the composition before and upon exposure to UV light and elevated temperature during the thermal cure is shown.

[0070] As shown in FIG. 1, component (A) and component (B) react in the presence of component (D) to form a pre-polymer.

[0071] As further shown in FIG. 2, the pre-polymer is modified in the presence of component (D) with component (C) to add functional blocking units to chain terminals. An acrylated blocked PU (ABPU) is thus formed.

[0072] Referring now to FIG. 3, the blocked PU, components (E), (F), and (G) are exposed to UV light. Polymerization is initiated and results in a formation of a crosslinked blocked diisocyanate prepolymer containing unreacted chain extenders, component (F).

[0073] And turning to FIG. 4, the photo-crosslinked blocked diisocyanate prepolymer having poly-urethane network and unreacted component (F) are exposed to elevated temperature during thermal cure. During thermal cure, the blocking functional unit is cleaved off and diisocyanate prepolymer is re-formed to quickly react with component (F). Thermal cure results in formation of segmented thermoplastic PU having partially substituted poly-urethane/poly-urea network.

[0074] Referring to FIG. 5, the additive manufacturing or 3D printing process may include preparing a bath suitable for forming a 3D article from the composition according to the teachings of the present disclosure. The process generally includes combining the components, which may be combined separately or at the same time. Alternatively, the process may include adding one or more components to the composition forming a bath later than the remaining components. For example, one or more reactive diluents, photoinitiator(s), or chain extender(s) may be mixed with the other components immediately before being placed in the bath for polymerization.

[0075] The 3D printing process generally includes mixing the combined components, placing the composition into a container, preparing a CAD file including data about an article to be formed, supplying the CAD data to software in a computer, initiating the 3D printing process, exposing the bath to UV light, polymerizing at least one or more portions of the bath according to the CAD data, forming the article layer-by-layer according to the CAD data, and exposing the formed article to additional UV cure and/or thermal cure.

[0076] The forming process may include one or more curing stages. The curing stages may include UV cure, and/or thermal cure. The UV cure may precede the thermal cure. Alternatively, the UV cure and the thermal cure may run consecutively for at least a portion of the process.

[0077] The length of the UV and/or thermal post-treatment depends on the dimensions and complexity of the article to be formed. The length of the UV cure may be about 5 second to 2 hours, 10 seconds to 1.5 hours, or 20 seconds to 1 hour. The temperature during the UV cure may be about room temperature (18 to 25°C). A higher or lower temperature is contemplated as photoinitiation and UV-cure are not temperature dependent.

[0078] The process includes raising the temperature to an elevated temperature during the thermal cure or prior to thermal cure. The thermal cure is initiated post-printing. Alternatively, the temperature may be elevated during the UV post-cure such that UV post-cure and thermal cure overlap, at least during a portion of the process. The temperature may be elevated gradually. Alternatively, the temperature may be raised intermittently. The elevated temperature during the thermal cure may be about 25°C to 350°C, 50°C to 200°C, or 100°C to 250°C. The length of the thermal cure may be about 5 minutes to 8 hours, 10 minutes to 4 hours, or 30 minutes to 20 hours.

[0079] The formed article may comply with a variety of automotive testing methods such as an exterior weathering test procedure ASTM D7869, resistance to interior weathering ISO 105 A-02, SAE J2412, soiling and cleanability ISO 105-A03, fogging SAE J1756, flammability ISO 3795, and/or other tests such as impact resistance at room temperature, scratch resistance, odor testing, stress cracking.

[0080] A number of additive manufacturing methods may be used to form a 3D article from the compositions disclosed herein. The additive manufacturing methods/processes, which are also referred to interchangeably as 3D printing methods or processes, utilizing the compositions disclosed herein cure the compositions by UV light, thermal radiation, or a combination thereof, among other sources for photocuring of the compositions. Example additive manufacturing technologies include stereolithography (SLA) or digital light processing (DLP). As known in the art, both SLA and DLP use light to turn a liquid resin into a solid article, a layer at a time. UV light is utilized to cause polymerization. SLA uses two motors, known as galvanometers or galvos, (one on the X axis and one on the Y axis) to rapidly aim a laser beam across the print area, solidifying resin as it goes along. This process breaks down the design, layer by layer, into a series of points and lines that are given to the galvos as a set of coordinates. In contrast, DLP uses a digital

projector screen to flash a single image of each layer across the entire platform at once. Because the projector is a digital screen, the image of each layer is composed of square pixels, resulting in a layer formed from small rectangular bricks called voxels. In comparison with SLA, DLP may achieve faster print times for some parts as each entire layer is exposed at once rather than drawn out with a laser. Since DLP resolution depends on the projector while a SLA printer's build volume is completely independent from the resolution of the print, the choice of a specific additive manufacturing technology depends on the complexity and amount of components to be manufactured. DLP has a shallower bath than SLA. While SLA and DLP are mentioned, the two named technologies are only example technologies, and the formulas described herein may likewise be applicable in other additive manufacturing techniques. After polymerization, the formed article may be exposed to elevated temperature or further UV radiation to continue and/or expedite cross-linking.

[0081] Similarly, while the discussion herein focuses on polymeric articles used within the interior of a vehicle, the formed article may be any suitable component in any vehicle. Non-limiting example types of applicable vehicles include land vehicles such automobiles, buses, vehicles for transportation of goods, motorcycles, off-road vehicles, tracked vehicles, trains, amphibious vehicles, aircrafts, space crafts, watercrafts, or the like. The suitable component may be an interior trim, handle(s), knob(s), bracket(s), console component(s), cup holder(s), gasket(s), electrical connector(s), and the like.

[0082] Unless otherwise expressly indicated herein, all numerical values indicating mechanical/thermal properties, compositional percentages, geometric dimensions and tolerances, or other characteristics are to be understood as modified by the word "about" or "approximately" in describing the scope of the present disclosure.

[0083] The description of the disclosure is merely exemplary in nature and, thus, variations that do not depart from the substance of the disclosure are intended to be within the scope of the disclosure. Such variations are not to be regarded as a departure from the spirit and scope of the disclosure.

CLAIMS

What is claimed is:

1. A photo-curable composition for use in additive manufacturing comprising: an isocyanate;
a bio-based polyol;
at least one functional blocking unit;
a catalyst;
a reactive diluent;
at least one chain extender; and
at least one photoinitiator.

2. The photo-curable composition according to Claim 1 further comprising at least one solvent.

3. The photo-curable composition according to Claim 1 further comprising at least one filler.

4. The photo-curable composition according to Claim 3, wherein the filler is selected from the group consisting of talc, fibers, and calcium carbonate.

5. The photo-curable composition according to Claim 1, wherein the bio-based polyol is selected from the group consisting of vegetable oil, soy bean oil, rapeseed oil, canola oil, peanut oil, cashew oil, walnut oil, almond oil, cotton seed oil, neem seed oil, sunflower oil, safflower oil, olive oil, canola oil, grape seed oil, coconut oil, palm oil, linseed oil, castor oil, fish oil, algae oil, and from animal fat oil.

6. The photo-curable composition according to Claim 1, wherein the bio-based polyol has average molecular weight from about 200 to 10,000.

7. The photo-curable composition according to Claim 1, wherein the bio-based polyol includes about 50 to 80% primary hydroxyl groups.

8. The photo-curable composition according to Claim 7, wherein the bio-based polyol has about 67% primary hydroxyl content.

9. The photo-curable composition according to Claim 1, wherein the bio-based polyol is a mixture of at least one bio-based polyol and at least one petroleum-based polyol.

10. The photo-curable composition according to Claim 1, wherein:
the isocyanate is about 50 to 80 wt.%;
the catalyst is about 0.01-0.5 wt.%;
the reactive diluent is greater than zero and up to about 20 wt.%;
the photoinitiator is about 0.1 to 2 wt.%; and
a balance of the isocyanate, the functional blocking unit, and the chain extender.

11. The photo-curable composition according to Claim 10, wherein the isocyanate is about 0.5 to 5 mol equivalent to polyol functionality, the at least one functional blocking unit is about 0.5 to 5 mol equivalent to polyol functionality, and the chain extender is about 0.1 to 1 mol equivalent to polyol functionality.

12. A method of forming an article using an additive manufacturing process comprising:

mixing a photo-curable composition comprising:

an isocyanate;

a bio-based polyol;

at least one functional blocking unit;

a catalyst;

a reactive diluent;

at least one chain extender; and

at least one photoinitiator;

placing the composition into a bath;

initiating the additive manufacturing process;

exposing the bath to UV light;

polymerizing at least one or more portions of the bath and forming the article layer-by-layer; and

exposing the formed article to an additional UV cure and/or thermal cure.

13. The method according to Claim 12, wherein the additive manufacturing process is one of stereolithography (SLA) or digital light processing (DLP).

14. The method according to Claim 12, wherein the reactive diluent is added to the composition during the polymerizing step.

15. The method according to Claim 12 further comprising an additional component selected from the group consisting of at least one solvent and at least one filler.

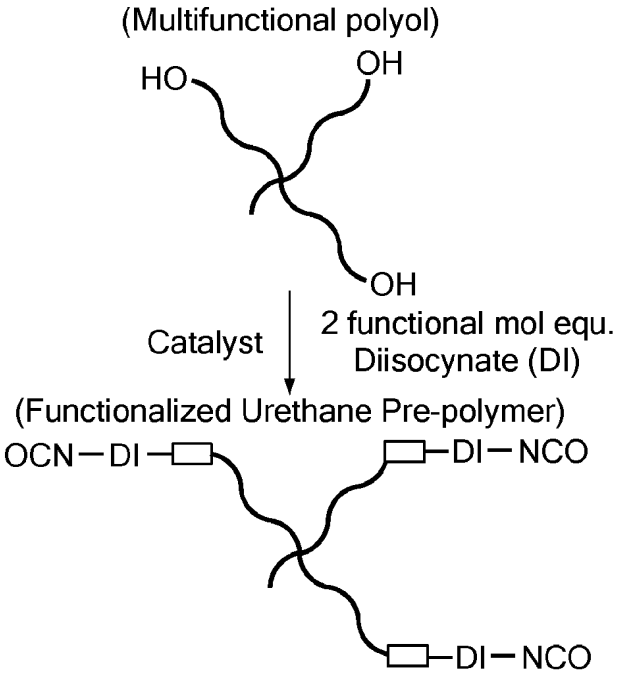

(Multifunctional polyol)
HO
OH
OH
Catalyst
2 functional mol equ.
Diisocynate (DI)
(Functionalized Urethane Pre-polymer)
OCN—DI—
—DI—NCO
—DI—NCO

FIG. 1

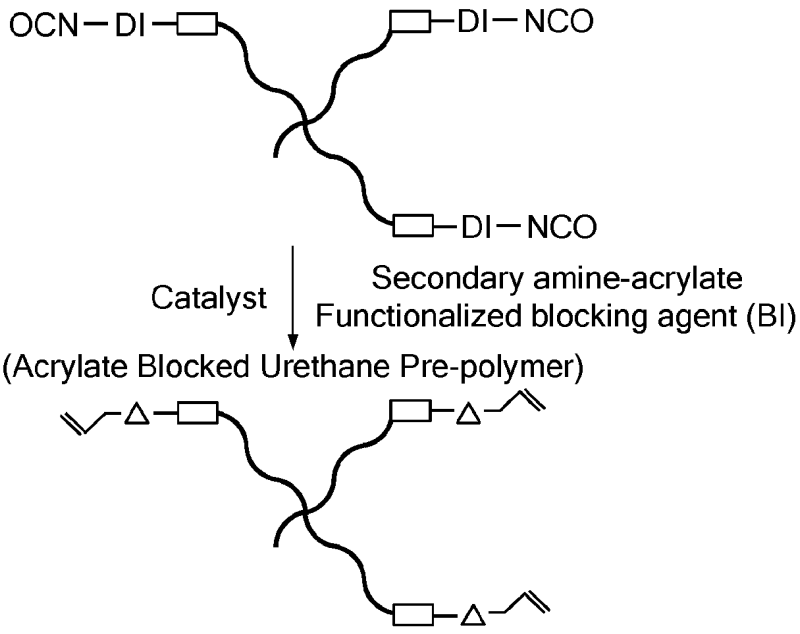

OCN—DI—
—DI—NCO
—DI—NCO
Catalyst
Secondary amine-acrylate
Functionalized blocking agent (BI)
(Acrylate Blocked Urethane Pre-polymer)

FIG. 2

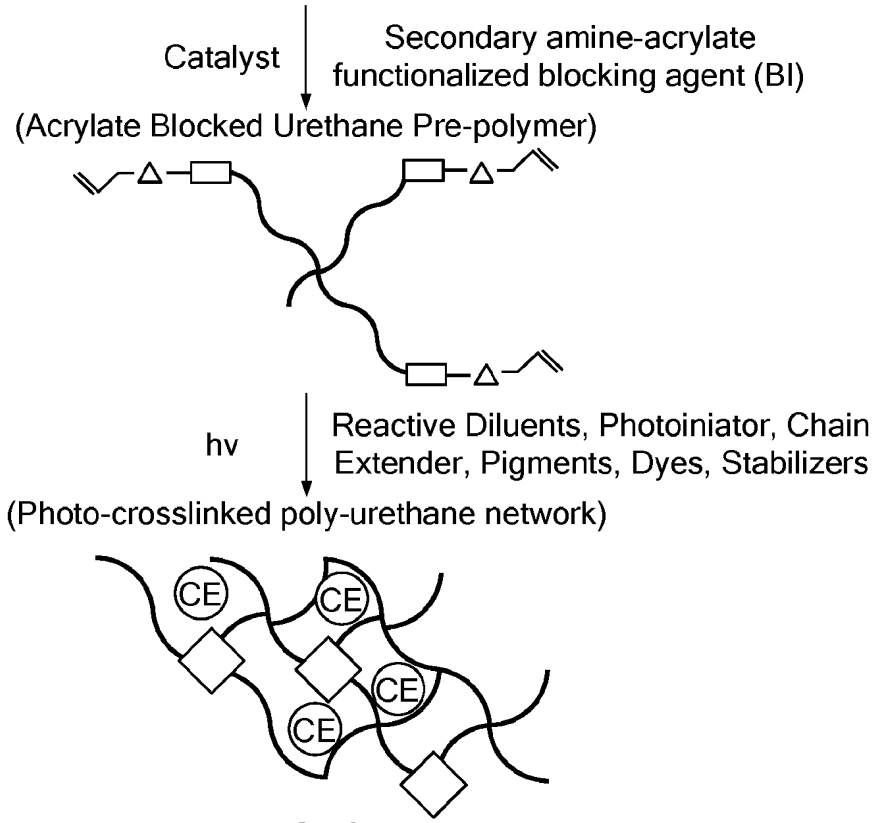

Catalyst
Secondary amine-acrylate functionalized blocking agent (BI)
(Acrylate Blocked Urethane Pre-polymer)
hv
Reactive Diluents, Photoiniator, Chain Extender, Pigments, Dyes, Stabilizers
(Photo-crosslinked poly-urethane network)
CE
CE
CE
CE

FIG. 3

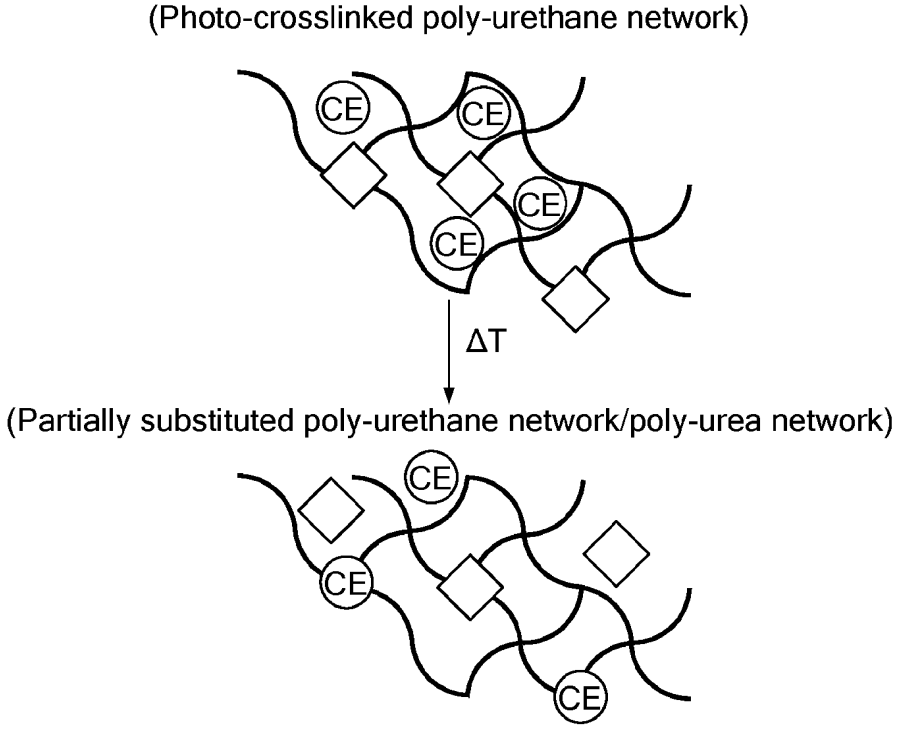

(Photo-crosslinked poly-urethane network)
CE
CE
CE
CE
ΔT
(Partially substituted poly-urethane network/poly-urea network)
CE
CE
CE

FIG. 4

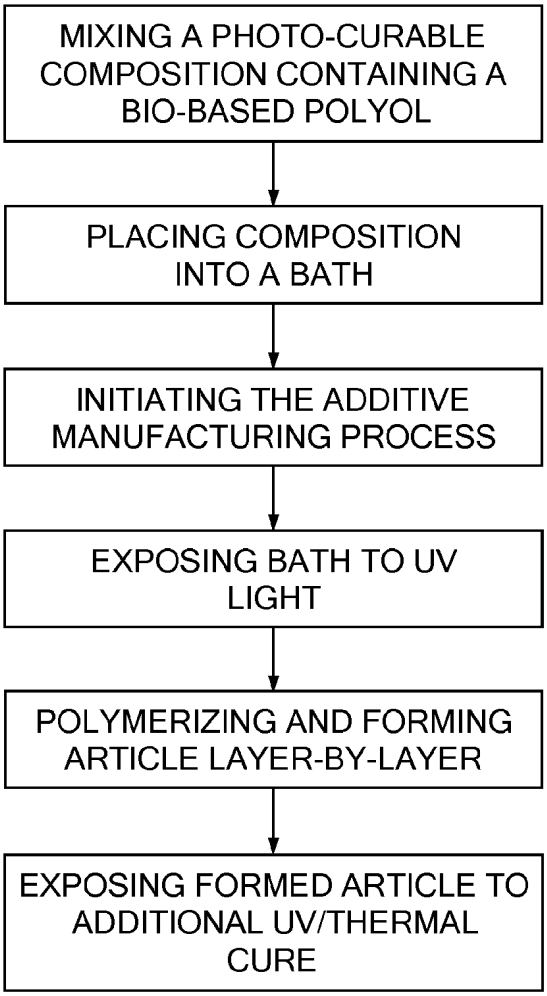

MIXING A PHOTO-CURABLE COMPOSITION CONTAINING A BIO-BASED POLYOL
PLACING COMPOSITION INTO A BATH
INITIATING THE ADDITIVE MANUFACTURING PROCESS
EXPOSING BATH TO UV LIGHT
POLYMERIZING AND FORMING ARTICLE LAYER-BY-LAYER
EXPOSING FORMED ARTICLE TO ADDITIONAL UV/THERMAL CURE

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/024754

A. CLASSIFICATION OF SUBJECT MATTER
INV. B29C64/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/369096 A1 (ROLLAND JASON P [US] ET AL) 22 December 2016 (2016-12-22) claim 1; figures 25B,25C examples 16,17 -----	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 June 2018	13/06/2018

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Bergmeier, Martin

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2018/024754

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2016369096 A1	22-12-2016	AU 2015280230 A1	08-12-2016
		AU 2015280283 A1	15-12-2016
		AU 2015280289 A1	08-12-2016
		BR 112016029755 A2	22-08-2017
		BR 112016029766 A2	22-08-2017
		BR 112016029793 A2	22-08-2017
		CA 2950209 A1	30-12-2015
		CA 2950213 A1	30-12-2015
		CA 2950215 A1	30-12-2015
		CN 106687861 A	17-05-2017
		CN 106796392 A	31-05-2017
		CN 107077064 A	18-08-2017
		EP 3157722 A1	26-04-2017
		EP 3158398 A1	26-04-2017
		EP 3158399 A1	26-04-2017
		EP 3158400 A1	26-04-2017
		JP 2017524565 A	31-08-2017
		JP 2017524566 A	31-08-2017
		JP 2017527637 A	21-09-2017
		KR 20170018067 A	15-02-2017
		KR 20170018451 A	17-02-2017
		KR 20170023977 A	06-03-2017
		SG 11201610189U A	27-01-2017
		SG 11201610191P A	27-01-2017
		SG 11201610192Y A	27-01-2017
		US 2016136889 A1	19-05-2016
		US 2016137838 A1	19-05-2016
		US 2016137839 A1	19-05-2016
		US 2016160077 A1	09-06-2016
		US 2016369096 A1	22-12-2016
		US 2017151718 A1	01-06-2017
		US 2017239887 A1	24-08-2017
		WO 2015200173 A1	30-12-2015
		WO 2015200179 A1	30-12-2015
		WO 2015200189 A1	30-12-2015
		WO 2015200201 A1	30-12-2015

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

To: MICHAEL N. MERCANTI
LUCAS & MERCANTI, LLP
30 BROAD STREET, 21 FLOOR
NEW YORK, NY 10004

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT AND THE WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

Applicant's or agent's file reference GRAN-1012-W	Date of mailing *(day/month/year)* 18 NOV 2020 **FOR FURTHER ACTION** See paragraphs 1 and 4 below
International application No. PCT/US 20/46170	International filing date *(day/month/year)* 13 August 2020 (13.08.2020)
Applicant GRANT INDUSTRIES, INC.	

1. ☒ The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

   Filing of amendments and statement under Article 19:
   The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

   When? The time limit for filing such amendments is normally two months from the date of transmittal of the international search report.

   How? Directly to the International Bureau preferably through ePCT, or on paper to:
   The International Bureau of WIPO, 34, chemin des Colombettes, 1211 Geneva 20, Switzerland

   For more detailed instructions, see the *PCT Applicant's Guide*, International Phase, paragraphs 9.004 – 9.011.

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.

3. ☐ **With regard to any protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:
   - ☐ the protest together with the decision thereon has been transmitted to the International Bureau together with any request to forward the texts of both the protest and the decision thereon to the designated Offices.
   - ☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Reminders**

   The applicant may **submit comments on an informal basis on the written opinion of the International Searching Authority** to the International Bureau. These comments will be made available to the public after international publication. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established.

   Shortly after the expiration of **18 months from the priority date, the international application will be published** by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau before the completion of the technical preparations for international publication (Rules 90*bis*.1 and 90*bis*.3).

   Within **19 months** from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase **until 30 months** from the priority date (in some Offices even later); otherwise, the applicant must, **within 20 months** from the priority date, perform the prescribed acts for **entry into the national phase** before those designated Offices. In respect of other designated Offices, the time limit of **30 months** (or later) will apply even if no demand is filed within 19 months. For details about the applicable time limits, Office by Office, see www.wipo.int/pct/en/texts/time_limits.html and the *PCT Applicant's Guide*, National Chapters.

   Within **22 months from the priority date, the applicant may request that a supplementary international search be carried out** by a different International Searching Authority that offers this service (Rule 45*bis*.1). The procedure for requesting supplementary international search is described in the *PCT Applicant's Guide*, International Phase, paragraphs 8.006-8.032.

Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Lee Young Telephone No. PCT Helpdesk: 571-272-4300

Form PCT/ISA/220 (revised January 2020)

Voluntary Amendment Due: January 18, 2021

Response to Search Report Due: February 18, 2021

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference		FOR FURTHER ACTION
GRAN-1012-W		see Form PCT/ISA/220 as well as, where applicable, item 5 below.
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US 20/46170	13 August 2020 (13.08.2020)	30 August 2019 (30.08.2019)
Applicant GRANT INDUSTRIES, INC.		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 2 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of:

☒ the international application in the language in which it was filed.

☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).

c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (see Box No. II).

3. ☐ **Unity of invention is lacking** (see Box No. III).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the **drawings**,

a. the figure of the **drawings** to be published with the abstract is Figure No._____

☐ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

b. ☒ none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 20/46170

A. CLASSIFICATION OF SUBJECT MATTER

IPC - A61K 8/02; A61K 8/06; A61K 8/19 (2020.01)

CPC - A61K 8/0241; A61K 8/062; A61K 8/19

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2015/0128335 A1 (Dehni) 14 May 2015 (14.05.2015) Para [0004]; [0025]; [0032]; [0033]; [0034]; [0036]; [0038]; [0042]; [0068]; [0087]; [0110]	1-10, 12, and 16-18 ---------- 11, 13-15, and 19-34
Y	US 2003/0092932 A1 (Tong et al.) 15 May 2003 (15.05.2003) Para [0001]; [0011]; [0012]; [0025]	11
Y	US 2018/0371149 A1 (Massachusetts Institute of Technology) 27 December 2018 (27.12.2018) Para [0004]; [0019]; [0035]; [0077]	13-15 and 19-20
Y	US 2013/0079486 A1 (Hidesaki et al.) 28 March 2013 (28.03.2013) Para [0017]	15
Y	US 2011/0045983 A1 (Healy et al.) 24 February 2011 (24.02.2011) Para [0005]; [0006]; [0021]; [0026]; [0043]; [0066]	21-34

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 October 2020	18 NOV 2020
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Lee Young Telephone No. PCT Helpdesk: 571-272-4300

Form PCT/ISA/210 (second sheet) (July 2019)

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To: MICHAEL N. MERCANTI
LUCAS & MERCANTI, LLP
30 BROAD STREET, 21 FLOOR
NEW YORK, NY 10004

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing *(day/month/year)*	18 NOV 2020
Applicant's or agent's file reference: GRAN-1012-W	FOR FURTHER ACTION: See paragraph 2 below

International application No.	International filing date *(day month year)*	Priority date *(day/month/year)*
PCT/US 20/46170	13 August 2020 (13.08.2020)	30 August 2019 (30.08.2019)

International Patent Classification (IPC) or both national classification and IPC

IPC - A61K 8/02; A61K 8/06; A61K 8/19 (2020.01)

CPC - A61K 8/0241; A61K 8/062; A61K 8/19

Applicant GRANT INDUSTRIES, INC.

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA/US	Date of completion of this opinion	Authorized officer
Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	25 October 2020	Lee Young PCT Help Desk Telephone No. 571-272-4300

Form PCT/ISA/237 (cover sheet) (revised January 2019)

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/46170

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed.

   ☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(b)).

3. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing:

   a. ☐ forming part of the international application as filed:

      ☐ in the form of an Annex C/ST.25 text file.

      ☐ on paper or in the form of an image file.

   b. ☐ furnished together with the international application under PCT Rule 13*ter*.1(a) for the purposes of international search only in the form of an Annex C/ST.25 text file.

   c. ☐ furnished subsequent to the international filing date for the purposes of international search only:

      ☐ in the form of an Annex C/ST.25 text file (Rule 13*ter*.1(a)).

      ☐ on paper or in the form of an image file (Rule 13*ter*.1(b) and Administrative Instructions, Section 713).

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that forming part of the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/46170

Box No. V **Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Claims	2, 5-6, 8-9, 11, 13-15, and 19-34	YES
	Claims	1, 3-4, 7, 10, 12, and 16-18	NO
Inventive step (IS)	Claims	none	YES
	Claims	1-34	NO
Industrial applicability (IA)	Claims	1-34	YES
	Claims	none	NO

2. Citations and explanations:

Claims 1,3-4, 7, 10, 12, 16-18 lack novelty under PCT Article 33(2) as being anticipated by US 2015/0128335 A1 to Dehni (hereinafter Dehni).

Regarding claim 1, Dehni discloses a cross-linked polyurethane elastomer rubber composition (Para [0042] In the hard foam, the hydrophilic silicone elastomer is cross-linked with another polymeric silicone and with polyurethane polymer. In the case of a Si-OH group reaction with an electrophilic group on a polyurethane compound...will result in a cross-linked elastomer-polyurethane composition), comprising a cross-linked polyurethane elastomer rubber (Para [0032] Flexible polyurethane foam is manufactured as a product of a reaction of two raw materials, a polyol and a diisocyanate. The general reaction is shown below. Each R1 group has multiple isocyanate groups; thus, there is a high degree of cross-linking in the polyurethane); a cosmetic emollient (Para [0087] In one embodiment, the polyurethane foam can include an emollient or humectant. Example emollients or humectants, include, but are not limited to include: hyaluronic acid); and a urethanation catalyst (Para [0033]-[0034] However, suitable catalysts that can be used include: a-tertiary amines such as N-methylimidazole; See instant specification Pg. 15 In 10-27 Preferred urethanation catalysts with reduced toxicity include...tertiary amines) wherein the cosmetic emollient forms a solvent matrix substantially surrounds the cross-linked polyurethane elastomer rubber (Para [0087] hyaluronic acid may be used to improve the tactile response and feel on surfaces of a final product. As a general guideline humectants can comprise from about 0.05% to about 4% by volume of the polyurethane).

Regarding claim 3, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the cross-linked polyurethane rubber is formed with a pre-polymer having at least two free hydroxyl groups (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol both of which contain an average two or more functional groups per molecule. By reacting two or more isocy anate groups per molecule (R(N=C=O)n) with a polyol containing on average two or more hydroxyl groups).

Regarding claim 4, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the solvent matrix comprises one or more cosmetic emollient (Para [0087] In one embodiment, the polyurethane foam can include an emollient or humectant. Example emollients or humectants, include, but are not limited to include: hyaluronic acid).

Regarding claim 7, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 3, wherein the prepolymer (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol) is a polyester reaction product of a diol and a dimer acid (Para [0004] Polyols can be polyether polyols or polyester polyols).

Regarding claim 10, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the urethanation catalyst is a bismuth, zinc, or amine catalyst (Para [0033]-[0034] However, suitable catalysts that can be used include: a-tertiary amines such as N-methylimidazole).

Regarding claim 12, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 6, wherein the overall molar ratio between the NCO in the polyisocyanate and the OH groups in the prepolymer is from 2:1 to 1:2 (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol both of which contain an average two or more functional groups per molecule).

Regarding claim 16, Dehni discloses a process (Para [0030] Any steps recited in any method or process claims may be executed in any order) for preparing a cross-linked polyurethane elastomer rubber composition (Para [0042] In the hard foam, the hydrophilic silicone elastomer is cross-linked with another polymeric silicone and with polyurethane polymer. In the case of a Si-OH group reaction with an electrophilic group on a polyurethane compound...will result in a cross-linked elastomer-polyurethane composition), comprising: reacting a polyisocyanate with a prepolymer having at least two free hydroxyl groups (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol both of which contain an average two or more functional groups per molecule. By reacting two or more isocyanate groups per molecule (R(N=C=O)n) with a polyol containing on average two or more hydroxyl groups) in the presence of a urethanation catalyst (Para [0033]-[0034] However, suitable catalysts that can be used include: a-tertiary amines such as N-methylimidazole; See instant specification Pg. 15 In 10-27 Preferred urethanation catalysts with reduced toxicity include...tertiary amines) and a cosmetic emollient (Para [0087] In one embodiment, the polyurethane foam can include an emollient or humectant. Example emollients or humectants, include, but are not limited to include: hyaluronic acid) under conditions sufficient to form a cross-linked polyurethane rubber (Para [0032] Flexible polyurethane foam is manufactured as a product of a reaction of two raw materials, a polyol and a diisocyanate. The general reaction is shown below. Each R1 group has multiple isocyanate groups; thus, there is a high degree of cross-linking in the polyurethane).

*******CONTINUED ON SUPPLEMENTAL PAGE********

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/46170

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of:
Box V(2): Citations and Explanations

Regarding claim 17, Dehni discloses the process of claim 16, wherein said conditions include reacting the prepolymer having at least two free hydroxyl groups (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol both of which contain an average two or more functional groups per molecule. By reacting two or more isocyanate groups per molecule (R((N=C=O)n) with a polyol containing on average two or more hydroxyl groups) the urethanation catalyst (Para [0033]-[0034] However, suitable catalysts that can be used include: a-tertiary amines such as N-methylimidazole; See instant specification Pg. 15 ln 10-27 Preferred urethanation catalysts with reduced toxicity include...tertiary amines) and cosmetic emollient (Para [0087] In one embodiment, the polyurethane foam can include an emollient or humectant. Example emollients or humectants, include, but are not limited to include: hyaluronic acid) at a temperature of from about 20 to about 100 degrees Celsius (Para [0031] unique composition of polyurethane formed from an isocyanate and a polyol...The initiator, and accelerator along with the optional gelling agent, surfactant, and reinforcement filler are added at room temperature).

Regarding claim 18, Dehni discloses the process of claim 16, wherein the urethanation catalyst is a bismuth, zinc, or amine catalyst (Para [0033]-[0034] However, suitable catalysts that can be used include: a-tertiary amines such as N-methylimidazole).

Claims 2, 5-6, 8-9 lack an inventive step under PCT Article 33(3) as being obvious over Dehni.

Regarding claim 2, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the polyurethane elastomer rubber composition has a hardness value from 15 to about 40A (Para [0038] This foam can have a shore hardness value from 15 to about 40A, and most often about 30) and high resilience (Para [0068] Reinforcement fillers are capable of cross-linking and contribute to the increased resilience, toughness, and comprehensive strength of the material) but does not disclose wherein the polyurethane elastomer rubber composition has a hardness force greater than 200 g as measured by a texture analyzer prior to any milling or dilution and that it has a resilience greater than or equal to 70%. However, it would have been obvious to one of ordinary skill in the art to change the hardness and resilience of the elastomer through routine experimentation (Para [0110] in conjunction with polyurethane, polysulfide polymers, natural and synthetic rubber and silk fibroin can be used to affect cell size, hardness, resiliency and toughness).

Regarding claim 5, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the polyurethane elastomer rubber is formed with from a prepolymer having at least two free hydroxyl group (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol both of which contain an average two or more functional groups per molecule. By reacting two or more isocyanate groups per molecule (R((N=C=O)n) with a polyol containing on average two or more hydroxyl groups) but does not disclose wherein the prepolymer comprises from about 5 to about 25 weight percent. However, it would have been obvious to one of ordinary skill in the art to change the amount of prepolymer in the polyurethane through routine experimentation.

Regarding claim 6, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the polyurethane elastomer rubber is formed with from an isocyanate functionalized molecule and a prepolymer having OH-groups (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol both of which contain an average two or more functional groups per molecule. By reacting two or more isocyanate groups per molecule (R((N=C=O)n) with a polyol containing on average two or more hydroxyl groups) but does not disclose wherein polyurethane elastomer rubber is formed with from about 1 to about 20 weight percent of an isocyanate functionalized molecule and a prepolymer having OH-groups. However, it would have been obvious to change the weight percentages of isocyanate and prepolymer in the composition through routine experimentation.

Regarding claim 8, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the polyurethane elastomer rubber is formed with a polyisocyanate (Para [0036] In one embodiment of the present disclosure, a methylene bisphenyl isocyanate (MDI) solution and a mixture of polyether polyol can be mixed...to form polyurethane) containing NCO (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol both of which contain an average two or more functional groups per molecule. By reacting two or more isocyanate groups per molecule (R((N=C=O)n)) but does not disclose wherein the polyisocyanate contains from about 15 to about 38 weight% NCO. However, it would have been obvious to one of ordinary skill in the art to change the weight percent of NCO through routine experimentation.

Regarding claim 9, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the amount of urethanation catalyst (Para [0033]-[0034] suitable catalysts that can be used include: a-tertiary amines such as N-methylimidazole; See Instant Specification Pg. 15 ln 10-27 urethanation catalysts with reduced toxicity include...tertiary amines) is about 10% by volume (Para [0039] the catalyst can compose about 10% by volume) but does not disclose wherein the catalyst is from about 0.1 to about 2.5 weight%. However, it would have been obvious to one of skill in the art to change the amount of the catalyst through routine experimentation.

Claim 11 lacks an inventive step under PCT Article 33(3) as being obvious over Dehni in view of US 2003/0092932 A1 to Tong et al. (hereinafter Tong)

Regarding claim 11, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, but does not disclose the composition further comprising an amount of a finisher containing an alcohol or an amine sufficient to quench unreacted isocyanate groups. However, Tong discloses a polyurethane (Para [0011] invention provides a method of reducing the amount of unreacted polyisocyanate from a polyurethane prepolymer) further comprising an amount of a finisher containing an alcohol or an amine (Para [0012] the process comprising reacting the composition with a quenching agent, the quenching agent comprising an arylalkyl alcohol and an alkoxysilane) sufficient to quench unreacted isocyanate groups (Para [0001] invention relates to a process for reducing residual monomeric polyisocyanate in a composition comprising a polymer or oligomer bearing isocyanate groups). It would have been obvious to one of ordinary skill in the art to combine these references to include a finisher in order to reduce isocyanate groups (Tong Para [0025] Reaction of the mixture of the arylalkyl alcohol and alkoxysilane with residual monomeric polyisocyanate eliminates at least one of the isocyanate groups of the residual monomeric polyisocyanate).

*********CONTINUED ON SUPPLEMENTAL PAGE********

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/46170

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:
Box V(2): Citations and Explanations

Claims 13-14 and 19-20 lack an inventive step under PCT Article 33(3) as being obvious over Dehni in view of US 2018/0371149 A1 to Massachusetts Institute of Technology (hereinafter Massachusetts)

Regarding claim 13, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, but does not disclose wherein the cross-linked polyurethane elastomer rubber is formed with a bio-based and biodegradable prepolymer. However, Massachusetts discloses a cross-linked polyurethane elastomer rubber (title; Para [0004] present disclosure provides elastomeric materials In particular, the present invention provides compositions comprising a polyester material together with and/or crosslinked by a polyisocyanate crosslinker. The present invention therefore provides elastomeric materials that include at least one urethane crosslink) is formed with a bio-based and biodegradable prepolymer (Para [0035] A pre-polymer, in some embodiments, is biodegradable and/or biocompatible). It would have been obvious to one of ordinary skill in the art to combine these references to use a bio-based and biodegradable prepolymer and so the polyurethane can be broken down (Para [0019] biodegradable materials are enzymatically broken down. Alternatively or additionally, in some embodiments, biodegradable materials are broken down by hydrolysis).

Regarding claim 14, Dehni in view of Massachusetts discloses the cross-linked polyurethane elastomer rubber composition of claim 13. Dehni discloses wherein the cosmetic emollient are bio-based and biodegradable (Para [0087] Example emollients or humectants, include, ...glycerin; See Instant Specification Pg. 12 In 17-41 Appropriate emollients or solvents include but are not limited to...glycerin) but does not disclose wherein the prepolymer and the polyisocyanate are bio-based and biodegradable and wherein the cross-linked polyurethane elastomer rubber composition is comprised of greater than about 85%, preferably greater than about 95% or, greater than about 99% renewable, bio-based feedstocks. However, Massachusetts discloses a cross-linked polyurethane elastomer rubber (Para [0004] disclosure provides elastomeric materials In particular, the present invention provides compositions comprising a polyester material together with and/or crosslinked by a polyisocyanate crosslinker. The present invention therefore provides elastomeric materials that include at least one urethane crosslink) wherein the prepolymer is bio-based and biodegradable (Para [0035] A pre-polymer, in some embodiments, is biodegradable and/or biocompatible) and the polyisocyanate is bio-based and biodegradable (Para [0077] In some embodiments, polyisocyanates for use in the present invention include...4,4'-dicyclohexylmethane diisocyanate; See Instant Specification Pg. 13 Para 3 to Pg. 14 Para 1 Appropriate functionalized isocyanates include but are not limited to....4,4'-dicyclohexylmethane diisocyanate) but does not disclose wherein the cross-linked polyurethane elastomer rubber composition is comprised of greater than about 85%, preferably greater than about 95% or, greater than about 99% renewable, bio-based feedstocks. However, it would have been obvious to one of skill in the art to change the weight percentage of renewable, bio-based feedstock through routine experimentation. It would have also been obvious to one of ordinary skill in the art to combine these references to use a bio-based and biodegradable prepolymer and polyisocyante so the polyurethane can be broken down (Massachusetts Para [0019] biodegradable materials are enzymatically broken down. Alternatively or additionally, in some embodiments, biodegradable materials are broken down by hydrolysis).

Regarding claim 19, Dehni discloses the process of claim 16 wherein the cosmetic is bio-based and biodegradable (Para [0087] Example emollients or humectants, include, but are not limited to include...glycerin; See Instant Specification Pg. 12 In 17-41 Appropriate emollients or solvents include but are not limited to...glycerin) but does not disclose wherein the prepolymer and the polyisocyanate are bio-based and biodegradable. However, Massachusetts discloses a cross-linked polyurethane elastomer rubber (title; Para [0004] present disclosure provides elastomeric materials In particular, the present invention provides compositions comprising a polyester material together with and/or crosslinked by a polyisocyanate crosslinker. The present invention therefore provides elastomeric materials that include at least one urethane crosslink) wherein the prepolymer is bio-based and biodegradable (Para [0035] A pre-polymer, in some embodiments, is biodegradable and/or biocompatible) and the polyisocyanate is bio-based and biodegradable (Para [0077] In some embodiments, polyisocyanates for use in the present invention include...4,4'-dicyclohexylmethane diisocyanate; See Instant Specification Pg. 13 Para 3 to Pg. 14 Para 1 Appropriate functionalized isocyanates include but are not limited to....4,4'-dicyclohexylmethane diisocyanate). It would have also been obvious to one of ordinary skill in the art to combine these references to use a bio-based and biodegradable prepolymer and polyisocyante so the polyurethane can be broken down (Massachusetts Para [0019] biodegradable materials are enzymatically broken down. Alternatively or additionally, in some embodiments, biodegradable materials are broken down by hydrolysis).

Regarding claim 20, Dehni in view of Massachusetts discloses the process of claim 19, but does not disclose wherein the cross-linked polyurethane elastomer rubber composition is comprised of greater than about 85%, preferably greater than about 95% or, greater than about 99%, bio-based feedstock. However, it would have been obvious to one of ordinary skill in the art to change the weight percentage of renewable, bio-based feedstock through routine experimentation.

Claims 21-34 lack an inventive step under PCT Article 33(3) as being obvious over Dehni in view of US 2011/0045983 A1 to Healy et al. (hereinafter Healy)

Regarding claim 21, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1 in micronized form (Para [0093] polymer polyols formed by the polymer ization process increase the load bearing capacity of the low density and high resiliency of the flexible polyure thane and add toughness to the microcellular foam structure) and at least one cosmetic emollient (Para [0087] Example emollients or humectants, include, but are not limited to include: hyaluronic acid, glyc erin) but does not disclose a gel composition composition comprising a mixture of the cross-linked polyurethane elastomer rubber. However, Healy discloses a polyurethane (Para [0026] Numerous commercially available block copoly mers may be used in embodiments of the invention. For example...polyes ter/polyurethane) elastomer rubber (Para [0021] In some embodiments of the invention, a block copolymer capable of forming a three-dimensional network through physical cross-linking...Upon cooling, removal of shear, or solvent evaporation, the rigid domains reform and harden, locking the elastomeric network in place) in a gel composition (Para [0006] the invention relates to a gel composition that includes an ester compound and a polymer compound). It would have been obvious to one of ordinary skill in the art to combine these references to include a geling agent to form a gel composition (Healy Para [0005] A gel composition typically is made by mixing one or more compounds to be gelled with a gelling agent).

********CONTINUED ON SUPPLEMENTAL PAGE*********

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/46170

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:
Box V(2): Citations and Explanations

Regarding claim 22, Dehni in view of Healy discloses the gel composition of claim 21. Dehni further discloses wherein the amount of the micronized (Para [0093] polyurethane/polyorganosiloxane foam and add toughness to the microcellular foam structure) cross-linked polyurethane elastomer rubber composition (Para [0042] In the case of a Si-OH group reaction with an electrophilic group on a polyurethane compound...will result in a cross-linked elastomer-polyurethane composition; Para [0032] Flexible polyurethane foam is manufactured as a product of a reaction a polyol and a diisocyanate. Each R1 group has multiple isocyanate groups thus, there is a high degree of cross-linking in the polyurethane) is from about 66 to 87% by volume(Para [0036] the present disclosure, a methylene bisphenyl isocyanate (MDI) solution and a mixture of polyether polyol can be mixed to form polyurethane. Although other proportions can be suitable, this mixture can often comprise about 66% to about 87% by volume) but does not disclose wherein the polyurethane elastomer rubber composition is from about 30 to about 5 weight. However, it would have been obvious to one of ordinary skill in the art to change the weight percentage of polyurethane elastomer rubber through routine experimentation.

Regarding claim 23, Dehni in view of Healy discloses the gel composition of claim 22. Dehni further discloses wherein the amount of the micronized (Para [0093]] polyurethane/polyorganosiloxane foam and add toughness to the microcellular foam structure) cross-linked polyurethane elastomer rubber composition (Para [0042] In the case of a Si-OH group reaction with an electrophilic group on a polyurethane compound...will result in a cross-linked elastomer-polyurethane composition; Para [0032] Flexible polyurethane foam is manufactured as a product of a reaction a polyol and a diisocyanate. Each R1 group has multiple isocyanate groups thus, there is a high degree of cross-linking in the polyurethane) is from about 66 to 87% by volume(Para [0036] the present disclosure, a methylene bisphenyl isocyanate (MDI) solution and a mixture of polyether polyol can be mixed to form polyurethane. Although other proportions can be suitable, this mixture can often comprise about 66% to about 87% by volume) but does not disclose wherein the polyurethane elastomer rubber composition is from about 5 to about 17 weight %. However, it would have been obvious to one of ordinary skill in the art to change the weight percentage of polyurethane elastomer rubber through routine experimentation.

Regarding claim 24, Dehni in view of Healy discloses the gel composition of claim 21. Dehni further discloses wherein the amount of the cosmetic emollient is from about 0.05% to about 4% by volume (Para [0087] Example emollients or humectants, include, but are not limited to include...glycerin. As a general guideline humectants can comprise from about 0.05% to about 4% by volume) but does not disclose wherein the amount of the cosmetic emollient is from about 70 to about 95 weight %. However, it would have been obvious to one of ordinary skill in the art to change the weight percentage of humectant through routine experimentation.

Regarding claim 25, Dehni in view of Healy discloses the gel composition of claim 22. Dehni further discloses wherein the amount of the cosmetic emollient is from about 0.05% to about 4% by volume (Para [0087] Example emollients or humectants, include, but are not limited to include...glycerin. As a general guideline humectants can comprise from about 0.05% to about 4% by volume) but does not disclose wherein the amount of the cosmetic emollient is from about 83 to about 95 weight %. However, it would have been obvious to one of ordinary skill in the art to change the weight percentage of humectant through routine experimentation.

Regarding claim 26, Dehni in view of Healy discloses the gel composition of claim 21. Healy further discloses the composition comprising a secondary solvent (Para [0043] Examples of the suitable naturally-occurring fats and oils include, but are not limited to...triheptanoin; See Instant Specification 27 the secondary solvent is selected from the group consisting of triheptanoin).

Regarding claim 27, Dehni in view of Healy discloses the gel composition of claim 21. Healy further discloses wherein the secondary solvent is selected from the group consisting of triheptanoin; undecane; tridecane; or wherein the secondary solvents are naturally derived alkanes or naturally derived esters (Para [0043] Examples of the suitable naturally-occurring fats and oils include, but are not limited to...triheptanoin).

Regarding claim 28, Dehni in view of Healy discloses the gel composition of claim 21. Healy further discloses the composition comprising an active composition, optionally selected from the group consisting of selected from vitamins, sunscreens, plant extracts fragrances and mixtures thereof (Para [0066] The gel compositions in accordance with embodiments of the invention also have a wide spectrum of cosmetic applications when the gel compositions include an effective amount of one or more...fragrance oils).

Regarding claim 29, Dehni in view of Healy discloses the gel composition of claim 21. Healy further discloses the composition comprising a member of the group consisting of fragrances, colorants, preservatives, active compositions, and mixtures thereof (Para [0066] The gel compositions in accordance with embodiments of the invention also have a wide spectrum of cosmetic applications when the gel compositions include an effective amount of one or more...fragrance oils).

Regarding claim 30, Dehni in view of Healy discloses the gel composition of claim 21, but does not disclose wherein the micronized cross-linked polyurethane elastomer rubber composition has a cross-sectional diameter of from about 1 to about 61 microns. However, it would have been obvious to one of ordinary skill in the art to change the diameter of the polyurethane elastomer rubber through routine experimentation.

Regarding claim 31, Dehni in view of Healy discloses the gel composition of claim 21, but does not disclose the composition having a viscosity ranging from about 15,000 cP to about 1,000,000 cP, preferably from about 40,000 to about 1,000,000 cP. However, it would have been obvious to one of ordinary skill in the art to change the viscosity of the gel through routine experimentation.

Regarding claim 32, Dehni in view of Healy discloses the gel composition of claim 21. Healy further discloses wherein the gel is a non-Newtonian fluid or a thixotropic fluid (Para [0021] The physical cross-linking via these rigid domains yields a continuous three-dimensional network. In the presence of heat, shear, or solvent, the rigid domains soften and permit flow. Upon cooling, removal of shear, or solvent evaporation, the rigid domains reform and harden).

*********CONTINUED ON SUPPLEMENTAL PAGE*********

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/46170

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of:
Box V(2): Citations and Explanations

Regarding claim 33, Dehni discloses a method (Para [0030] Any steps recited in any method or process claims may be executed in any order and are not limited to the order presented) comprising: a) micronizing (Para [0093] novel polymer polyols formed by the polymerization process above, increase the load bearing capacity of the low density and high resiliency of the flexible polyurethane and add toughness to the microcellular foam structure) the cross-linked polyurethane elastomer rubber composition of claim 1 (Para [0042] In the case of a Si-OH group reaction with an electrophilic group on a polyurethane compound...will result in a cross-linked elastomer-polyurethane composition; Para [0032] Flexible polyurethane foam is manufactured as a product of a reaction a polyol and a diisocyanate. Each R1 group has multiple isocyanate groups thus, there is a high degree of cross-linking in the polyurethane) in the presence of a cosmetic emollient (Para [0087] Example emollients or humectants, include, but are not limited to include...glycerin) but does not disclose a method of preparing a gel composition and optionally, b) combining the mixture resulting from step a) with a secondary solvent. However, Healy discloses a polyurethane (Para [0026] Numerous commercially available block copoly mers may be used in embodiments of the invention. For example...polyes ter/polyurethane) elastomer rubber (Para [0021] In some embodiments of the invention, a block copolymer capable of forming a three-dimensional network through physical cross-linking...Upon cooling, removal of shear, or solvent evaporation, the rigid domains reform and harden, locking the elastomeric network in place) in a gel composition (Para [0006] the invention relates to a gel composition that includes an ester compound and a polymer compound) and optionally, b) combining the mixture resulting from step a) with a secondary solvent (Para [0043] Examples of the suitable naturally-occurring fats and oils include, but are not limited to...triheptanoin). It would have been obvious to one of ordinary skill in the art to combine these references to include a geling agent to form a gel composition (Healy Para [0005] A gel composition typically is made by mixing one or more compounds to be gelled with a gelling agent).

Regarding claim 34, Dehni in view of Healy discloses the process of claim 33. Healy further discloses wherein the secondary solvent is the secondary solvent is selected from the group consisting of triheptanoin; undecane; tridecane; or wherein the secondary solvents are naturally derived alkanes or naturally derived esters (Para [0043] Examples of the suitable naturally-occurring fats and oils include, but are not limited to...triheptanoin).

Claim 15 lack an inventive step under PCT Article 33(3) as being obvious over Dehni in view of Massachusetts and further in view of US 2013/0079486 A1 to Hidesaki et al. (hereinafter Hidesaki)

Regarding claim 15, Dehni in view of Massachusetts discloses the cross-linked polyurethane elastomer rubber composition of claim 14, but does not disclose wherein the bio-based and biodegradable polyisocyanate is 1,5-pentamethylene diisocyanate trimer. However, Hidesaki discloses a polyurethane (Para [0017] a polyurethane resin obtained by using 1,5-pentamethylene diisocyanate and the polyisocyanate composition) wherein the bio-based and biodegradable polyisocyanate is 1,5-pentamethylene diisocyanate trimer (Para [0017] a polyurethane resin obtained by using 1,5-pentamethylene diisocyanate and the polyisocyanate composition). It would have been obvious to one of ordinary skill in the art to combine these references to use 1,5-pentamethylene diisocyanate trimer to form polyurethane because the isocyante groups also for crosslinking (Dehni Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol...By reacting two or more isocy anate groups with a polyol a flexible polyurethane foam is produced).

Claims **1**-34 have industrial applicability as defined by PCT Article 33(4) because the subject matter can be made or used in industry.

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
18/066,105	**12/14/2022 05:17:52 PM ET**	**GRAN-1012-U-D**

Title of Invention

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	1563	FILED BY	Carla Curado
PATENT CENTER #	61300708	FILING DATE	-
CUSTOMER #	20311	FIRST NAMED INVENTOR	Anna K. CROOM
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Michael Mercanti

Documents

TOTAL DOCUMENTS: 20

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
ADS_GRAN1012UD.pdf	9	Application Data Sheet	2174 KB
IDSSB08_GRAN1012UD.PDF	7	Information Disclosure Statement (IDS) Form (SB08)	1235 KB
WO2018183440.PDF	25	Foreign Reference	1089 KB
WO2014167518.PDF	20	Foreign Reference	1064 KB
JP6892253B2.PDF	25	Foreign Reference	532 KB
WO2021007489.PDF	53	Foreign Reference	2729 KB
WO2021231527.PDF	37	Foreign Reference	1728 KB

WO2021257937.PDF	71	Foreign Reference	3031 KB
EP1142959A1.PDF	44	Foreign Reference	2531 KB
JP3631542B2.PDF	9	Foreign Reference	3063 KB
ISR_WO_GRAN1012U.PDF	10	Other reference-Patent/Application/Search Documents	734 KB
IPRP.PDF	9	Other reference-Patent/Application/Search Documents	619 KB
PCTWrittenOpinionPCTUS2020041540.PDF	14	Other reference-Patent/Application/Search Documents	1247 KB
Becker.PDF	96	Other reference-Patent/Application/Search Documents	5866 KB
WO2013074655.PDF	44	Foreign Reference	3075 KB
Declaration_GRAN1012UD.PDF	3	Oath or Declaration filed	2942 KB
Specification_GRAN1012UD.PDF	38	Specification	215 KB
POA_GRAN1012UD.pdf	2	Power of Attorney	418 KB
Drawing_GRAN_1012UD.PDF	1	Drawings-only black and white line drawings	621 KB
IDSLetterGRAN1012UD.PDF	2	Transmittal Letter	85 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
ADS_GRAN1012UD.pdf	47BB602E8F534AC937F2C8B8F23EE5ABD7DEC9A2E04BB19C DF33103B2B550F27EEC9AB8A685930BBA7F6BA4F7BCB8A41 A2A0F1A15DD44B6E414BF2A00F11539C
IDSSB08_GRAN1012UD.PDF	AAA594AA3FE0319F5A2B3EB289698EA008CF1960CC4BD68A0 9ABD3C487EE7EC0086D93CE6052724BCDEAE16E730DDE2C0 322148864DF844664A1690AEF67D796
WO2018183440.PDF	9A6437634BCB67DCB2912B33D8F938099F767BDEB108FFC3A FEA97C025AA11B5757BCE9355E81BA30E633848C89FA6DBE1 5D7EFC06CCD3615115E9DE312F3F92
WO2014167518.PDF	28F1B6A33ED49090FAAB768F60047CB50A594EAB28F56E94F 7B0828254AF9ED63C77F7986CB8AFB3BDBD57342CC3E1C6D 51CD57C7E5C529C1BA6F07EBB6199D3
JP6892253B2.PDF	0CA56997FE54EC6F147E790305BA0242FDA94B2B132364291D 1E08C09FD684EA9E4078F627FEC475268BFE8D5879108B9959 1AD7EDC39CA266C3C0B7469746AE
WO2021007489.PDF	AB0648DEE8EABEF7B15FCBAE88EB1D8DECDA5B328D3A143 52F3F33063A83C8A60207A8698D0603AE7A24FFE42BA78E669 0DEB6E74D21E360B5B1A0812A1E0A47
WO2021231527.PDF	351E86A77A1F8C0A4D326ADDEF8CD004E6616178835C57070 6DD0DB84CE919A90EE6611AE1FB2AD96DA396EFECC3377B0 848FE18D05081AA5E966ACAC8A3219E
WO2021257937.PDF	D95E080BD1BD2D4AAE8162826F685AA4ADA97EC174E653A9 F4CE55E6941BF384FEA46E5EFDAD8E9DF834083659A9FAEF9 F18CA9C6F14765B4A306C8ECE494B0F
EP1142959A1.PDF	960759305F82A3BB1FEF660FABA2E3DED661EFE2C9FBC0DF 15EF30F6E3FC3BC886D0066F3ABFF319AC218D7836AF17834 C926EA1F541F8C4E15ED41585AFDFB1
JP3631542B2.PDF	B2AFED8309B1B6C9853CC3570198DCAC43D7E10ED748292F ACA5CF858FD372E0A096510C554A5561A5C5573F08F20B43C

	AD304683C90819C35E1C4CDE7837ACC
ISR_WO_GRAN1012U.PDF	8E590B87AA3646B9A2BCB5AEBF1FE0232AAB9AEAA6B51F3BF51DBC9BF7D34129CB826E9D343BF5E6B5BE275128CB78022404AAB7F73FF2D64DDFAA741C1FEDA1
IPRP.PDF	D287D2ADD34D2A6D6E02663B8CC93798B375FE76AEA587138C73B936ECDE0FC318AF62B2594E399B74B1229191BF9BD08FAD435FC36BBE65AE14D8C98623C902
PCTWrittenOpinionPCTUS2020041540.PDF	8EE853D48D472F561BBCF9EEC0E4FE28F30F32645A4820A7F288629985D4D6CFF9B9F5B48E79BD1D6CD0E842462E7B9D198E3D7280E20C02747335F352DBCC17
Becker.PDF	1AFF1A64A56672AD8FCEC1D820A6669C701DCBF2880520BE29131C0663B1D839B1966AF5145BA5DCCAA610DB4B3E43845389A44BF32970AE84D759300D764995
WO2013074655.PDF	4088E4829C83906DD72D76EB9F32D714F60900DD6FC26637D26984AA4EB7A736345000AD23C90AEB991ED0E39F146E4DF6F6E3AD4C1BBC9533D2051D66A246E3
Declaration_GRAN1012UD.PDF	1A277E976D46EA11CC304A23F886A8580C741F2F8A7F435D13267B35F0551178CB68EE0AB6BA891C7B7344257A824D2A2D825741D481451911A621F9E2FC3F2F
Specification_GRAN1012UD.PDF	D4DB168589C0D233C09DD133D5B4639D5C668E95532E4F5BB98D13DCAB11A0CC06CF65DFC55290189E3A77C7F712BE8C6C88A58E71B6BCC0FA12D23B7FBA1B1E
POA_GRAN1012UD.pdf	5B3E2BB692D546E8F62375F9F6C44FF728CDA3E2917EFD90318F3D5762A98EB8D4DA4B521980D96B8A67AE9305FCC578F84EC5ACC51C2996840926FA777A8BCF
Drawing_GRAN_1012UD.PDF	BD972DE2CA64FBEDCB3740AB11B1C1BB9DA468FFE50897ABB4A63473EB498C4B26B4F6A17A869B725E179A1DAD2793F5BF5536674695478D941E32E2E30ED270
IDSLetterGRAN1012UD.PDF	7C2AD4D223155BCD14A6F31A0B5DAD9E8CDFF65A13486EED4C1339C8C1DA226E535C6945E09228CA1559AA26005A977877

67D4277E3AB45C07ABD8592F89AAA7

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Espacenet

JP6892253B2 ポリウレタンゲルおよびその製造方法

Applicants: 三井化学株式会社

Inventors: 中川 亜弥,中川 俊彦,山下 達也,森田 広一,山崎 聡

Classifications:
IPC ***C08G18/08; C08G18/73; C08G18/79;***

Priorities: JP2016232583A 2016-11-30

Application: JP2016232583A·2016-11-30

Publication: JP6892253B2·2021-06-23

Published as: **JP2018090662A**; JP6892253B2

ポリウレタンゲルおよびその製造方法

Abstract

PROBLEM TO BE SOLVED: To provide a polyurethane gel that is excellent in transparency, and is excellent in tactile sensation, absorbency, holding power and volatility, and furthermore is excellent in shape retention, heat resistance and quick curability, and to provide a production process therefor.SOLUTION: In a polyurethane gel containing a reaction product of a polyisocyanate component containing a polyfunctional aliphatic polyisocyanate having an average functional group number of more than 2.0 and not more than 3.5 and a polyol component containing a bifunctional polyol by 80 mass% or more, and a solvent, the content ratio of the solvent is set to 50 mass% or more and 95 mass% or less with respect to the total amount of polyurethane gel.SELECTED DRAWING: None

(19)日本国特許庁(JP)　(12)特　許　公　報(B2)　(11)特許番号
特許第6892253号
(P6892253)
(45)発行日　令和3年6月23日(2021.6.23)　(24)登録日　令和3年5月31日(2021.5.31)

(51)Int.Cl.　　F I
C08G 18/08 (2006.01)　C08G 18/08 042
C08G 18/73 (2006.01)　C08G 18/73
C08G 18/79 (2006.01)　C08G 18/79 020

請求項の数 7　(全 24 頁)

(21)出願番号　特願2016-232583(P2016-232583)
(22)出願日　平成28年11月30日(2016.11.30)
(65)公開番号　特開2018-90662(P2018-90662A)
(43)公開日　平成30年6月14日(2018.6.14)
審査請求日　令和1年9月6日(2019.9.6)

(73)特許権者　000005887
三井化学株式会社
東京都港区東新橋一丁目５番２号
(74)代理人　100103517
弁理士　岡本　寛之
(72)発明者　中川　亜弥
千葉県袖ヶ浦市長浦５８０番地３２　三井化学株式会社内
(72)発明者　中川　俊彦
千葉県袖ヶ浦市長浦５８０番地３２　三井化学株式会社内
(72)発明者　山下　達也
千葉県袖ヶ浦市長浦５８０番地３２　三井化学株式会社内

最終頁に続く

(54)【発明の名称】ポリウレタンゲルおよびその製造方法

(57)【特許請求の範囲】
【請求項１】
平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有するポリイソシアネート成分と、２官能性ポリオールを８０質量％以上含有するポリオール成分との反応生成物と、
溶媒と
を含有するポリウレタンゲルであって、
前記反応生成物において、ポリオール成分の水酸基に対する、前記ポリイソシアネート成分のイソシアネート基の当量比（ＮＣＯ／ＯＨ）が、０．７以上１未満であり、
前記溶媒の含有割合は、前記ポリウレタンゲルの総量に対して、５０質量％以上９５質量％以下である
ことを特徴とする、ポリウレタンゲル。
【請求項２】
前記２官能性ポリオールが、ポリエーテルジオールである
ことを特徴とする、請求項１に記載のポリウレタンゲル。
【請求項３】
前記ポリウレタンゲルがウレタン化触媒を含有し、
前記ウレタン化触媒の含有割合が、前記ポリイソシアネート成分および前記ポリオール成分の総量１００質量部に対して、０．１質量部を超過し１質量部以下である
ことを特徴とする、請求項１または２に記載のポリウレタンゲル。

【請求項４】
前記多官能性脂肪族ポリイソシアネートが、イソシアヌレート誘導体を含有する
ことを特徴とする、請求項１～３のいずれか一項に記載のポリウレタンゲル。
【請求項５】
前記多官能性脂肪族ポリイソシアネートが、ペンタメチレンジイソシアネートの誘導体である
ことを特徴とする、請求項１～４のいずれか一項に記載のポリウレタンゲル。
【請求項６】
ポリウレタンと溶媒とを含有するポリウレタンゲルの製造方法であって、
平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有するポリイソシアネート成分と、２官能性ポリオールを８０質量％以上含有するポリオール成分と、ウレタン化触媒と、前記ポリウレタンゲルの総量に対して５０質量％以上９５質量％以下の溶媒とを配合する工程と、
それらを室温で反応させる工程と
を備え、
前記ポリオール成分の水酸基に対する、前記ポリイソシアネート成分のイソシアネート基の当量比（ＮＣＯ／ＯＨ）が、０．７以上１未満である
ことを特徴とする、ポリウレタンゲルの製造方法。
【請求項７】
前記ウレタン化触媒の配合割合が、前記ポリイソシアネート成分および前記ポリオール成分の総量１００質量部に対して、０．１質量部を超過し１質量部以下である
ことを特徴とする、請求項６に記載のポリウレタンゲルの製造方法。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は、ポリウレタンゲルおよびその製造方法に関する。
【背景技術】
【０００２】
従来、香料、防虫剤、殺虫剤、抗菌剤、殺菌剤、忌避剤、農薬などの揮散性有効成分と、溶剤とが、ポリウレタンなどの樹脂中に内包されてなるゲル状物質が、提案されている。
【０００３】
このようなゲル状物質では、揮散性有効成分が徐々に樹脂から放出（揮散）されるため、揮散性有効成分の効果を長期間にわたって継続的に発現させることができる。
【０００４】
このようなゲル状物質としては、例えば、揮散性薬剤とポリウレタンとを含有するゲル状樹脂成形体組成物が提案されており、より具体的には、イソシアヌレート型ヘキサメチレンジイソシアネートと、ヒマシ油（グリセリルトリリシノレート）と、イソチオシアン酸アリル、薄荷油、ジャスミンオイルなどの揮散性薬剤とを種々の比率で配合し、ジブチル錫ジラウレートの存在下で反応させることにより、ポリウレタン樹脂のゲル状樹脂成形体組成物を得ることが、提案されている（例えば、特許文献１（表１～１３）参照。）。
【先行技術文献】
【特許文献】
【０００５】
【特許文献１】特開２００６－２６５５５８号公報
【発明の概要】
【発明が解決しようとする課題】
【０００６】
しかし、特許文献１に記載のゲル状樹脂成形体組成物では、ポリウレタン樹脂の原料としてヒマシ油（グリセリルトリリシノレート）が用いられている。そのため、ゲル状樹脂

成形体組成物が変色し易く、透明性が十分ではない場合がある。

【０００７】

また、ポリウレタン樹脂の原料として上記のヒマシ油（グリセリルトリリシノレート）が用いられていると、ポリウレタン樹脂のネットワークが過度に強固になるため、ゲル状樹脂成形体組成物の触感（柔軟性、弾力）、デザイン性（透明感、潤い感、ぷるぷる感など）や、揮散性薬剤の吸収性および保持力が十分ではなく、また、揮散性薬剤の揮散性に劣る場合がある。

【０００８】

また、このようなゲル状樹脂成形体組成物としては、さらに、保型性（形状保持性）、耐熱性などが要求され、さらに、生産効率の観点から、速硬化性も要求される。

【０００９】

本発明の目的は、透明性に優れ、また、触感、デザイン性、吸収性、保持力および揮散性に優れ、さらには、保型性、耐熱性および速硬化性に優れるポリウレタンゲル、および、その製造方法を提供することにある。

【課題を解決するための手段】

【００１０】

本発明［１］は、平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有するポリイソシアネート成分と、２官能性ポリオールを８０質量％以上含有するポリオール成分との反応生成物と、溶媒とを含有するポリウレタンゲルであって、前記溶媒の含有割合は、前記ポリウレタンゲルの総量に対して、５０質量％以上９５質量％以下である、ポリウレタンゲルを含んでいる。

【００１１】

本発明［２］は、前記２官能性ポリオールが、ポリエーテルジオールである、上記［１］に記載のポリウレタンゲルを含んでいる。

【００１２】

本発明［３］は、前記ポリウレタンゲルがウレタン化触媒を含有し、前記ウレタン化触媒の含有割合が、前記ポリイソシアネート成分および前記ポリオール成分の総量１００質量部に対して、０．１質量部を超過し１質量部以下である、上記［１］または［２］に記載のポリウレタンゲルを含んでいる。

【００１３】

本発明［４］は、前記多官能性脂肪族ポリイソシアネートが、イソシアヌレート誘導体を含有する、上記［１］～［３］のいずれか一項に記載のポリウレタンゲルを含んでいる。

【００１４】

本発明［５］は、前記多官能性脂肪族ポリイソシアネートが、ペンタメチレンジイソシアネートの誘導体である、上記［１］～［４］のいずれか一項に記載のポリウレタンゲルを含んでいる。

【００１５】

本発明［６］は、ポリウレタンと溶媒とを含有するポリウレタンゲルの製造方法であって、平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有するポリイソシアネート成分と、２官能性ポリオールを８０質量％以上含有するポリオール成分と、ウレタン化触媒と、前記ポリウレタンゲルの総量に対して５０質量％以上９５質量％以下の溶媒とを配合する工程と、それらを室温で反応させる工程とを備える、ポリウレタンゲルの製造方法を含んでいる。

【００１６】

本発明［７］は、前記ウレタン化触媒の配合割合が、前記ポリイソシアネート成分および前記ポリオール成分の総量１００質量部に対して、０．１質量部を超過し１質量部以下である、上記［６］に記載のポリウレタンゲルの製造方法を含んでいる。

【００１７】

本発明［８］は、前記ポリオール成分の水酸基に対する、前記ポリイソシアネート成分

のイソシアネート基の当量比（ＮＣＯ／ＯＨ）が、０．７以上１未満である、上記［６］または［７］に記載のポリウレタンゲルの製造方法を含んでいる。

【発明の効果】

【００１８】

本発明のポリウレタンゲルは、平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有するポリイソシアネート成分と、２官能性ポリオールを８０質量％以上含有するポリオール成分とが反応してなり、また、特定割合で溶媒を含有するため、透明性に優れ、また、触感（柔軟性、弾力）、デザイン性（透明感、潤い感、ぷるぷる感など）、吸収性、保持力および揮散性に優れ、さらには、保型性、耐熱性および速硬化性に優れる。

【００１９】

また、本発明のポリウレタンゲルの製造方法によれば、透明性に優れ、また、触感、デザイン性、吸収性、保持力および揮散性に優れ、さらには、保型性、耐熱性および速硬化性に優れるポリウレタンゲルを、得ることができる。

【発明を実施するための形態】

【００２０】

本発明のポリウレタンゲルは、ポリイソシアネート成分とポリオール成分との反応生成物であるポリウレタン（分散質）と、溶媒（分散媒）とを含有し、ポリウレタンの３次元ネットワークにより、高い粘性を有し、溶媒がポリウレタン中に内包されることにより流動性を失い、系全体としては固体状となっているものである。

【００２１】

ポリウレタンゲルの２５℃における剪断弾性率は、１×１０^{3}～１×１０^{7} Ｐａである。剪断弾性率は、固体粘弾性測定装置により測定される。

【００２２】

なお、以下において、ポリイソシアネート成分の官能基とは、イソシアネート基を示し、ポリオール成分の官能基とは、水酸基を示す。

【００２３】

ポリイソシアネート成分は、必須成分として、多官能性脂肪族ポリイソシアネートを含有しており、具体的には、平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有している。

【００２４】

平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートとしては、例えば、脂肪族ジイソシアネート（２官能性モノマー）の誘導体が挙げられる。

【００２５】

すなわち、多官能性脂肪族ポリイソシアネートとして、具体的には、平均官能基数が上記の特定範囲となるように脂肪族ジイソシアネート（２官能性モノマー）を変性して得られる誘導体が挙げられる。

【００２６】

脂肪族ジイソシアネート（２官能性モノマー）としては、例えば、１，３－トリメチレンジイソシアネート、１，２－プロピレンジイソシアネート、１，４－ブチレンジイソシアネート、１，５－ペンタメチレンジイソシアネート（ＰＤＩ）、１，６－ヘキサメチレンジイソシアネート（ＨＤＩ）、２，４，４－または２，２，４－トリメチルヘキサメチレンジイソシアネート、２，６－ジイソシアネートメチルカプエートなどが挙げられる。

【００２７】

これら脂肪族ジイソシアネート（２官能性モノマー）は、単独使用または２種類以上併用することができる。

【００２８】

脂肪族ジイソシアネートとして、透明性の向上を図る観点から、好ましくは、１，５－ペンタメチレンジイソシアネート（ＰＤＩ）、１，６－ヘキサメチレンジイソシアネート

（ＨＤＩ）が挙げられ、さらに、保型性、耐熱性および速硬化性の向上を図る観点から、より好ましくは、１，５－ペンタメチレンジイソシアネート（ＰＤＩ）が挙げられる。換言すれば、脂肪族ジイソシアネートとして、１，５－ペンタメチレンジイソシアネート（ＰＤＩ）を用いれば、透明性に優れ、さらには、速硬化性に優れるポリウレタンゲルを得ることができる。

【００２９】

脂肪族ジイソシアネートの誘導体は、平均官能基数が上記の特定範囲となるように、上記の脂肪族ジイソシアネートを公知の方法で変性することにより、得ることができる。

【００３０】

脂肪族ジイソシアネートの誘導体としては、例えば、脂肪族ジイソシアネートの３量体（例えば、イソシアヌレート誘導体、イミノオキサジアジンジオン誘導体など）、アロファネート誘導体（例えば、上記した脂肪族ジイソシアネートと２価アルコール（後述）とをアロファネート化触媒存在下で反応させることにより生成するアロファネート誘導体など。）、ビウレット誘導体（例えば、上記した脂肪族ジイソシアネートと、水やアミン類との反応により生成するビウレット誘導体など。）、オキサジアジントリオン誘導体（例えば、上記した脂肪族ジイソシアネートと炭酸ガスとの反応により生成するオキサジアジントリオン誘導体など。）、ウレトンイミン誘導体、ポリオール誘導体（例えば、上記した脂肪族ジイソシアネートと３価以上のポリオール（好ましくは、トリメチロールプロパンなどの３価アルコール（後述））との反応より生成するポリオール誘導体（アルコール付加体）などが挙げられ、好ましくは、脂肪族ジイソシアネートの３量体が挙げられ、より好ましくは、脂肪族ジイソシアネートのイソシアヌレート誘導体が挙げられる。

【００３１】

脂肪族ジイソシアネートのイソシアヌレート誘導体は、例えば、脂肪族ジイソシアネートを、公知のイソシアヌレート化触媒（例えば、Ｎ－（２－ヒドロキシプロピル）－Ｎ，Ｎ，Ｎ－トリメチルアンモニウム－２－エチルヘキサノエートなど）の存在下において反応させ、３量化反応させることにより、得ることができる。

【００３２】

なお、３量化反応における反応条件は、特に制限されず、適宜設定される。

【００３３】

また、脂肪族ジイソシアネートのイソシアヌレート誘導体は、必要により、アルコール類により変性される。

【００３４】

アルコール類としては、特に制限されないが、例えば、脂肪族アルコール、芳香族アルコールなどが挙げられ、好ましくは、脂肪族アルコールが挙げられ、具体的には、例えば、メタノール、エタノール、ｎ－プロパノール、イソプロパノール、ｎ－ブタノール、イソブタノール（別名：イソブチルアルコール）、ｓｅｃ－ブタノール、ｔｅｒｔ－ブタノール、ペンタノール、ヘキサノール、２－エチルヘキサノール、オクタノール、デカノールなどの１価脂肪族アルコール、例えば、エチレングリコール、１，２－プロパンジオール、１，３－プロパンジオール、１，３－ブチレングリコール、１，４－ブチレングリコール、１，５－ペンタンジオール、１，６－ヘキサンジオールなどの２価脂肪族アルコール、例えば、グリセリン、トリメチロールプロパンなどの３価脂肪族アルコール、例えば、テトラメチロールメタンなどの４価以上の脂肪族アルコールなどが挙げられる。

【００３５】

また、アルコール類としては、例えば、分子量２５０～３０００のポリエステルポリオール、ポリエーテルポリオール、ポリカーボネートポリオールなども挙げられる。

【００３６】

これらアルコール類は、単独使用または２種類以上併用することができる。アルコール類として、好ましくは、１価脂肪族アルコールが挙げられ、より好ましくは、炭素数１～４の１価脂肪族アルコールが挙げられ、さらに好ましくは、イソブタノール（別名：イソブチルアルコール）が挙げられる。

【００３７】
脂肪族ジイソシアネートのイソシアヌレート誘導体を、アルコール類により変性する方法としては、例えば、まず、脂肪族ジイソシアネートとアルコール類とを反応させ、次いで、イソシアヌレート化触媒の存在下にイソシアヌレート化反応させる方法や、例えば、まず、脂肪族ジイソシアネートのみをイソシアヌレート化した後、得られたポリイソシアヌレートとアルコール類とを反応させる方法などが挙げられる。
【００３８】
好ましくは、まず、脂肪族ジイソシアネートとアルコール類とを反応させ、次いで、イソシアヌレート化触媒の存在下にイソシアヌレート化反応させる。
【００３９】
このような反応において、脂肪族ジイソシアネートとアルコール類との配合割合は、目的および用途に応じて、適宜設定されるが、脂肪族ジイソシアネート１００質量部に対して、アルコール類が、例えば、０．０５質量部以上、好ましくは、０．１質量部以上であり、また、例えば、１０質量部以下、好ましくは、５質量部以下である。
【００４０】
また、脂肪族ジイソシアネートとアルコール類との反応条件は、目的および用途に応じて、適宜設定される。また、イソシアネート基（ウレタン化後の残存イソシアネート基）の転化率（アロファネート基またはトリマー基への転化率）が、所定の割合（例えば、５～２０％）に達した時点で、例えば、リン酸、モノクロル酢酸、塩化ベンゾイル、ドデシルベンゼンスルホン酸、オルトトルエンスルホン酸、パラトルエンスルホン酸などの反応停止剤を反応液に添加して、触媒を失活させて反応を停止させることもできる。
【００４１】
なお、脂肪族ジイソシアネートとアルコール類との反応は、ウレタン化反応およびアロファネート化反応であり、脂肪族ジイソシアネートのアロファネート誘導体が、副生成物として生成する場合がある。すなわち、アルコール類により変性された脂肪族ジイソシアネートのイソシアヌレート誘導体は、イソシアヌレート基と、アロファネート基とを併有する場合がある。
【００４２】
そのような場合、アロファネート基のモル比率は、イソシアヌレート基のモル比率より少なく、具体的には、イソシアヌレート基１モルに対して、アロファネート基が、例えば、０．０５モル以上であり、例えば、１．０モル未満、好ましくは，０．５モル以下である。
【００４３】
アロファネート基のモル比率が上記範囲であれば、耐熱性の向上を図ることができる。
【００４４】
なお、アロファネート基とイソシアヌレート基とのモル比率は、後述する実施例に準拠して求めることができる。
【００４５】
さらに、多官能性脂肪族ポリイソシアネートとしては、上記の他、例えば、３官能性の脂肪族ポリイソシアネートモノマーが挙げられる。３官能性の脂肪族ポリイソシアネートモノマーとしては、例えば、１，６，１１－ウンデカメチレントリイソシアネート、１，３，６－ヘキサメチレントリイソシアネート、１，８－ジイソシアネート－４－イソシアナトメチルオクタン、２，５，７－トリメチル－１，８－ジイソシアネート－５－イソシアナトメチルオクタン、リシントリイソシアネートなどの脂肪族トリイソシアネートなどが挙げられる。
【００４６】
これら多官能性脂肪族ポリイソシアネートは、単独使用または２種類以上併用することができる。
【００４７】
多官能性脂肪族ポリイソシアネートは、耐熱性の向上を図る観点から、好ましくは、脂

肪族ジイソシアネートのイソシアヌレート誘導体、より好ましくは、ペンタメチレンジイソシアネートのイソシアヌレート誘導体の単独使用が挙げられる（ただし、イソシアヌレート誘導体の製造時に副生するアロファネート誘導体およびウレトジオン誘導体の含有を許容する。）。

【００４８】

多官能性脂肪族ポリイソシアネートの平均官能基数は、２．０を超過し、好ましくは、２．５以上、より好ましくは、２．８以上、さらに好ましくは、３．０以上であり、また、３．５以下、好ましくは、３．３以下である。

【００４９】

多官能性脂肪族ポリイソシアネートの平均官能基数は、後述する実施例に準拠して算出される。

【００５０】

多官能性脂肪族ポリイソシアネートの平均官能基数を上記の範囲とすることにより、後述するように、ポリオール成分と相まってポリウレタンに適度な３次元ネットワークを形成することができる。

【００５１】

なお、また、多官能性脂肪族ポリイソシアネートは、本発明の優れた効果を阻害しない範囲で、官能基数が２．０以下の脂肪族ポリイソシアネートや、官能基数が３．５を超過する脂肪族ポリイソシアネートを含有することができる。このような場合も、多官能性脂肪族ポリイソシアネートの平均官能基数は、上記の範囲に調整される。

【００５２】

また、ポリイソシアネート成分は、任意成分として、上記した平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネート以外のポリイソシアネート（以下、その他のポリイソシアネートと称する。）を含有することができる。

【００５３】

その他のポリイソシアネートとしては、例えば、芳香族ポリイソシアネート、芳香脂肪族ポリイソシアネート、脂環族ポリイソシアネートなどのポリイソシアネートモノマー（すなわち、脂肪族ポリイソシアネート以外のポリイソシアネートモノマー）が挙げられる。

【００５４】

芳香族ポリイソシアネートとしては、例えば、トリレンジイソシアネート（２，４－または２，６－トリレンジイソシアネートもしくはその混合物）（ＴＤＩ）、フェニレンジイソシアネート（ｍ－、ｐ－フェニレンジイソシアネートもしくはその混合物）、４，４’－ジフェニルジイソシアネート、１，５－ナフタレンジイソシアネート（ＮＤＩ）、ジフェニルメタンジイソシネート（４，４’－、２，４’－または２，２’－ジフェニルメタンジイソシネートもしくはその混合物）（ＭＤＩ）、４，４’－トルイジンジイソシアネート（ＴＯＤＩ）、４，４’－ジフェニルエーテルジイソシアネートなどの芳香族ジイソシアネートなどが挙げられる。

【００５５】

芳香脂肪族ポリイソシアネートとしては、例えば、キシリレンジイソシアネート（１，３－または１，４－キシリレンジイソシアネートもしくはその混合物）（ＸＤＩ）、テトラメチルキシリレンジイソシアネート（１，３－または１，４－テトラメチルキシリレンジイソシアネートもしくはその混合物）（ＴＭＸＤＩ）、ω，ω’－ジイソシアネート－１，４－ジエチルベンゼンなどの芳香脂肪族ジイソシアネートなどが挙げられる。

【００５６】

脂環族ポリイソシアネートとしては、例えば、１，３－シクロペンタンジイソシアネート、１，３－シクロペンテンジイソシアネート、シクロヘキサンジイソシアネート（１，４－シクロヘキサンジイソシアネート、１，３－シクロヘキサンジイソシアネート）、３－イソシアナトメチル－３，５，５－トリメチルシクロヘキシルイソシアネート（イソホロンジイソシアネート）（ＩＰＤＩ）、メチレンビス（シクロヘキシルイソシアネート）

（４，４’－、２，４’－または２，２’－メチレンビス（シクロヘキシルイソシアネート、これらのＴｒａｎｓ，Ｔｒａｎｓ－体、Ｔｒａｎｓ，Ｃｉｓ－体、Ｃｉｓ，Ｃｉｓ－体、もしくはその混合物））（$Ｈ_{12}$ＭＤＩ）、メチルシクロヘキサンジイソシアネート（メチル－２，４－シクロヘキサンジイソシアネート、メチル－２，６－シクロヘキサンジイソシアネート）、ノルボルナンジイソシアネート（各種異性体もしくはその混合物）（ＮＢＤＩ）、ビス（イソシアナトメチル）シクロヘキサン（１，３－または１，４－ビス（イソシアナトメチル）シクロヘキサンもしくはその混合物）（$Ｈ_{6}$ＸＤＩ）などの脂環族ジイソシアネートなどが挙げられる。

【００５７】

また、その他のポリイソシアネートとしては、上記したポリイソシアネートモノマー（すなわち、脂肪族ポリイソシアネート以外のポリイソシアネートモノマー）の誘導体も挙げられる。そのような誘導体としては、例えば、ポリイソシアネートモノマーの多量体（例えば、２量体、３量体（例えば、イソシアヌレート変性体、イミノオキサジアジンジオン変性体）、５量体、７量体など）、アロファネート誘導体、ビウレット誘導体、オキサジアジントリオン誘導体、ウレトンイミン誘導体などが挙げられる。

【００５８】

これらその他のポリイソシアネートは、単独使用または２種類以上併用することができる。

【００５９】

その他のポリイソシアネートの含有割合は、本発明の優れた効果を損なわない観点から、ポリイソシアネート成分の総量に対して、例えば、５０質量％未満、好ましくは、３０質量％以下、より好ましくは、１０質量％以下、さらに好ましくは、５質量％以下、とりわけ好ましくは、０質量％である。

【００６０】

すなわち、ポリイソシアネート成分は、好ましくは、その他のポリイソシアネートを含有せず、平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを単独で含有する。

【００６１】

ポリイソシアネート成分の平均官能基数は、例えば、２．０を超過し、好ましくは、２．５以上、より好ましくは、２．８以上、さらに好ましくは、３．０以上であり、また、例えば、３．５以下、好ましくは、３．３以下である。

【００６２】

また、ポリイソシアネート成分のイソシアネート基濃度は、例えば、２０．０質量％以上、好ましくは、２３．０質量％以上であり、例えば、３０．０質量％以下、好ましくは、２５．０質量％以下、より好ましくは、２４．６質量％以下である。

【００６３】

ポリオール成分は、必須成分として、２官能性ポリオールを特定割合（後述）で含有する。

【００６４】

本発明では、ポリイソシアネート成分の平均官能基数が上記の範囲である一方、ポリオール成分が２官能性ポリオールを特定割合（後述）で含有するため、得られるポリウレタンが適度なネットワークを形成し、後述するように、溶媒を比較的多く含有することができる。そのため、本発明によれば、優れた触感（柔軟性、弾力）およびデザイン性（透明感、潤い感、ぷるぷる感など）と、優れた保型性を両立することができ、また、溶媒の揮散性に優れ、さらには、溶媒の揮散に伴うポリウレタンゲルの収縮性にも優れる。

【００６５】

２官能性ポリオールとしては、例えば、低分子量ジオール、高分子量ジオールが挙げられる。

【００６６】

低分子量ジオールは、水酸基を２つ有する数平均分子量４００未満、４０以上の化合物

であって、具体的には、例えば、エチレングリコール、プロピレングリコール（１，２－プロパンジオール）、１，３－プロパンジオール、１，４－ブチレングリコール、１，３－ブチレングリコール、１，２－ブチレングリコール、１，５－ペンタンジオール、１，６－ヘキサンジオール、ネオペンチルグリコール、３－メチル－１，５－ペンタンジオール、２，２，２－トリメチルペンタンジオール、３，３－ジメチロールヘプタン、アルカン（Ｃ７～２０）ジオール、１，３－または１，４－シクロヘキサンジメタノールおよびそれらの混合物、１，３－または１，４－シクロヘキサンジオールおよびそれらの混合物、水素化ビスフェノールＡ、１，４－ジヒドロキシ－２－ブテン、２，６－ジメチル－１－オクテン－３，８－ジオール、ビスフェノールＡ、ジエチレングリコール、トリエチレングリコール、ジプロピレングリコールなどの２価アルコールなどが挙げられる。

【００６７】

これら低分子量ジオールは、単独使用または２種類以上併用することができる。

【００６８】

高分子量ジオールは、水酸基を２つ有する数平均分子量４００以上、１００００以下の化合物であって、例えば、ポリエーテルジオール、ポリエステルジオール、ポリカーボネートジオールなどが挙げられる。

【００６９】

ポリエーテルジオールとしては、例えば、ポリオキシアルキレンジオール、ポリテトラメチレンエーテルグリコール、ポリトリメチレンエーテルグリコールなどが挙げられる。

【００７０】

ポリオキシアルキレンジオールとしては、上記した２価アルコールを開始剤とする、エチレンオキサイド、プロピレンオキサイドなどのアルキレンオキサイドの付加重合物（２種以上のアルキレンオキサイドのランダムおよび／またはブロック共重合体を含む。）が挙げられる。より具体的には、例えば、ポリエチレングリコール、ポリプロピレングリコール、ポリオキシエチレン・ポリオキシプロピレン（ランダムおよび／またはブロック）共重合体などが挙げられる。

【００７１】

ポリテトラメチレンエーテルグリコールとしては、例えば、テトラヒドロフランのカチオン重合により得られる開環重合物や、テトラヒドロフランの重合単位に上記した２価アルコールを共重合した非晶性ポリテトラメチレンエーテルグリコール（平均官能基数２）などが挙げられる。

【００７２】

非晶性ポリテトラメチレンエーテルグリコールは、例えば、テトラヒドロフランと、アルキル置換テトラヒドロフラン（例えば、３－メチルテトラヒドロフランなど）との共重合体（テトラヒドロフラン／アルキル置換テトラヒドロフラン（モル比）＝１５／８５～８５／１５、数平均分子量５００～４０００、好ましくは、８００～２５００）や、例えば、テトラヒドロフランと、分岐状グリコール（例えば、ネオペンチルグリコールなど）との共重合体（テトラヒドロフラン／分岐状グリコール（モル比）＝１５／８５～８５／１５、数平均分子量５００～４０００、好ましくは、８００～２５００）などとして、得ることができる。

【００７３】

なお、非晶性（非結晶性）とは、常温（２５℃）において液状であることを示す（以下同様）。

【００７４】

また、フルフラールなどの植物由原料をもとに製造されたテトラヒドロフランを出発原料とした植物由来のポリテトラメチレンエーテルグリコールも使用することができる。

【００７５】

ポリトリメチレンエーテルグリコールとしては、例えば、植物由来の１，３－プロパンジオールの縮重合により製造されるポリオールが挙げられる。

【００７６】

ポリエステルジオールは、ジカルボン酸と、上記した２価アルコールとの縮合反応や、ジカルボン酸のアルキルエステルと、上記した２価アルコールとのエステル交換反応により得ることができる。

【００７７】

ジカルボン酸としては、例えば、シュウ酸、マロン酸、コハク酸、メチルコハク酸、グルタール酸、アジピン酸、１，１－ジメチル－１，３－ジカルボキシプロパン、３－メチル－３－エチルグルタール酸、アゼライン酸、セバシン酸、その他の飽和脂肪族ジカルボン酸（炭素数１１～１３）、例えば、マレイン酸、フマル酸、イタコン酸、その他の不飽和脂肪族ジカルボン酸、例えば、オルソフタル酸、イソフタル酸、テレフタル酸、トルエンジカルボン酸、ナフタレンジカルボン酸、その他の芳香族ジカルボン酸、例えば、ヘキサヒドロフタル酸、その他の脂環族ジカルボン酸、例えば、ダイマー酸、水添ダイマー酸、ヘット酸などのその他のカルボン酸などが挙げられる。さらには、ジカルボン酸から誘導される酸無水物、例えば、無水シュウ酸、無水コハク酸、無水メチルコハク酸、無水マレイン酸、無水フタル酸、無水ヘキサヒドロフタル酸、または、これらのジカルボン酸から誘導される酸ハライド、例えば、シュウ酸ジクロライド、アジピン酸ジクロライド、セバシン酸ジクロライドなどが挙げられる。

【００７８】

また、ジカルボン酸のアルキルエステルとしては、例えば、上記したジカルボン酸のＣ１～４アルキルエステルが挙げられる。

【００７９】

ポリカーボネートジオールとしては、例えば、上記した２価アルコールを開始剤とするエチレンカーボネートの開環重合物や、例えば、１，４－ブタンジオール、１，５－ペンタンジオール、３－メチル－１，５－ペンタンジオールや１，６－ヘキサンジオールなどの２価アルコールと、開環重合物とを共重合した非晶性ポリカーボネートジオールなどが挙げられる。

【００８０】

また、ポリカーボネートジオールとして、例えば、植物由来のポリカーボネートジオールが挙げられ、具体的には、植物由来原料であるグルコースなどから誘導されたイソソルビドなどの脂環式ジヒドロキシ化合物や、上記した２価アルコールを、炭酸ジフェニルとエステル交換反応させて得られるポリカーボネートジオールなどが挙げられる。

【００８１】

これら高分子量ジオールは、単独使用または２種類以上併用することができる。

【００８２】

ポリウレタンゲルの製造時における溶媒との相溶性の観点から、好ましくは、非晶性の高分子量ジオールが挙げられ、より好ましくは、ポリオキシアルキレングリコール、非晶性ポリテトラメチレンエーテルグリコール、非晶性ポリカーボネートジオール、ポリエステルポリオールが挙げられる。

【００８３】

また、耐熱性および透明性の向上を図る観点から、好ましくは、ポリエーテルジオールが挙げられ、より好ましくは、ポリテトラメチレンエーテルグリコールが挙げられ、さらに好ましくは、非晶性ポリテトラメチレンエーテルグリコールが挙げられる。

【００８４】

これら２官能性ポリオールは、単独使用または２種類以上併用することができる。

【００８５】

２官能性ポリオールとして、好ましくは、高分子量ジオールが挙げられる。

【００８６】

また、ポリオール成分は、任意成分として、その他のポリオール（３官能性以上のポリオール）や、モノオールを含有することができる。

【００８７】

その他のポリオール（３官能性以上のポリオール）としては、３官能性以上の低分子量

ポリオール、３官能性以上の高分子量ポリオールが挙げられる。

【００８８】

３官能性以上の低分子量ポリオールは、水酸基を３つ以上有する数平均分子量４００未満、４０以上の化合物であって、具体的には、例えば、グリセリン、トリメチロールプロパン、トリイソプロパノールアミンなどの３価アルコール、例えば、テトラメチロールメタン（ペンタエリスリトール）、ジグリセリンなどの４価アルコール、例えば、キシリトールなどの５価アルコール、例えば、ソルビトール、マンニトール、アリトール、イジトール、ダルシトール、アルトリトール、イノシトール、ジペンタエリスリトールなどの６価アルコール、例えば、ペルセイトールなどの７価アルコール、例えば、ショ糖などの８価アルコールなどが挙げられる。

【００８９】

これら３官能性以上の低分子量ポリオールは、単独使用または２種類以上併用することができる。

【００９０】

３官能性以上の高分子量ポリオールは、水酸基を３つ以上有する数平均分子量４００以上、１００００以下の化合物であって、例えば、ポリエーテルトリオール（上記３価アルコールを開始剤とした炭素数２～３のアルキレンオキサイドの付加重合体など）、ポリエーテルテトラオール（上記４価アルコールを開始剤とした炭素数２～３のアルキレンオキサイドの付加重合体など）、ポリエステルトリオール（２塩基酸および／またはそのアルキルエステルと、上記３価アルコール（および２価アルコール）との反応生成物など）、ポリエステルテトラオール（２塩基酸および／またはそのアルキルエステルと、上記４価アルコール（および２～３価アルコール）との反応生成物など）、ポリカーボネートトリオール（上記３価アルコールを開始剤とするエチレンカーボネートの開環重合物など）、ポリカーボネートテトラオール（上記４価アルコールを開始剤とするエチレンカーボネートの開環重合物など）などが挙げられる。

【００９１】

これら３官能性以上の高分子量ポリオールは、単独使用または２種類以上併用することができる。

【００９２】

モノオールとしては、例えば、メタノール、エタノール、プロパノール、イソプロパノール、ブタノール、イソブタノール、ｓ－ブタノール、ｔ－ブタノール、ペンタノール、ヘキサノール、ヘプタノール、オクタノールなどの１価アルコールが挙げられる。

【００９３】

また、モノオールとしては、例えば、上記した高分子量ジオールの片末端の水酸基がアルキルエステル基に置換されたモノアルキルエステルや、例えば、上記した高分子量ジオールの片末端の水酸基がアルキルエーテル基に置換されたモノアルキルエーテル（例えば、ポリオキシエチレンモノアルキルエーテルなど）が挙げられる。

【００９４】

これらモノオールは、単独使用または２種類以上併用することができる。

【００９５】

ポリオール成分において、２官能性ポリオールの含有割合は、透明性、触感、デザイン性、吸収性、保持力、揮散性、保型性、耐熱性および速硬化性の向上を図る観点から、ポリオール成分の総量に対して、８０質量％以上、好ましくは、８５質量％以上、より好ましくは、９０質量％以上、さらに好ましくは、９５質量％以上、とりわけ好ましくは、１００質量％である。

【００９６】

すなわち、ポリオール成分は、好ましくは、３官能性以上のポリオールおよびモノオールを含有せず、２官能性ポリオールを単独で含有する。

【００９７】

ポリオール成分の平均官能基数は、３．０以下、好ましくは、２．５以下であり、通常

、２．０以上である。ポリオールの平均官能基数として、とりわけ好ましくは、２．０である。

【００９８】

また、ポリオール成分の水酸基価（ＯＨ価）は、例えば、１０ｍｇＫＯＨ／ｇ以上、好ましくは、１２ｍｇＫＯＨ／ｇ以上、より好ましくは、１５ｍｇＫＯＨ／ｇ以上であり、例えば、１５０ｍｇＫＯＨ／ｇ以下、好ましくは、１２０ｍｇＫＯＨ／ｇ以下、より好ましくは、１００ｍｇＫＯＨ／ｇ以下である。

【００９９】

なお、ポリオール成分の平均官能基数は、仕込みの配合処方から算出され、ポリオールの水酸基価は、ＪＩＳ　Ｋ　１５５７－１（２００７年）の記載に準拠して測定される。

【０１００】

そして、ポリウレタンゲルは、上記のポリイソシアネート成分と上記のポリオール成分とがウレタン化触媒および溶媒の存在下においてウレタン化反応した反応生成物として得られる。

【０１０１】

ポリウレタンゲルの製造方法として、より具体的には、まず、上記したポリイソシアネート成分と、上記したポリオール成分と、ウレタン化触媒と、溶媒とを配合する（配合工程）。

【０１０２】

より具体的には、この工程では、ポリイソシアネート成分と、ポリオール成分と、ウレタン化触媒と、溶媒とを、順次配合するのではなく、一括で配合する。

【０１０３】

ポリイソシアネート成分およびポリオール成分の配合割合は、ポリオール成分の水酸基に対する、ポリイソシアネート成分のイソシアネート基の当量比（ＮＣＯ／ＯＨ）が、例えば、０．６以上、好ましくは、０．７以上、より好ましくは、０．７５以上、さらに好ましくは、０．８以上であり、例えば、１．２以下、好ましくは、１以下、比較的緩いネットワークを形成して、より多くの溶媒をポリウレタン中に内包する観点から、より好ましくは、１未満、より好ましくは、０．９５以下、さらに好ましくは、０．９以下である。

【０１０４】

ウレタン化触媒としては、公知のウレタン化触媒が挙げられ、具体的には、アミン類、有機金属化合物、カリウム塩が挙げられる。

【０１０５】

アミン類としては、例えば、トリエチルアミン、トリエチレンジアミン、ビス－（２－ジメチルアミノエチル）エーテル、Ｎ－メチルモルホリンなどの３級アミン類、例えば、テトラエチルヒドロキシルアンモニウムなどの４級アンモニウム塩、例えば、イミダゾール、２－エチル－４－メチルイミダゾールなどのイミダゾール類などが挙げられる。

【０１０６】

有機金属化合物としては、例えば、酢酸錫、オクチル酸錫、オレイン酸錫、ラウリル酸錫、ジブチル錫ジアセテート、ジメチル錫ジラウレート、ジブチル錫ジラウレート、ジブチル錫ジメルカプチド、ジブチル錫マレエート、ジブチル錫ジラウレート（ジラウリン酸ジブチル錫（ＩＶ））、ジブチル錫ジネオデカノエート、ジオクチル錫ジメルカプチド、ジオクチル錫ジラウリレート、ジブチル錫ジクロリドなどの有機錫化合物、例えば、オクタン酸鉛、ナフテン酸鉛などの有機鉛化合物、例えば、ナフテン酸ニッケルなどの有機ニッケル化合物、例えば、ナフテン酸コバルトなどの有機コバルト化合物、例えば、オクテン酸銅などの有機銅化合物、例えば、オクチル酸ビスマス、ネオデカン酸ビスマスなどの有機ビスマス化合物などが挙げられる。

【０１０７】

カリウム塩としては、例えば、炭酸カリウム、酢酸カリウム、オクチル酸カリウムなどが挙げられる。

【０１０８】
これらウレタン化触媒は、単独使用または２種類以上併用することができる。
【０１０９】
ウレタン化触媒として、好ましくは、有機金属化合物が挙げられ、より好ましくは、有機錫化合物が挙げられ、とりわけ好ましくは、ジブチル錫ジラウレートが挙げられる。
【０１１０】
ウレタン化触媒の配合割合は、室温での反応性の向上を図る観点から、通常のポリウレタン製造における配合割合よりも相対的に多く、具体的には、ポリイソシアネート成分およびポリオール成分の総量１００質量部に対して、例えば、０．０５質量部以上、好ましくは、０．１質量部を超過し、より好ましくは、０．２質量部以上であり、例えば、１．５質量部以下、好ましくは、１質量部以下、より好ましくは、０．５質量部以下である。
【０１１１】
溶媒としては、例えば、アセトン、メチルエチルケトン、メチルイソブチルケトン、シクロヘキサノンなどのケトン類、例えば、アセトニトリルなどのニトリル類、酢酸メチル、酢酸エチル、酢酸ブチル、酢酸イソブチル、乳酸メチルなどのアルキルエステル類、例えば、ｎ－ヘキサン、ｎ－ヘプタン、オクタンなどの脂肪族炭化水素類、例えば、シクロヘキサン、メチルシクロヘキサンなどの脂環族炭化水素類、例えば、トルエン、キシレン、エチルベンゼンなどの芳香族炭化水素類、例えば、メチルセロソルブアセテート、エチルセロソルブアセテート、メチルカルビトールアセテート、エチルカルビトールアセテート、エチレングリコールメチルエーテルアセテート、エチレングリコールエチルエーテルアセテート、プロピレングリコールメチルエーテルアセテート（ＰＭＡ）、３－メチル－３－メトキシブチルアセテート、ジプロピレングリコールメチルエーテルアセテート、プロピレングリコールジアセテート、エチル－３－エトキシプロピオネートなどのグリコールエーテルエステル類、例えば、ジエチルエーテル、テトラヒドロフラン、ジオキサン、１，２－ジメトキシエタン、ジエチレングリコールジメチルエーテル、ジエチレングリコールジエチルエーテル、ジプロピレングリコールジメチルエーテル、ジプロピレングリコールジエチルエーテル、エチレングリコールジエチルエーテル１，２－ジエトキシエタン、１，８－シネオール、バニリン、エチルバニリンなどのエーテル類、例えば、塩化メチル、塩化メチレン、クロロホルム、四塩化炭素、臭化メチル、ヨウ化メチレン、ジクロロエタンなどのハロゲン化脂肪族炭化水素類、例えば、Ｎ－メチルピロリドン、Ｎ，Ｎ’－ジメチルホルムアミド、Ｎ，Ｎ’－ジメチルアセトアミド、ジメチルスルホキシド、ヘキサメチルホスホニルアミドなどの極性非プロトン類、さらには、植物油脂、天然由来油脂などが挙げられる。
【０１１２】
これら溶媒は、単独使用または２種類以上併用することもできる。
【０１１３】
溶媒として、揮散性の観点から、好ましくは、グリコールエーテルエステル類、エーテル類が挙げられ、より好ましくは、グリコールエーテルエステル類が挙げられる。
【０１１４】
溶剤の配合割合は、得られるポリウレタンゲルの総量に対して、透明性、触感、デザイン性および揮散性の向上を図る観点から、ポリウレタンゲルにより多く含まれることが好ましく、具体的には、５０質量％以上、好ましくは、５０質量％を超過し、より好ましくは、７０質量％以上であり、触感、デザイン性、吸収性、保持力、揮散性、保型性、耐熱性および速硬化性の向上を図る観点から、９５質量％以下、好ましくは、９３質量％以下、より好ましくは、９０質量％以下である。
【０１１５】
次いで、この方法では、上記のように配合されたポリイソシアネート成分およびポリオール成分を、ウレタン化触媒および溶媒の存在下、ウレタン化反応させる（反応工程）。
【０１１６】
より具体的には、ウレタン化反応における反応温度は、溶媒の揮発を抑制する観点から

、室温（加熱することのない室内環境雰囲気温度）であり、例えば、１５℃以上、好ましくは、１８℃以上であり、例えば、３５℃以下、好ましくは、３０℃以下である。また、反応時間が、例えば、２時間以上、好ましくは、４時間以上であり、例えば、４８時間以下、好ましくは、２４時間以下である。

【０１１７】

これにより、ポリイソシアネート成分およびポリオール成分の反応により得られるポリウレタンのネットワーク中に、溶媒が内包されるポリウレタンゲルが得られる。

【０１１８】

得られるポリウレタンゲルにおいて、溶媒の含有割合は、ポリウレタンゲルの総量に対して、５０質量％以上、好ましくは、５０質量％を超過し、より好ましくは、７０質量％以上であり、９５質量％以下、好ましくは、９３質量％以下、より好ましくは、９０質量％以下である。

【０１１９】

溶媒の含有割合が上記範囲であれば、透明性に優れ、また、触感、デザイン性、吸収性、保持力および揮散性に優れ、さらには、保型性、耐熱性および速硬化性に優れるポリウレタンゲルが得られる。

【０１２０】

また、得られるポリウレタンゲルにおいて、ウレタン化触媒の含有割合は、ポリイソシアネート成分およびポリオール成分の総量１００質量部に対して、例えば、０．０５質量部以上、好ましくは、０．１質量部を超過し、より好ましくは、０．２質量部以上であり、例えば、２質量部以下、好ましくは、１質量部以下、より好ましくは、０．５質量部以下である。

【０１２１】

ウレタン化触媒の含有割合が上記範囲であれば、揮散性、保型性および速硬化性に優れるポリウレタンゲルが得られる。

【０１２２】

また、ポリウレタンゲルは、必要に応じて、公知の添加剤を含有することができる。添加剤としては、例えば、香料、防虫剤、殺虫剤、抗菌剤、殺菌剤、忌避剤、農薬などの揮散性有効成分、さらには、貯蔵安定剤（ｏ－トルエンスルホンアミド、ｐ－トルエンスルホンアミドなど）、ブロッキング防止剤、耐熱安定剤、耐光安定剤、紫外線吸収剤、酸化防止剤、消泡剤、離型剤、顔料、染料、滑剤、フィラー、加水分解防止剤などが挙げられる。

【０１２３】

これら添加剤は、単独使用または２種類以上併用することができる。

【０１２４】

また、添加剤の添加量は、特に制限されず、目的および用途に応じて、適宜設定される。

【０１２５】

なお、ポリウレタンゲルに添加剤を含有させる方法は、特に制限されず、例えば、ポリイソシアネート成分、ポリオール成分、ウレタン化触媒および溶媒からなる群から選択される１種以上に対して、予め添加してもよく、また、それらの配合と同時に添加してもよく、さらには、それらを配合した後に、別途添加してもよい。また、添加剤の添加割合は、特に制限されず、目的および用途に応じて、適宜設定される。

【０１２６】

また、ポリウレタンゲルの形状およびサイズは、特に制限されず、目的および用途に応じて、所定の金型を用いることにより、適宜設定される。具体的には、例えば、立方体状、直方体状、多角柱状、球状、塊状など、種々の形状が挙げられる。

【０１２７】

そして、このようなポリウレタンゲルは、平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有するポリイソシアネート成分と、２官能性

ポリオールを８０質量％以上含有するポリオール成分とが反応してなり、また、特定割合で溶媒を含有するため、透明性に優れ、また、触感（柔軟性、弾力）、デザイン性（透明感、潤い感、ぷるぷる感など）、吸収性、保持力および揮散性に優れ、さらには、保型性、耐熱性および速硬化性に優れる。

【０１２８】

また、上記したように、溶媒が揮散性である場合、溶媒の放出に伴ってポリウレタンゲルが収縮する。すなわち、溶媒の含有量が多い状態では、ポリウレタンゲルの体積が比較的大きく、また、溶媒が揮散するに従って、ポリウレタンゲルの体積が小さくなる。そのため、溶媒の残量が外観で判断可能である。

【０１２９】

そのため、ポリウレタンゲルは、例えば、揮散性の溶媒とともに揮散性有効成分を含有することにより、種々の産業分野において好適に用いられる。具体的には、添加剤として香料を含有するポリウレタンゲルは、芳香ゲルとして好適に用いられ、また、添加剤として防虫剤や忌避剤を含有するポリウレタンゲルは、防虫ゲルとして好適に用いられ、例えば、添加剤として抗菌剤、殺菌剤を含有するポリウレタンゲルは、抗菌ゲル、殺菌ゲルとして好適に用いられる。

【実施例】

【０１３０】

次に、本発明を、製造例、実施例および比較例に基づいて説明するが、本発明は、下記の実施例によって限定されるものではない。なお、「部」および「％」は、特に言及がない限り、質量基準である。また、以下の記載において用いられる配合割合（含有割合）、物性値、パラメータなどの具体的数値は、上記の「発明を実施するための形態」において記載されている、それらに対応する配合割合（含有割合）、物性値、パラメータなど該当記載の上限値（「以下」、「未満」として定義されている数値）または下限値（「以上」、「超過」として定義されている数値）に代替することができる。

【０１３１】

また、各製造例、各実施例および各比較例において採用される測定方法を下記する。

１．測定方法

＜イソシアネート基濃度（単位：質量％）、イソシアネート基の転化率（単位：質量％）＞

電位差滴定装置（京都電子工業社製、型番：ＡＴ－５１０）を用いて、ＪＩＳ　Ｋ－１６０３－１（２００７年）に準拠したトルエン／ジブチルアミン・塩酸法によりイソシアネート基濃度（イソシアネート基含有率）を測定し、以下の式により、測定試料のイソシアネート基の転化率を算出した。

【０１３２】

イソシアネート基の転化率＝［（反応前の反応液のイソシアネート基濃度－反応終了後の反応液のイソシアネート基濃度）／反応前の反応液のイソシアネート基濃度］×１００

＜^{1}Ｈ－ＮＭＲによるアロファネート基とイソシアヌレート基とのモル比率＞

下記の装置および条件にて^{1}Ｈ－ＮＭＲを測定し、イソシアヌレート基１モルに対するアロファネート基の含有割合（アロファネート基／イソシアヌレート基のモル比率）を以下の式により算出した。なお、化学シフトｐｐｍの基準として、Ｄ^{6}－ＤＭＳＯ溶媒中のテトラメチルシラン（０ｐｐｍ）を用いた。

装置；　ＪＮＭ－ＡＬ４００（ＪＥＯＬ製）

条件；　測定周波数：４００ＭＨｚ、溶媒：Ｄ^{6}－ＤＭＳＯ、溶質濃度：５質量％

イソシアヌレート基（イソシアヌレート基に直接結合するメチレン基（CH_2基））のプロトンの帰属ピーク（６Ｈ）：３．８ｐｐｍ

アロファネート基（アロファネート基内のＮＨ基）のプロトンの帰属ピーク（１Ｈ）：８．３～８．７ｐｐｍ

アロファネート基／イソシアヌレート基（モル比率）＝アロファネート基のプロトン

の帰属ピークの積分値／（イソシアヌレート基のプロトンの帰属ピークの積分値／６）

＜平均イソシアネート基数（平均官能基数）＞

ポリイソシアネートの平均イソシアネート基数を、イソシアネート基濃度、固形分濃度（ＮＶ）、および、以下の装置および条件にて測定されるゲルパーミエーションクロマトグラフィーの数平均分子量から、下記式により算出した。

【０１３３】

平均イソシアネート基数＝Ａ／Ｂ×Ｃ／４２．０２

（式中、Ａは、イソシアネート基濃度を示し、Ｂは、固形分濃度を示し、Ｃは、数平均分子量を示す。）

装置：ＨＬＣ－８２２０ＧＰＣ（東ソー製）

カラム：ＴＳＫｇｅｌＧ１０００ＨＸＬ、ＴＳＫｇｅｌＧ２０００ＨＸＬ、およびＴＳＫｇｅｌＧ３０００ＨＸＬ（東ソー製）を直列に連結した。

検出器：　示差屈折率計

測定条件

注入量：１００μＬ

溶離液：テトラヒドロフラン

流量：０．８ｍＬ／ｍｉｎ

温度：４０℃

検量線：１０６～２２４５０の範囲の標準ポリエチレンオキシド（東ソー製、商品名：ＴＳＫ標準ポリエチレンオキシド）

製造例１（ペンタメチレンジイソシアネート（ａ）の製造）

国際公開パンフレットＷＯ２０１２／１２１２９１号の明細書における実施例１と同様の操作にて、９９．９質量％のペンタメチレンジイソシアネート（以後ＰＤＩと略する場合がある。）（ａ）を得た。

【０１３４】

製造例２（ＰＤＩのイソシアヌレート誘導体（Ａ））

温度計、撹拌装置、還流管、および、窒素導入管を備えた４つ口フラスコに、製造例１により得られたペンタメチレンジイソシアネート（ａ）を５００質量部、イソブチルアルコールを０．５２質量部、２，６－ジ（ｔｅｒｔ－ブチル）－４－メチルフェノールを０．３質量部、トリス（トリデシル）ホスファイトを０．３質量部、それぞれ装入し、８０℃で２時間反応させた。

【０１３５】

次いで、イソシアヌレート化触媒としてＮ－（２－ヒドロキシプロピル）－Ｎ，Ｎ，Ｎ－トリメチルアンモニウム－２－エチルヘキサノエートを０．０５質量部配合した。イソシアネート基濃度を測定し、その濃度が４８．９質量％（すなわち、転化率１０質量％）に至るまで反応を継続した。５０分後に所定の転化率（転化率１０質量％）に達したところで、ｏ－トルエンスルホンアミド（貯蔵安定剤）を０．１２質量部添加した。

【０１３６】

その後、得られた反応混合液を薄膜蒸留装置（温度：１５０℃、真空度：０．０９３ｋＰａ）に通液して、未反応の１，５－ペンタメチレンジイソシアネートを除去した。

【０１３７】

さらに、得られたろ物１００質量部に対し、ｏ－トルエンスルホンアミド（貯蔵安定剤）０．０２質量部、および、塩化ベンゾイル（反応停止剤）０．００３質量部を添加し、ＰＤＩのイソシアヌレート誘導体（Ａ）（以下、ＰＤＩ誘導体（Ａ）とする。）を得た。

【０１３８】

このＰＤＩ誘導体（Ａ）におけるＰＤＩモノマー濃度は０．５質量％、イソシアネート基濃度は２４．６質量％、イソシアネート基の平均官能基数は３．１、２５℃における粘度は２０００ｍＰａ・ｓであった。

【０１３９】

また、このＰＤＩ誘導体（Ａ）の^{1}Ｈ－ＮＭＲ測定によるアロファネート基とイソシア

ヌレート基とのモル比率は、アロファネート基／イソシアヌレート基＝８／１００（すなわち、アロファネート基の含有割合は、イソシアヌレート基１モルに対して、０．０８モル）であった。

【０１４０】

製造例３（ＰＤＩのイソシアヌレート誘導体（Ｂ））

温度計、撹拌装置、還流管、および、窒素導入管を備えた４つ口フラスコに、製造例１により得られた１，５－ペンタメチレンジイソシアネート（ａ）を５００質量部、イソブチルアルコールを９．８質量部、２，６－ジ（ｔｅｒｔ－ブチル）－４－メチルフェノールを０．３質量部、トリス（トリデシル）ホスファイトを０．３質量部、それぞれ、装入し、８０℃で２時間反応させた。

【０１４１】

次いで、イソシアヌレート化触媒としてＮ－（２－ヒドロキシプロピル）－Ｎ，Ｎ，Ｎ－トリメチルアンモニウム－２－エチルヘキサノエートを０．０５質量部配合した。イソシアネート基濃度を測定し、その濃度が、４７．１質量％（すなわち、転化率１０質量％）に至るまで反応を継続した。２０分後に所定の転化率（転化率１０質量％）に達したため、ｏ－トルエンスルホンアミド（貯蔵安定剤）を０．１２質量部添加した。

【０１４２】

その後、得られた反応混合液を薄膜蒸留装置（温度：１５０℃、真空度：０．０９３ｋＰａ）に通液して未反応の１，５－ペンタメチレンジイソシアネートモノマーを除去した。

【０１４３】

さらに、得られたろ物１００質量部に対し、ｏ－トルエンスルホンアミド（貯蔵安定剤）０．０２質量部、および、塩化ベンゾイル（反応停止剤）０．００３質量部を添加し、ＰＤＩのイソシアヌレート誘導体（Ｂ）（以下、ＰＤＩ誘導体（Ｂ）とする。）を得た。

【０１４４】

ＰＤＩ誘導体（Ｂ）におけるＰＤＩモノマー濃度は０．６質量％、イソシアネート基濃度は２３．５質量％、イソシアネート基の平均官能基数は２．８、２５℃における粘度は９００ｍＰａ・ｓであった。

【０１４５】

また、このＰＤＩ誘導体（Ｂ）の^{1}Ｈ－ＮＭＲ測定によるアロファネート基とイソシアヌレート基とのモル比率は、アロファネート基／イソシアヌレート基＝５５／１００（すなわち、アロファネート基の含有割合は、イソシアヌレート基１モルに対して、０．５５モル）であった。

【０１４６】

製造例４（ＰＤＩのウレトジオン誘導体（Ｃ））

温度計、撹拌装置、還流管、および、窒素導入管を備えた４つ口フラスコに、窒素雰囲気下、製造例１により得られたペンタメチレンジイソシアネートを５００質量部、２，６－ジ（ｔｅｒｔ－ブチル）－４－メチルフェノールを０．３質量部、トリス（トリデシル）ホスファイト（商品名：ＪＰ－３３３Ｅ、城北化学社製）を０．３質量部、それぞれ装入し、１５０℃に昇温した。次いで、同温度で１０時間反応継続した後、反応を終了した。

【０１４７】

そして、得られた反応混合液を、薄膜蒸留装置（温度：１２０℃、真空度：９３．３Ｐａ）に通液して、未反応の１，５－ペンタメチレンジイソシアネートモノマーを除去し、ＰＤＩのウレトジオン誘導体（Ｃ）（以下、ＰＤＩ誘導体（Ｃ）とする。）を得た。

【０１４８】

ＰＤＩ誘導体（Ｃ）におけるＰＤＩモノマー濃度は０．５質量％、イソシアネート基濃度は２６．５質量％、イソシアネート基の官能基数は２．０、２５℃における粘度は８０ｍＰａ・ｓであった。

【０１４９】

また、このＰＤＩ誘導体（Ｃ）の^{1}Ｈ－ＮＭＲ測定ではアロファネート基とイソシアヌレート基は検出されなかった。

【０１５０】

製造例５（ＨＤＩのイソシアヌレート誘導体（Ｄ））

１，５－ペンタメチレンジイソシアネートに代えてヘキサメチレンジイソシアネート（三井化学社製　タケネート７００（以後ＨＤＩと略する場合がある。））を用いた以外は、製造例３と同様の操作にて、ＨＤＩのイソシアヌレート誘導体（Ｄ）（以下、ＨＤＩ誘導体（Ｄ）とする。）を得た。

【０１５１】

ＨＤＩ誘導体（Ｄ）におけるＨＤＩモノマー濃度は０．７質量％、イソシアネート基濃度は２２．３質量％、イソシアネート基の官能基数は２．８、２５℃における粘度は１，２００ｍＰａ・ｓであった。

【０１５２】

また、このＨＤＩ誘導体（Ｄ）の^{1}Ｈ－ＮＭＲ測定によるアロファネート基とイソシアヌレート基とのモル比率は、アロファネート基／イソシアヌレート基＝５５／１００（すなわち、アロファネート基の含有割合は、イソシアヌレート基１モルに対して、０．５５モル）であった。

【０１５３】

実施例１～１９、参考例２０、比較例１～６

ポリイソシアネート成分、ポリオール成分、溶媒およびウレタン化触媒を、表１～表３に記載の配合処方（総量２０ｇ）となるように、６０ｍｌで密栓ができるガラススクリュービンにて一括で配合した。

【０１５４】

次いで、ガラススクリュービンを密栓し、マグネチックスターラーで均一になるように１分撹拌した後、マグネチックスターラーを取り出した。

【０１５５】

その後、２３℃で２４時間の恒温槽内で所定時間反応および硬化させ、ポリウレタンゲルを得た。

【０１５６】

得られたポリウレタンゲルの２５℃における剪断弾性率は、1×10^{3}～1×10^{5}Ｐａの範囲であった。

【０１５７】

＜＜評価＞＞

ポリウレタンゲルを、以下の方法で評価した。その結果を、表１～表３に示す。

【０１５８】

＜透明性＞

２３℃で２４時間硬化後のポリウレタンゲルの外観を、目視で判断し、以下の基準に従って評価した。

３：透明。

２：やや白濁。

１：白濁。

【０１５９】

＜保型性＞

２３℃で２４時間硬化後のポリウレタンゲルを取り出し、形状の変化を目視で確認し、以下の基準に従って評価した。

３：崩れなし。

２：一部崩れ。

１：崩れて広がる。

【０１６０】

＜触感・デザイン性＞

２３℃で２４時間硬化後のポリウレタンゲルを触診し、以下の基準に従って評価した。
３：弾力感・ぷるぷる感あり。
２：弾力感あり、ぷるぷる感なし。
１：弾力感なし。
【０１６１】
＜未含浸溶媒（吸収性および保持力）＞
２３℃で２４時間硬化後のポリウレタンゲルを取り出し、ポリウレタンゲル中に含浸されずに残存した溶媒を目視で確認し、以下の基準に従って評価した。
３：なし。
２：ゲル上にうっすらあり。
１：ゲル周辺にあり。
【０１６２】
＜硬化性＞
ポリウレタンゲルの製造時において２３℃で２４時間放置した後の硬化状態、および、１０℃で４８時間放置した後の硬化状態を確認し、以下の基準に従って評価した。
３：硬化。
２：一部未硬化。
１：未硬化。
＜耐熱性＞
２３℃で２４時間硬化後のポリウレタンゲルを、密閉状態のまま８０℃７２時間静置した。その後、外観を目視で確認し、以下の基準に従って評価した。
３：変化なし。
２：やや変色、または、一部溶解。
１：変色。
＜揮散性＞
２３℃で２４時間硬化後のポリウレタンゲルを取り出し、常温および常圧環境下に開放した状態にて、４０℃で１週間保管した。その後の外観を目視で確認し、以下の基準に従って評価した。
３：収縮変形　大
２：収縮変形　中
１：収縮変形　小
【０１６３】

【表１】

【０１６４】

表１

No.		官能基数	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7	実施例8	実施例9	実施例10
ポリイソシアネート成分（NCO当量比）	PDI誘導体(A)	3.1	0.75	0.8	0.9	0.9	0.95	–	–	–	0.9	0.9
	PDI誘導体(B)	2.8	–	–	–	–	–	0.9	0.75	–	–	–
	PDI誘導体(C)	2.0	–	–	–	–	–	–	–	–	–	–
	HDI誘導体(D)	2.8	–	–	–	–	–	–	–	0.9	–	–
	TDI誘導体(E)	3.2	–	–	–	–	–	–	–	-	–	–
ポリオール成分（OH当量比）	PTXG-1800	2.0	1	1	1	1	1	1	1	1	1	1
	T-5652	2.0	–	–	–	–	–	–	–	–	–	–
	P-2010	2.0	–	–	–	–	–	–	–	–	–	–
	T-3000	3.0	–	–	–	–	–	–	–	–	–	–
	ひまし油	2.7	–	–	–	–	–	–	–	–	–	–
ウレタン化触媒（ポリイソシアネート成分とポリオール成分との総量100質量部に対する質量）	DBTDL		0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.8	1
溶媒（総質量に対する質量割合(%)）	PMA		85	85	85	–	85	85	85	85	85	85
	DMM		–	–	–	85	–	–	–	–	–	–
外観 23℃24時間後	透明性		3	3	3	3	3	3	3	3	3	3
	保型性		2	3	3	3	3	3	2	2	3	3
	触感・デザイン性		3	3	3	3	3	3	3	3	3	3
	未含浸溶媒（吸収性・保持力）		3	3	3	3	3	3	3	3	3	3
硬化性	23℃×24時間 硬化性		3	3	3	3	3	3	3	2	3	3
	10℃×48時間 硬化性		2	3	3	3	3	3	2	2	3	3
耐熱性	80℃×72時間後 外観		3	3	3	3	3	3	3	2	3	2
揮散性	40℃×1週間後 外観		3	3	3	3	3	3	3	3	3	3

【0165】

表2

【表2】

No.		官能基数	実施例11	実施例12	実施例13	実施例14	実施例15	実施例16	実施例17	実施例18	実施例19	参考例20
ポリイソシアネート成分（NCO当量比）	PDI誘導体(A)	3.1	0.9	0.9	0.9	0.9	0.8	0.9	0.9	0.9	0.6	1
	PDI誘導体(B)	2.8	–	–	–	–	–	–	–	–	–	–
	PDI誘導体(C)	2.0	–	–	–	–	–	–	–	–	–	–
	HDI誘導体(D)	2.8	–	–	–	–	–	–	–	–	–	–
	TDI誘導体(E)	3.2	–	–	–	–	–	–	–	–	–	–
ポリオール成分（OH当量比）	PTXG-1800	2.0	1	1	1	1	1	–	–	0.9	1	1
	T-5652	2.0	–	–	–	–	–	1	–	–	–	–
	P-2010	2.0	–	–	–	–	–	–	1	–	–	–
	T-3000	3.0	–	–	–	–	–	–	–	0.1	–	–
	ひまし油	2.7	–	–	–	–	–	–	–	-	–	–
ウレタン化触媒（ポリイソシアネート成分とポリオール成分との総量100質量部に対する質量）	DBTDL		0.05	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
溶媒（総質量に対する質量割合(%)）	PMA		85	80	90	93	60	85	85	85	90	90
	DMM		–	–	–	–	–	–	–	–	–	–
外観 23℃24時間後	透明性		3	3	3	3	3	3	3	2	3	2
	保型性		2	3	3	2	3	3	3	2	1	3
	触感・デザイン性		3	3	2	2	2	3	3	2	1	3
	未含浸溶媒（吸収性・保持力）		3	3	3	3	3	3	3	2	1	2
硬化性	23℃×24時間 硬化性		3	3	3	2	3	3	3	3	3	3
	10℃×48時間 硬化性		2	3	2	1	3	3	3	1	1	3
耐熱性	80℃×72時間後 外観		3	3	2	1	3	3	2	3	2	3
揮散性	40℃×1週間後 外観		3	3	3	3	2	2	2	2	3	2

【表３】

表3

No.		官能基数	比較例1	比較例2	比較例3	比較例4	比較例5	比較例6	比較例7
ポリイソシアネート成分（NCO当量比）	PDI誘導体(A)	3.1	0.9	0.9	—	0.9	0.9	0.9	—
	PDI誘導体(B)	2.8	—	—	—	—	—	—	—
	PDI誘導体(C)	2.0	—	—	—	—	—	—	0.9
	HDI誘導体(D)	2.8	—	—	—	—	—	—	—
	TDI誘導体(E)	3.2	—	—	0.9	—	—	—	—
ポリオール成分（OH当量比）	PTXG-1800	2.0	1	1	1	—	—	0.7	1
	T-5652	2.0	—	—	—	—	—	—	—
	P-2010	2.0	—	—	—	—	—	—	—
	T-3000	3.0	—	—	—	1	—	0.3	—
	ひまし油	2.7	—	—	—	—	1	—	—
ウレタン化触媒（ポリイソシアネート成分とポリオール成分との総量100質量部に対する質量）	DBTDL		0.3	0.3	0.05	0.3	0.3	0.3	0.3
溶媒（総質量に対する質量割合(%)）	PMA		40	97	90	85	85	85	85
	DMM		—	—	—	—	—	—	—
外観 23℃24時間後	透明性		1	3	3	—	1	2	—
	保型性		3	1	2	—	2	3	—
	触感・デザイン性		1	1	1	—	1	2	—
	未含浸溶媒（吸収性・保持力）		3	1	1	—	1	1	—
硬化性	23℃×24時間 硬化性		3	1	3	1	3	3	1
	10℃×48時間 硬化性		3	1	1	1	3	1	1
耐熱性	80℃×72時間後 外観		3	1	1	—	1	3	—
撹散性	40℃×1週間後 外観		1	1	3	—	1	2	—

【０１６６】

表中の略号の詳細を下記する。

・ポリイソシアネート成分

ＴＤＩ誘導体（Ｅ）：トリレンジイソシアネートのトリメチロールプロパン付加体

・ポリオール成分

ＰＴＸＧ１８００：旭化成せんい社製　非晶性ポリエーテルジオール　分子量１８００　平均官能基数２

Ｔ－５６５２：エターナコールＴ－５６５２　旭化成社製　非晶性ポリカーボネートジオール　分子量２０００　平均官能基数２
Ｐ－２０１０：クラレポリオールＰ－２０１０　クラレ社製　非晶性ポリエステルポリオール　分子量２０００　平均官能基数２
Ｔ－３０００：三井化学社製　ポリエーテルポリオール　分子量３０００　官能基数３
ひまし油：伊藤製油社製　精製ひまし油　平均官能基数　２．７
・ウレタン化触媒
ＤＢＴＤＬ：ジブチル錫ジラウレート
・溶媒
ＰＭＡ：ダワノールＰＭＡ　プロピレングリコールメチルエーテルアセテート　ダウ・ケミカル社製
ＤＭＭ：プログライドＤＭＭ　ジプロピレングリコールジメチルエーテルダウ・ケミカル社製

フロントページの続き

(72)発明者　森田　広一
千葉県袖ケ浦市長浦５８０番地３２　三井化学株式会社内
(72)発明者　山崎　聡
千葉県袖ケ浦市長浦５８０番地３２　三井化学株式会社内

審査官　吉田　早希

(56)参考文献　特開２０１１－２１６４４３（ＪＰ，Ａ）
特開２００７－１４３９４６（ＪＰ，Ａ）
特開昭６０－００６７１８（ＪＰ，Ａ）
特開２０１１－１９８６９１（ＪＰ，Ａ）
特開２００１－２７６２０３（ＪＰ，Ａ）
特公昭４７－０００９１４（ＪＰ，Ｂ１）
特開２０１１－０７９９８５（ＪＰ，Ａ）
特開２０１２－０１５２０７（ＪＰ，Ａ）
特開昭５７－１５５２５１（ＪＰ，Ａ）
特開２００６－２６５５５８（ＪＰ，Ａ）

(58)調査した分野(Int.Cl.，ＤＢ名)

ＩＰＣ	Ｃ０８Ｇ	１８／００ －	１８／８７
	Ｃ０８Ｇ	７１／００ －	７１／０４
	Ｃ０８Ｋ	３／００ －	１３／０８
	Ｃ０８Ｌ	１／００ －	１０１／１４
	Ａ０１Ｎ	１／００ －	６５／４８
	Ａ０１Ｐ	１／００ －	２３／００

ＤＢ名　ＣＡｐｌｕｓ／ＲＥＧＩＳＴＲＹ（ＳＴＮ

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 January 2021 (14.01.2021)

WIPO | PCT

(10) International Publication Number
WO 2021/007489 A1

(51) International Patent Classification:
A61K 8/87 (2006.01) *C08G 18/72* (2006.01)
A61Q 19/00 (2006.01)

(21) International Application Number:
PCT/US2020/041540

(22) International Filing Date:
10 July 2020 (10.07.2020)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/872,588 10 July 2019 (10.07.2019) US
62/872,592 10 July 2019 (10.07.2019) US
63/018,859 01 May 2020 (01.05.2020) US

(71) Applicant: **NANOMETICS LLC (D.B.A. PHD BIOSCIENCES)** [US/US]; 180 Varick Street, 6th Floor, New York, New York 10014 (US).

(72) Inventors: **ISAACMAN, Michael J.**; 50 East 8th Street, Apt. 4U, New York, New York 10003 (US). **ISAACMAN, Steven**; 248 Oak Beach Rd., Oak Beach, New York 11702 (US). **MAHON, Andrew B.**; 217 West 106th St., Apt. 2A, New York, New York 10025 (US).

(74) Agent: **RAO, Minxi**; MEDLER FERRO WOODHOUSE & MILLS PLLC, 8201 Greensboro Dr., Ste. 1060, McLean, Virginia 22102 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(54) Title: POLYURETHANE GELS

FIG. 1

Biolastomer Compatibility with Common Carriers

	Biolastomer A (12.5%)		Biolastomer C (11%)		Biolastomer D (14%)		Velvesil DM (17.5%)		DOWSIL 9040 (12%)	
Wt% emollients	20%	30%	20%	30%	20%	30%	10%	20%	20%	30%
Triglyceride	Clarity, Gel strength	Clarity, Gel strength	Clarity, Gel strength	Clarity, Gel strength	Clarity, Gel strength	Clarity, Gel strength	Clarity, Gel strength	Clarity, Gel strength	Clarity, Gel strength	Clarity, Gel strength
Caprylic/capric triglyceride	Translucent 5	Hazy 1	Hazy 3	Hazy 1	Hazy 3	Hazy 3	Not Compatible	Not Compatible	Clear 1	Compatible
Esters										
Isopropyl palmitate	Hazy 3	Hazy 1	Hazy 2	Hazy 2	Hazy 1	Not Compatible	Not Compatible	Not Compatible	Clear 3	Not Compatible
Fatty alcohol										
Octyl dodecanol	Translucent 5	Hazy 1	Translucent 5	Hazy 1	Translucent 5	Translucent 5	Not Compatible	Not Compatible	Not Compatible	Not Compatible
Hydrophilics										
EtOH	Translucent 5	Hazy 2	Translucent 5	Hazy 3	Translucent 5	Translucent 5	TBD	Not Compatible	TBD	TBD
Hydrocarbons										
Hemisqualane	Hazy 1	Hazy 1	Hazy 1	Not Compatible	Not Compatible	Not Compatible	Not Compatible	Not Compatible	Clear 3	Not Compatible
Silicones										
Dimethicone 350 cst	Not Compatible	Not Compatible	Not Compatible	Not Compatible	Not Compatible	Not Compatible	Not Compatible	Not Compatible	Clear 1	Compatible

(57) **Abstract:** The present invention relates to gel compositions comprising a polyurethane elastomer. The polyurethane elastomer is formed from the reaction of a polyol, a polyisocyanate, and optionally a polyurethane reaction catalyst, optionally in the presence of a topically acceptable carrier fluid. In some embodiments, the gel composition comprises a personal active ingredient or a healthcare active ingredient, which may be incorporated into the gel composition via a pre-load method or a post-load method. Also provided herein are gel pastes and topical formulations comprising the polyurethane elastomers, and methods of making the same.

[Continued on next page]

WO 2021/007489 A1

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

POLYURETHANE GELS

FIELD OF THE INVENTION

[001] The present invention relates to gel compositions comprising a polyurethane elastomer.

BACKGROUND OF THE INVENTION

[002] Elastomer gels consist of a cross-linked three-dimensional polymer network suspended in an emollient. Elastomer gels are capable of swelling in emollients and are useful as oil phase thickeners in cosmetic formulations. These elastomer gels have a ball bearing-like feel on skin and provide for enhanced aesthetics and feel. These desirable attributes cannot be achieved with traditional oil gels or linear polymers, making elastomer gels unique cosmetic application vehicles.

[003] Silicone elastomer gels are widely utilized ingredients in personal care products for their thickening and gelling efficiency, and unique silky and powdery sensory profile. When incorporated into formulations they provide a smooth, dry, and non-oily feel. Silicone elastomers are compatible with silicone-based fluids. Recently, concerns have been raised regarding the negative environmental impact of silicone-based ingredients in personal care products. Silicones are resistant to oxidative and chemical attack and are therefore not biodegradable. In addition, silicones are sourced from fossil fuels and are not considered to be a renewable resource. As consumers become increasingly educated with the environmental impact of cosmetics, the demand for biodegradable and renewably sourced ingredients that are silicone-free has rapidly increased.

[004] Silicone replacements derived from biomass have begun to enter the personal care market to meet these demands. However, these linear polymers and emollients do not provide the unique aesthetics that elastomer gels provide. Therefore, a need exists for a silicone-free elastomer gel that has a favorable environmental profile.

[005] The present invention consists of a polyurethane elastomer gel that is silicone-free and comprised of >99% bio-based materials. The polyurethane elastomer gel provides the aesthetic benefits of silicone-based elastomers while meeting a market demand for renewably sourced materials that are silicone-free.

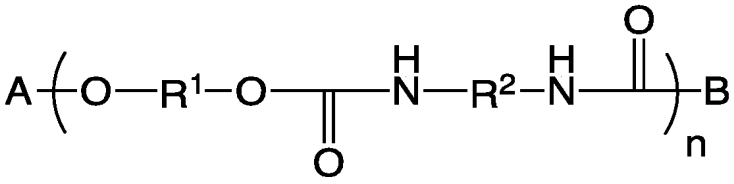
[006] The invention further relates to a method for preparing the polyurethane elastomer gel. A bio-based polyol is reacted with a bio-based polyisocyanate using a polyurethane catalyst at elevated temperature in a reaction medium of bio-based emollient or a mixture of bio-based emollients to give a polyurethane elastomer rubber. A bio-based emollient is then added to the rubber, and the mixture is processed into a polyurethane elastomer gel.

SUMMARY OF THE INVENTION

[007] In some embodiments, the invention provides a gel composition comprising a polyurethane elastomer requiring no purification and formed in a topically acceptable solvent from the reaction of: A) a polyol; B) a polyisocyanate; C) an optional polyurethane reaction catalyst; and D) a topically acceptable carrier fluid.

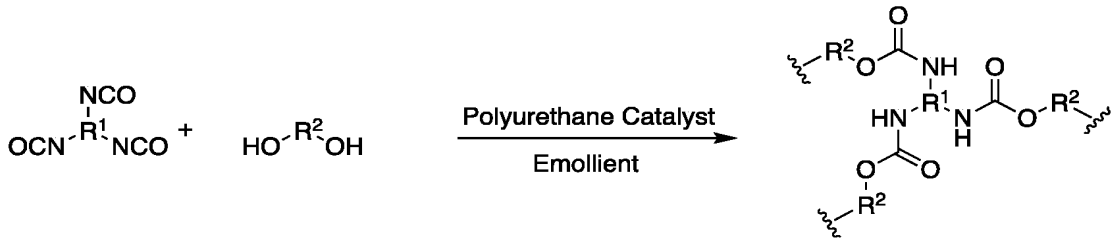
[008] In embodiments, a personal care or healthcare active ingredient (E) is incorporated into the polyurethane elastomer gel by dissolving it in the topically acceptable carrier fluid during the formation of the polyurethane elastomer gel (pre-load method) or admixing it with a formed polyurethane elastomer gel (post-load method).

[009] In further embodiments, the invention further provides a cross-linked polyurethane elastomer network with the following general structure:



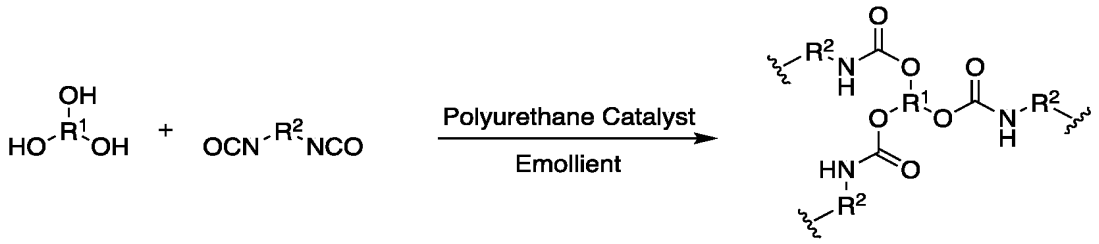
wherein: n is 2 to 10000000; A is an end group selected from a hydrogen, an isocyanate and a hydroxyl; R^1 is a C1-C60 substituted or unsubstituted linear or branched aliphatic group, cycloaliphatic group, aryl group, heterocycloaliphatic group, or heteroaryl group, optionally comprising a heteroatom; R^2 is a C1-C60 substituted or unsubstituted linear or branched aliphatic group, cycloaliphatic group, aryl group, heterocycloaliphatic group, or heteroaryl group, optionally comprising a heteroatom; and B is an end group selected from an isocyanate and a hydroxyl.

[010] In some embodiments, the invention provides a cross-linked polyurethane elastomer network according to the following general reaction scheme:



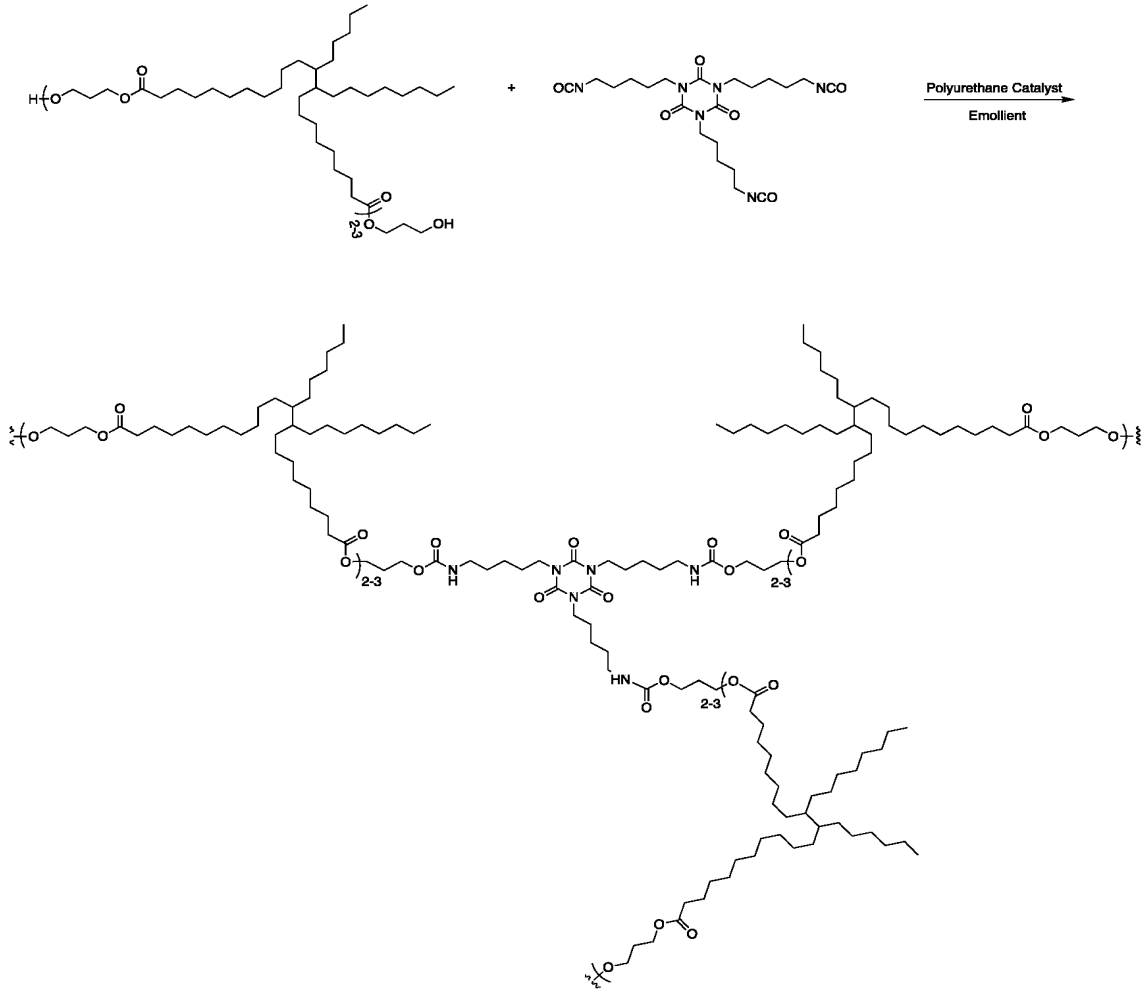
where R is a polyol with two or more functional groups and where R^1 is an isocyanate with three or more functional groups, and the emollient is topically acceptable.

[011] In further embodiments, the invention provides a cross-linked polyurethane elastomer network according to the following general reaction scheme:



where R is a polyol with three or more functional groups and where R^1 is an isocyanate with two or more functional groups, and the emollient is topically acceptable.

[012] In further embodiments, the invention provides a cross-linked polyurethane elastomer network according to the following general reaction scheme:



where the emollient is topically acceptable.

[013] In still further embodiments, the invention provides a process for making a polyurethane elastomer gel comprising: Adding to a container a cosmetically acceptable emollient, polyol, and polyisocyanate; stirring the mixture at room temperature until a clear, homogeneous solution

is obtained; adding a polyurethane catalyst with stirring, and heating the reaction to about 60 °C for about 23 hours, at which point a soft rubber is formed; allowing the rubber to cool to room temperature, and adding a cosmetically acceptable emollient and processing the mixture into a smooth gel.

[014] In embodiments, the rubber is formed at room temperature. In embodiments, the polyol, polyisocyanate and emollient are bio-based. In embodiments, the polyol, polyisocyanate and emollient are not bio-based. In embodiments, a bismuth, tin, zinc, or amine isocyanate catalyst is used. In embodiments, the concentration of bio-based emollient is between 70-85% by weight based on the total combined weight of bio-based polyol, bio-based isocyanate, bismuth catalyst, and a bio-based emollient or mixture of bio-based emollients. In embodiments, said polyol has a molecular weight ranging from about 500-10,000. In embodiments, the number of OH units per polyol is about 2-20. In embodiments, the number of NCO units per polyol is about 2-6. In embodiments, said bio-based emollient is selected from a group of esters, hydrocarbons, carbonate, vegetable oils, or modified vegetable oils. In embodiments, said bio-based emollient has a spreading value (mm^2/10 min) between 500-2500. In embodiments, said bio-based emollient has an average molecular weight of 240-1200.

[015] In some embodiments, the invention provides a process for making a polyurethane elastomer gel comprising: adding to a reaction kettle triheptanoin, coco-caprylate/caprate, dilinoleic acid/propane diol copolymer, and 1,5-pentamethylene diisocyanate based polyisocyanates; stirring the mixture at room temperature until a clear, homogeneous solution is obtained; adding bismuth neodecanoate with stirring, and heating the reaction to 60 °C, at which point a colorless rubber is formed.

[016] In further embodiments, the invention provides a process for making a polyurethane elastomer gel comprising: placing the polyurethane elastomer rubber in a drum, adding triheptanoin, milling the mixture with a Cowles mixer; running the resulting suspension through a disperser and allowing the resulting gel to cool to room temperature; and adding undecane and/or tridecane with mixing until the desired viscosity was achieved.

[017] In embodiments, the rubber is formed without stirring at room temperature over 24 hours. In embodiments, a finisher containing an alcohol or amine may be added to quench unreacted isocyanate groups. In embodiments, said polyurethane elastomer rubber has a hardness as described herein. In embodiments, said polyurethane elastomer gel has a viscosity as described herein.

[018] In some embodiments, the invention provides a gel composition comprising a polyurethane elastomer from the reaction of: A) castor oil; B) isophorone diisocyanate, wherein

the molar ratio of isocyanate groups to hydroxyl groups is between 1:1 and 1:2; C) an optional polyurethane reaction catalyst; and D) a carrier fluid, which is cosmetically acceptable (examples of such carrier fluids include diisooctyl succinate, heptyl undecylenate, neopentyl glycol diheptanoate, coco-caprylate/caprate, triheptanoin, C13-15 alkane, squalene, undecane, tridecane), wherein solvent concentration is between 60% (w/w) and 99.9% (w/w); wherein a personal care or healthcare active ingredient may be incorporated into the polyurethane elastomer gel by dissolving it in the topically acceptable solvent during the formation of the polyurethane elastomer gel (pre-load method) or admixing it with a formed polyurethane elastomer gel (post-load method).

[019] In embodiments, the polyurethane catalyst is a bismuth group containing catalyst. In embodiments, the carbon content of the topically acceptable solvent is >50% derived from plant sources.

[020] In further embodiments, the invention provides a process for preparing the polyurethane elastomer gel comprising: I) reacting: A) castor oil; B) isophorone diisocyanate; and (C) an optional polyurethane reaction catalyst, in the presence of D) a topically acceptable carrier fluid. In still further embodiments, the invention provides a gel composition prepared according to the process herein.

[021] In yet further embodiments, the invention provides a process for preparing a gel paste composition, comprising: I) shearing the polyurethane elastomer gel herein; and II) combining the sheared polyurethane elastomer gel with additional quantities of the carrier fluid to form a gel paste composition.

[022] In yet further embodiments, the invention provides a process for preparing a gel paste composition, comprising: I) shearing the polyurethane elastomer gel herein; and II) combining the sheared polyurethane elastomer gel with an active ingredient.

BRIEF DESCRIPTION OF THE DRAWINGS

[023] FIG. 1 shows a table describing biolastomer compatibility with common carrier fluids described in embodiments herein.

[024] FIG. 2 shows a FTIR spectrograph of dilinoleic acid/propane diol copolymer based pentamethylene diisocyanate trimer elastomer, as described in embodiments herein.

[025] FIG. 3 shows a FTIR spectrograph of dilinoleic acid/propane diol copolymer based hexamethylene diisocyanate trimer elastomer, as described in embodiments herein.

[026] FIG. 4 shows a FTIR spectrograph of castor oil based pentamethylene diisocyanate trimer elastomer, as described in embodiments herein.

[027] FIG. 5 shows a FTIR spectrograph of castor oil based hexamethylene diisocyanate trimer elastomer, as described in embodiments herein.

[028] FIG. 6 shows a FTIR spectrograph of dilinoleic acid/dilinoleic diol copolymer based pentamethylene diisocyanate trimer elastomer, as described in embodiments herein.

[029] FIG. 7 shows a FTIR spectrograph of dilinoleic acid/dilinoleic diol copolymer based hexamethylene diisocyanate trimer elastomer, as described in embodiments herein.

[030] FIG. 8 shows a FTIR spectrograph of castor oil based isophorone diisocyanate trimer elastomer, as described in embodiments herein.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[031] As used herein, "a" or "an" may mean one or more. As used herein, when used in conjunction with the word "comprising," the words "a" or "an" may mean one or more than one. As used herein, "another" or "a further" may mean at least a second or more.

[032] The term "about" as used herein means approximately ± 10%. When the term "about" is used in conjunction with a numerical value or range, it modifies that value or range by extending the boundaries above and below the numerical values set forth. In general, the term "about" is used herein to modify a numerical value above and below the stated value by a variance of 10 percent, up or down (higher or lower), i.e., ± 10%, unless a different variance is indicated (e.g., ± 30%, ± 20%, ± 5%, ± 1%, etc.).

[033] The use of the term "or" in the claims is used to mean "and/or", unless explicitly indicated to refer only to alternatives or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and "and/or."

[034] As used herein, the terms "comprising" (and any variant or form of comprising, such as "comprise" and "comprises"), "having" (and any variant or form of having, such as "have" and "has"), "including" (and any variant or form of including, such as "includes" and "include") or "containing" (and any variant or form of containing, such as "contains" and "contain") are inclusive or open-ended and do not exclude additional, unrecited, elements or method steps. It is contemplated that any embodiment discussed in this specification can be implemented with respect to any method, and/or composition of the present disclosure.

[035] The use of the term "for example" and its corresponding abbreviation "e.g." (whether italicized or not) means that the specific terms recited are representative examples and embodiments of the disclosure that are not intended to be limited to the specific examples referenced or cited unless explicitly stated otherwise.

[036] As used herein, "between" is a range inclusive of the ends of the range. For example, a number between x and y explicitly includes the numbers x and y, and any numbers that fall within x and y.

[037] As used herein the term "polyurethane" indicates materials formed by reacting a polyol with an isocyanate in the presence of an appropriate catalyst.

[038] The term "polyol" refers to materials having functional groups containing an active hydrogen atom that can undergo a reaction with an isocyanate. Preferably, polyols contain at least two hydroxyls, amines, carboxylic acids, and/or thiol groups per molecule.

[039] The term "polyisocyanate" refers to a substance containing two or more isocyanate functional groups.

[040] The term "bio-based" refers to materials that mainly consist of a substance derived from living matter, also known as biomass.

[041] The term "polyurethane elastomer rubber" refers to the reaction product of a polyol, an isocyanate, and a polyurethane catalyst in an emollient medium.

[042] The term "polyurethane elastomer gel" refers to the product of the processed polyurethane elastomer rubber.

[043] The present invention further relates to a polyurethane elastomer gel comprised of a bio-based polyol cross-linked with a bio-based polyisocyanate in a bio-based topically acceptable carrier fluid or mixture of bio-based topically acceptable carrier fluids. In some embodiments, the reaction is catalyzed by a topically acceptable bismuth polyurethane catalyst. The polyurethane elastomer gel described herein has good compatibility with cosmetic and natural oils and can be used as a thickener for these oils. The polyurethane elastomer gel further provides a smooth, non-tacky, non-oily, moisturizing skin feel with enhanced playtime to cosmetic formulations. The polarity of the polyurethane elastomer gel allows for its incorporation into polar cosmetic formulation mediums. Silicone elastomer gels, which are typically used in many formulations, are non-polar and are generally not compatible with polar formulation mediums, and therefore the polyurethane elastomer gels meet a critical need in the personal care industry.

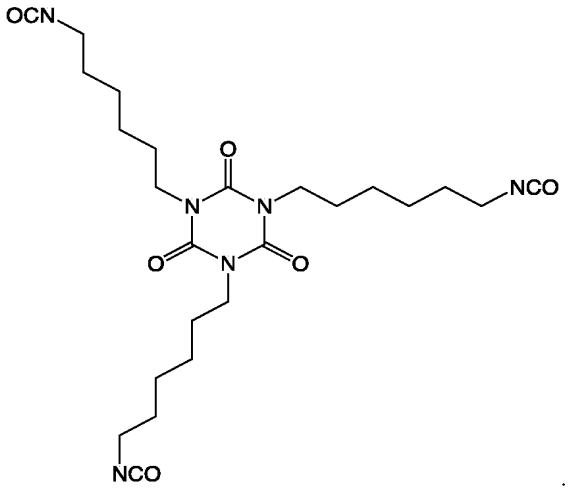
[044] By using a bio-based polyol, a bio-based polyisocyanate, and a bio-based carrier fluid, a polyurethane elastomer gel is produced comprising >99% bio-based material. Silicone elastomer gels are derived from fossil fuels which are not a renewable resource. It is generally recognized that cosmetic ingredients derived from biomass are considered to be "natural," and the market demand for natural cosmetics has fueled the industries need for a bio-based elastomer that is silicone-free.

[045] The present invention relates to a gel composition comprising a polyurethane elastomer requiring no purification and formed in a topically acceptable solvent from the reaction of component (A), a polyisocyanate; component (B), a polyol; component (C), an optional polyurethane reaction catalyst; optionally in component (D), a topically acceptable carrier fluid.

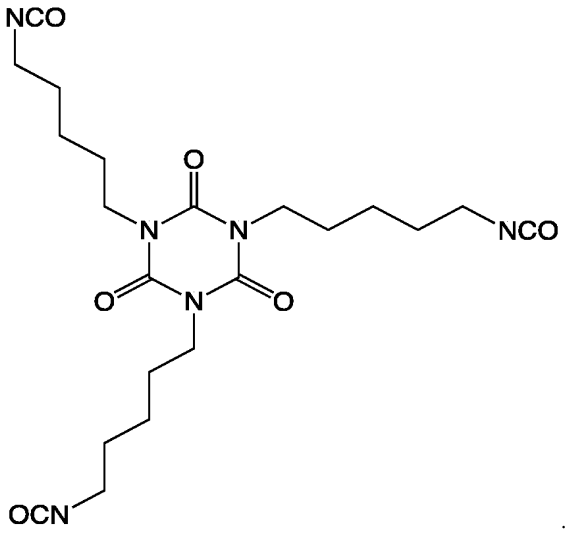
Component (A) - Polyisocyanate

[046] In some embodiments, component (A) has a molecular structure containing more than one isocyanate and can be produced by a number of methods from polyamines or the polymerization of polyisocyanates and should have two or more reactive isocyanate functional groups in its molecular structure. In some embodiments, the polyisocyanate comprises three isocyanate functional groups. The polyisocyanate serves as a cross-linker in the reaction, which allows the use of a bi-functional polyol copolymer to create a three-dimensional polymer network.

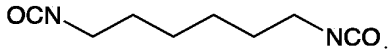
[047] One preferred example of a polyisocyanate is hexamethylene diisocyanate trimer and has the following structure:



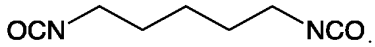
[048] Another preferred example of a polyisocyanate is pentamethylene diisocyanate trimer and has the following structure:



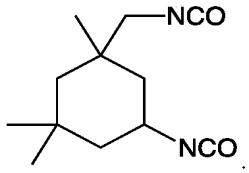
[049] Another preferred example of a polyisocyanate is hexamethylene diisocyanate and has the following structure:



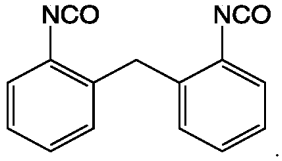
[050] Another preferred example of a polyisocyanate is pentamethylene diisocyanate and has the following structure:



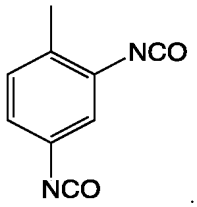
[051] Another preferred example of a polyisocyanate is isophorone diisocyanate and has the following structure:



[052] Another preferred example of a polyisocyanate is 4,4'-methylenebis(phenyl isocyanate) and has the following structure:



[053] Another preferred example of a polyisocyanate is toluene diisocyanate and has the following structure:



[054] Another preferred example of a polyisocyanate is hexamethylene diisocyanate biuret.

[055] Further non-limiting examples of polyisocyanates containing two isocyanate groups include bis(Isocyanatomethyl)benzene; 1,3-bis(Isocyanatomethyl)cyclohexane; Diphenylmethane diisocyanate; Hexamethylenediisocyanate; Hexamethylenediisocyanate based polyisocyanates; 1,5-pentamethylene diisocyanate; Isocyanato methylethylbenzene; Isophorone diisocyanate; Methylene bis-(4-cyclohexylisocyanate); M-Tetramethylene diisocyanate; meta-Tetramethylenexylenediisocyanate; Saturated methylene diphenyldiisocyanate; and Toluene diisocyanate.

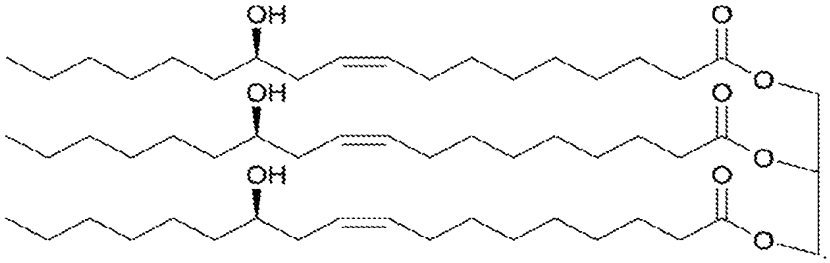
Component (B) - Polyol

[056] In some embodiments, component (B) has a molecular structure containing more than one hydroxyl group that can undergo a reaction with an isocyanate. In certain embodiments, component (B) contains nucleophilic groups other than hydroxyl and the term "polyol" refers to materials having a reactive hydrogen that can react with isocyanates. Preferably, polyols contain at least two hydroxyls, amines, carboxylic acids, and/or thiol groups per molecule.

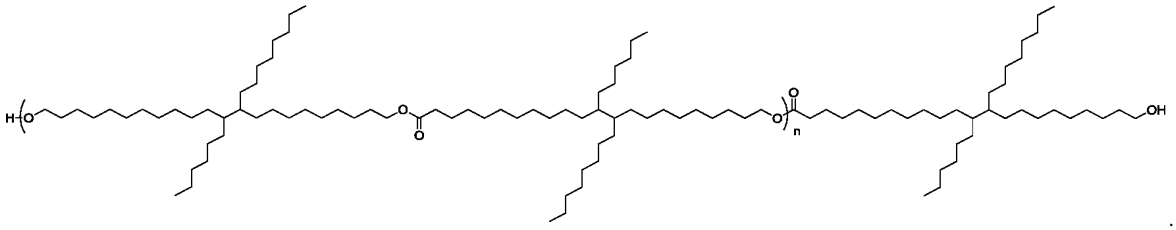
[057] When polyols containing three or more functional groups are used, a di-functional isocyanate (e.g., containing two isocyanate functional groups) may be used for synthesis of polyurethane elastomer gels. Exemplary di-functional isocyanates are provided herein and include bis(Isocyanatomethyl)benzene; 1,3-bis(Isocyanatomethyl)cyclohexane; Diphenylmethane diisocyanate; Hexamethylenediisocyanate; Hexamethylenediisocyanate based polyisocyanates; 1,5-pentamethylene diisocyanate; Isocyanato methylethylbenzene; Isophorone diisocyanate; Methylene bis-(4-cyclohexylisocyanate); M-Tetramethylene diisocyanate; meta-Tetramethylenexylenediisocyanate; Saturated methylene diphenyldiisocyanate; Toluene diisocyanate.

[058] One preferred example of a polyol is castor oil, which naturally contains multiple hydroxyl groups and is bio-based. The molecular structure of natural castor oil is a triglyceride with three pendant carbon chains. Generally, each carbon has a double bond at the 9,10 position and a hydroxyl group on the 12th carbon. Castor oil in nature has a hydroxyl value of approximately 160-165 with a fatty acid distribution of approximately 89% $C_{18}OH$ and 9% C_{18}. Thus, not all of the carbon chain lengths in natural or untreated castor oil contain an OH group,

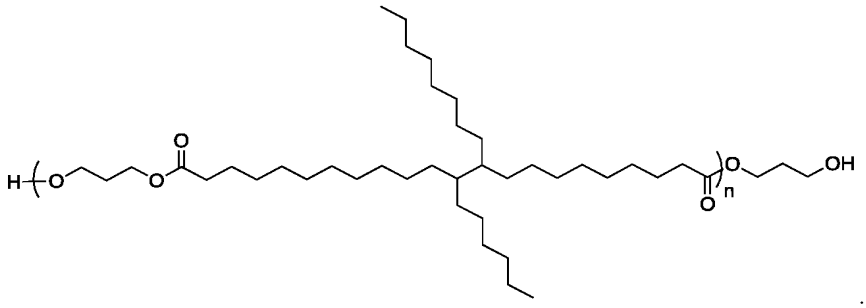
and on average, only about 90% of said chains contain an OH group. The principal component of castor oil is ricinolein and has the following structure:



[059] Another preferred example of a polyol is dilinoleic acid/dilinoleic diol copolymer, and is reported to have the following structure:

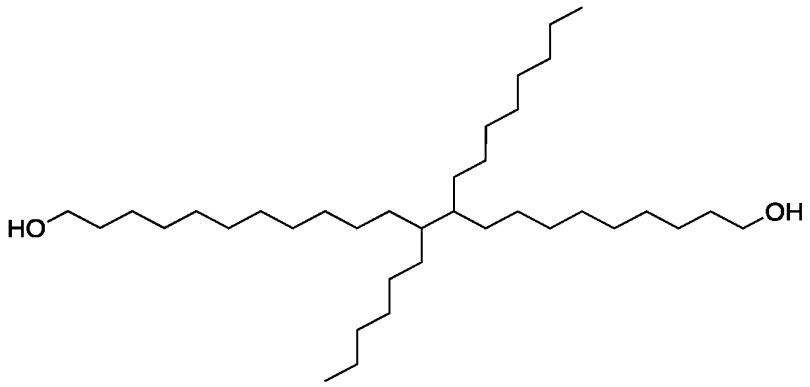


[060] Another preferred example of a polyol is dilinoleic acid/propane diol copolymer (also called "dilinoleic acid/propane diol copolymer"), and is reported to have the following structure:

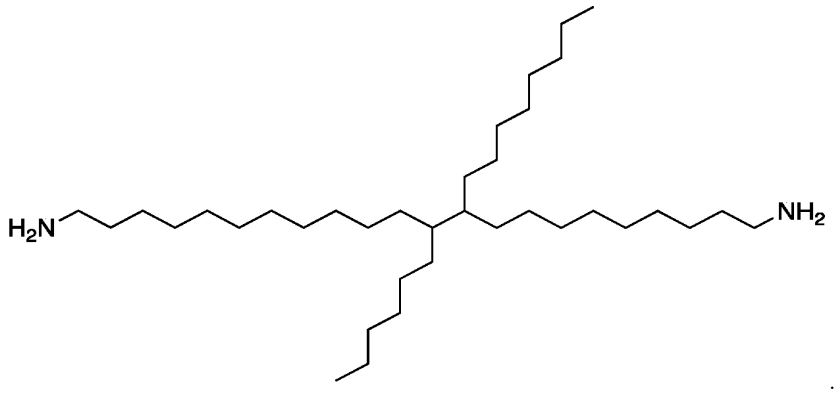


[061] Dilinoleic acid/propane diol copolymer is 100% bio-based, has film forming properties, is non-tacky, and has good compatibility with cosmetic and natural oils. Preferably, the dilinoleic acid/propane diol copolymer should be terminated in hydroxy groups and have a low acid value, as hydroxyl groups react more readily with isocyanates than carboxylic acids. The molecular weight of the dilinoleic acid/propane diol copolymer can be between 500-10000 g/mol, and preferably between 1000-3000 g/mol. Castor oil polyurethane elastomer gels and dilinoleic acid/propane diol polyurethane elastomer gels demonstrate similar properties.

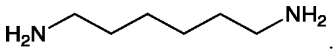
[062] Another preferred example of a polyol is dilinoleic diol, and is reported to have the following structure:



[063] Another preferred example of a polyol is dilinoleic diamine, and is reported to have the following structure:



[064] Another preferred example of a polyol is hexamethylene diamine, and has the following structure:



[065] Other appropriate polyols include glycerol, polyglycerol, pentaerythritol, pentaerythritol tetrakis(3-mercaptopropionate), trimethylol propane, mercaptanized soybean oil, glycerol propoxylate, glyceryl poly(oxypropylene) triamine, and melamine.

[066] Further exemplary polyols include, but are not limited to, Dilinoleic acid/propanediol copolymer; Propylene glycol/azelaic acid copolymer; Azelate Polyol; Propylene glycol/sebacic acid copolymer; 1,3-Propane diol/azelaic acid copolymer; 1,3-Propane diol/sebacic acid copolymer; 1,3-Butane diol/azelaic acid copolymer; 1,3-Butane diol/sebacic acid copolymer; 1,4-Butane diol/azelaic acid copolymer; 1,4-Butane diol/sebacic acid copolymer; Propylene glycol/apidic acid copolymer; 1,3-Propane diol/apidic acid copolymer; 1,3-Butane diol/apidic acid copolymer; 1,4-Butane diol/apidic acid copolymer; Capryloyl Glycerin/sebacic acid copolymer; Trimethylpentanediol/apidic acid copolymer; Capryloyl glycerin/sebacic acid copolymer; Diheptyl succinate (and) capryloyl glycerin/sebacic acid copolymer;

Polyhydroxystearic acid; Polyether; Polybutylene succinate; Polylactic acid; Polyethylene terephthalate; Polyester; Polydimethylsiloxane, hydroxy terminated; Polyethylene Glycol; Polyoxazoline; Polyglycerol; Polystyrenes; Polyhydroxyalkanoates; Polysaccharides; Polylactides; Polyethylene; Starch; Cellulose; Chitin; Chitosan; Pullulan; Collagen; Gelatin; Lignin; Polysaccharides; Alginate; Polyethylene terephthalate; Polytrimethylene terephthalate; Poly(ethylene 2,5-furandicarboxylate); Polyamides; Polyterpenes; Polyethylene 2,5-furandicarboxylate; Polycaprolactone; Polytetrahydrofuran; Polylactides; Polyglycolides; Polydioxanones; Polycarbonates; Polylactide-co-glycolides; Polyanhydrides; Polyphosphazenes; Polyphophoesters; Glycerol; Castor Oil; Jatropha Oil; Multi-hydroxy soybean oil; Palm oil; Hydrogenated Castor Oil; Caprylyl glycol; Glyceryl caprylate; Ethylhexylglycerin; 1,2-hexanediol; Hexylene glycol; Glyceryl undecylenate; Methylpropanediol; 1,2-hexanediol; Pentaerythritol; Dipentaerythritol; Tripentaerythritol; Trimethyoyl propane; Isosorbide; Ethylene glycol; Diethylene glycol; Triethylene glycol; Tetraethylene glycol; Propylene glycol; Dipropylene glycol; Tripropylene glycol; 1,3-Butanediol; 1,4-Butanediol; Neopentyl glycol; 1,6-hexanediol; 1,4-Cyclohexanedimethanol; Ethanolamine; Diethanolamine; Methyldiethanolamine; Phenyldiethanolamine; 1,2,6-Hexanetriol; Triethanolamine; Diethyltoluenediamine; Dimethylthiotoluenediane; Citric acid; Lactic acid; Polylactic acid; Dilinoleic acid; Trilinoleic acid; Azelaic acid; and Sebacic acid.

Component (C) - Polyurethane Reaction Catalyst:

[067] In some embodiments, component (C), the polyurethane reaction catalyst, is optionally used to increase the rate of polyurethane elastomer formation. Bismuth carboxylates are the preferred catalysts for the synthesis of the polyurethane elastomer gel due to their favorable toxicity profile and acceptable use in topical products.

[068] Preferably, bismuth neodecanoate is used as the polyurethane catalyst. Zinc, tin, and amine based polyurethane catalysts can also be used. Appropriate polyurethane catalysts include but are not limited to: Triethylenediamine, N,N,N',N",N"-Pentamethyldiethylenetriamine, 1,2-Dimethylimidazole, N,N,N',N'-Tetramethyl-1,6-hexanediamine, N,N',N'-Trimethylaminoethylpiperazine, 1,1'-[[3-(dimethylamino)propyl]imino]bispropan-2-ol, N,N,N'-Trimethylaminoethylethanolamine, N,N',N"-Tris(3-dimethylaminopropyl)-hexahydro-s-triazine, 1,4-diazabicyclo[2.2.2]octane, Stannous octoate, Stannous oxalate, Stannous oxide, Stannous chloride, Dioctyltin di(2-hexylhexanoate)-solution, Dioctyltin dithioglycolate, Dioctyltin dilaurate, Dioctyltin oxide blend, Dibutyltin dilaurate, Monobutyl tin tris-(2-ethylhexanoate), Dioctyltin diketanoate, Dioctyltin diacetate, Dioctyltin oxide, Dibutyltin diacetate, Modified dibutyltin diacetate, Dibutyltin oxide, Monobutyltin dihydroxychloride, Organotin oxide, Monobutyltin oxide, Dioctyltin dicarboxylate, Dioctyltin carboxylate, Dioctyltin stannoxane,

Zinc neodecanoate, Zinc octoate, Zinc acetylacetonate, Zinc oxalate, Zinc acetate, Bismuth carboxylates, and Zinc neodecanoate.

Component (D) - Carrier Fluid

[069] In some embodiments, the polyurethane elastomer is contained in an optional carrier fluid (D) that is topically acceptable. In exemplary embodiments, the carrier fluid is a "topically acceptable carrier fluid" which is a solvent for topical use on cutaneous surfaces i.e. skin, lips, mucous membranes, etc. The terms "topically acceptable" and "cosmetically acceptable" can be used interchangeably herein, and the topically acceptable carrier fluid can also be referred to herein as an "emollient." Although it is not required, typically the carrier fluid may be the same as the solvent used for conducting the polyurethane elastomer reaction as described above. The topically acceptable carrier fluid used for the synthesis of the polyurethane elastomer rubber and gel can be fully, partially, or not bio-based. As described herein, "bio-based" refers to materials that mainly consist of a substance/s derived from living matter, also known as biomass.

[070] The topically acceptable carrier fluid should be compatible with the reaction to form the polyurethane elastomer rubber described herein, such that the rubber is not too hard and/or brittle to process into a gel. When processing the polyurethane elastomer rubber into a gel, a carrier fluid with the appropriate polarity should be used in order to swell the elastomer granules while milling. If the emollient is not able to swell the granules, the polyurethane elastomer rubber cannot be processed into a smooth gel. Triglycerides, esters, and ethers with appropriate polarity can be used to swell the elastomer granules during the milling process. In some embodiments, the topically acceptable carrier fluid comprises a triglyceride, ester, alkane, ether, or a mixture thereof. Preferably, the topically acceptable carrier fluid is triheptanoin or a mixture of triheptanoin and coco-caprylate/caprate. Triheptanoin is a preferred carrier fluid for swelling the elastomers granules as described herein. Triheptanoin has relatively high polarity, is 100% bio-based, and has a low viscosity and a light non-oily skin feel.

[071] Once the polyurethane elastomer rubber is processed into a smooth gel, volatile carrier fluids with a dry skin feel can be added to the gel with high sheer mixing until the desired viscosity is achieved. Volatile carrier fluids serve to enhance the dry feeling of polyurethane elastomer gels on the skin. Triglycerides, esters, ethers, and alkanes can be used during this process. Preferably, undecane and/or tridecane and/or coconut alkanes are used.

[072] The stability of the polyurethane elastomer gel is partially dependent on the carrier fluid or mixture of carrier fluids used in the synthesis of the polyurethane elastomer rubber and gel. If the polarity of the carrier fluid is too low, the gel may initially form but will separate over time. Generally, triglycerides, esters, ethers, and alkanes can be used in various combinations.

Preferably, a mixture of triheptanoin, coco-caprylate/caprate, and undecane and/or tridecane in a ratio of about 1/1/0.5 is used. Surfactants may also be used to maintain gel stability if separation occurs.

[073] The topically acceptable carrier fluids preferably have a viscosity between 1-65 mPas at 20 °C. The spreading value of the topically acceptable carrier fluid is preferably between 500-2500 $mm^2/10$ min. Appropriate topically acceptable carrier fluids for the synthesis of the polyurethane elastomer rubber and processing of the polyurethane elastomer gel include but are not limited to: Bis-Diglyceryl Polyacyladipate-1, Bis-Diglyceryl Polyacyladipate-1, Bis-Diglyceryl Polyacyladipate-2, Butylene Glycol Dicaprylate/Dicaprate, Butyrospermum Parkii Butter, Caprylic/Capric Glycerides, Caprylic/Capric Triglyceride, Caprylic/Capric/Myristic/Stearic Triglyceride, Caprylic/Capric/Succinic Triglyceride, Caprylyl Methicone, Coco-Caprylate/Caprate, Decamethylcyclopentasiloxane, Decyl Oleate, Dimethiconol, Diphenylsilanediol, Dodecamethylcyclohexasiloxane, Ethyl trisiloxane, Glyceryl Caprylate, Glyceryl Caprylate, Glyceryl Citrate/Lactate/Linoleate/Oleate, Glyceryl Citrate/Lactate/Linoleate/Oleate, Glyceryl Cocoate, Glyceryl Isostearate, Glyceryl Oleate, Glyceryl Ricinoleate, Glyceryl Ricinoleate, Tocopherol, Glyceryl Stearate, Glyceryl Stearate, Glyceryl Stearate Citrate, Hexamethyldisilazane, Hexamethyldisiloxane, Hydrogenated Coco-Glycerides, Hydrogenated Palm Oil, Hydroxytrimethylsilane, Isopropoxytrimethylsilane, Methylheptyl Isostearate, Octamethylcyclotetrasiloxane, Oleyl Erucate, Olus Oil, Organo-modified Siloxanes, Organosilicone Fluids, PCA Glyceryl Oleate, PEG-6 Caprylic/Capric Glycerides, Phenyltrichlorosilane, Poly(dimethyl siloxane), Poly(ethylene glycol)-containing siloxanes, Polydimethylsiloxane, Polyglyceryl-2 Caprate, Polyglyceryl-3 Caprate, Polyglyceryl-3 Caprate, Polyglyceryl-3 Diisostearate, Polyglyceryl-3 Polyricinoleate, Polyglyceryl-4 Cocoate, Polyglyceryl-4 Cocoate, Propylene Carbonate, Propylene Carbonate, Propylene Carbonate, Propylene Carbonate, Propylene Glycol Dicaprylate/Dicaprate, Propylene Glycol Dicaprylate/Dicaprate, Propylene Glycol Dicaprylate/Dicaprate, Silicone oil, Stearalkonium Bentonite, Stearalkonium Hectorite, Stearalkonium Hectorite, Stearalkonium Hectorite, Triheptanoin, Trimethyl(bromodifluoromethyl)silane, Trimyristin, and Tristearin.

[074] In some embodiments, the topically acceptable carrier fluid is at a concentration of about 0% to about 99.9% (w/w) of the gel composition, about 1% (w/w) to about 99.9% (w/w) of the gel composition, about 10% (w/w) to about 99.9% (w/w) of the gel composition, about 20% (w/w) to about 99.9% (w/w) of the gel composition, about 30% (w/w) to about 99.9% (w/w) of the gel composition, about 40% (w/w) to about 99.9% (w/w) of the gel composition, about 50% (w/w) to about 99.9% (w/w) of the gel composition, about 60% (w/w) to about 99.9% (w/w) of the gel composition, about 70% (w/w) to about 99.9% (w/w) of the gel composition, about 80%

(w/w) to about 99.9% (w/w) of the gel composition, or about 90% (w/w) to about 99.9% (w/w) of the gel composition. In certain embodiments, the gel composition does not comprise a topically acceptable carrier fluid. In some embodiments, a process for preparing the gel composition herein is conducted in the presence of a topically acceptable carrier fluid. In further embodiments, a process for preparing the gel composition herein is not conducted in the presence of a topically acceptable carrier fluid.

Component (E) - Active Ingredient

[075] In some embodiments, the gel compositions herein further comprise component (E), an active ingredient.

[076] In some embodiments, component (E) is a "pharmaceutically active ingredient" selected from any personal or health care active ingredient. As used herein, a "pharmaceutically active ingredient" means any compound or mixtures of compounds that are known in the art as additives in the personal care formulations that are typically added for the purpose of treating skin, lips or to provide a cosmetic and/or aesthetic benefit. A "healthcare active ingredient" means any compound or mixtures of compounds that are known in the art to provide a pharmaceutical or medical benefit. Thus, "healthcare active ingredient" includes materials considered an active ingredient or active drug ingredient as generally used and defined by the United States Department of Health & Human Services Food and Drug Administration, contained in Title 21, Chapter I, of the Code of Federal Regulations, Parts 200-299 and Parts 300-499. Thus, active ingredient can include any component that is intended to furnish pharmacological activity or other direct effect in the diagnosis, cure, mitigation, treatment, or prevention of disease, or to affect the structure or any function of the body of a human or other animals. The phrase can include those components that may undergo chemical change in the manufacture of drug products and be present in drug products in a modified form intended to furnish the specified activity or effect.

[077] Some representative examples of active ingredients include: drugs, vitamins, minerals, hormones, topical antimicrobial agents such as antibiotic active ingredients, antifungal active ingredients for the treatment of athlete's foot, jock itch, or ringworm, and acne active ingredients, astringent active ingredients, deodorant active ingredients, wart remover active ingredients, corn and callus remover active ingredients, pediculicide active ingredients for the treatment of head, pubic (crab) and body lice, active ingredients for the control of dandruff, seborrheic dermatitis, or psoriasis, and sunburn prevention and treatment agents.

[078] Useful active ingredients for use in processes according to the invention include Vitamins and its derivatives, including "pro-vitamins." Vitamins useful herein include, but are

not limited to, Vitamin A, retinol, C-C esters of retinol, Vitamin E, tocopherol, esters of vitamin E, and mixtures thereof. Retinol includes trans-retinol, 1.3-cis-retinol, 11-cis-retinol, 9-cis-retinol, and 3,4-didehydro-retinol, Vitamin C and its derivatives, Vitamin B, Vitamin B. Pro Vitamin B5, panthenol, Vitamin B, Vitamin B2, niacin, folic acid, biotin, and pantothenic acid. Other suitable vitamins and the INCI names for the vitamins considered included herein are ascorbyl dipalmitate, ascorbyl methylsilanol pectinate, ascorbyl palmitate, ascorbyl Stearate, ascorbyl glucoside, sodium ascorbyl phosphate, sodium ascorbate, disodium ascorbyl sulfate, potassium (ascorbyl/tocopheryl)phosphate.

[079] Retinol, it should be noted, is an International Nomenclature Cosmetic Ingredient Name (INCI) designated by The Cosmetic, Toiletry, and Fragrance Association (CTFA), Washington D.C., for vitamin A. Other suitable vitamins and the INCI names for the vitamins considered included herein are retinylacetate, retinyl palmitate, retinyl propionate, o-tocopherol, tocophersolan, tocopheryl acetate, tocopheryl linoleate, tocopheryl nicotinate, and tocopheryl succinate.

[080] The pharmaceutically active ingredient used in processes according to the invention can be an active drug ingredient. Representative examples of some suitable active drug ingredients which can be used are hydrocortisone, ketoprofen, timolol, pilocarpine, adriamycin, mitomycin C, morphine, hydromorphone, diltiazem, theophylline, doxorubicin, daunorubicin, heparin, penicillin G, carbenicillin, cephalothin, cefoxitin, cefotaxime, 5-fluorouracil, cytarabine, 6-azauridine, 6-thioguanine, vinblastine, Vincristine, bleomycin sulfate, aurothioglucose, suramin, mebendazole; clonidine, scopolamine, propranolol, phenylpropanolamine hydrochloride, ouabain, atropine, haloperidol, isosorbide, nitroglycerin, ibuprofen, ubiquinones, indomethacin, prostaglandins, naproxen, Salbutamol, guanaben Z, labetalol, pheniramine, metrifonate, and steroids.

[081] Considered to be included herein as active drug ingredients for purposes of the present invention are antiacne agents such as benzoyl peroxide and tretinoin; antibacterial agents such as chlorohexadiene gluconate; antifungal agents such as miconazole nitrate; anti-inflammatory agents; corticosteroidal drugs; non-steroidal anti-inflammatory agents such as diclofenac; antipsoriasis agents such as clobetasol propionate; anesthetic agents such as lidocaine; antipruritic agents; antidermatitis agents; and agents generally considered barrier films.

[082] The pharmaceutically active ingredient E) of the present invention can be a protein, such as an enzyme. The internal inclusion of enzymes in the polyurethane elastomer gel have advantages to prevent enzymes from deactivating and maintain bioactive effects of enzymes for a longer time. Enzymes include, but are not limited to, commercially available types, improved

types, recombinant types, wild types, variants not found in nature, and mixtures thereof. For example, suitable enzymes include hydrolases, cutinases, oxidases, transferases, reductases, hemicellulases, esterases, isomerases, pectinases, lactases, peroxidases, laccases, catalases, and mixtures thereof. Hydrolases include, but are not limited to, proteases (bacterial, fungal, acid, neutral or alkaline), amylases (alpha orbeta), lipases, mannanases, cellulases, collagenases, lisozymes, superoxide dismutase, catalase, and mixtures thereof. Said proteases include, but are not limited to, trypsin, chymotrypsin, pepsin, pancreatin and other mammalian enzymes; papain, bromelain and other botanical enzymes; subtilisin, epidermin, nisin, naringinase(L-rhammnosidase) urokinase and other bacterial enzymes. Said lipases include, but are not limited to, triacyl-glycerol lipases, monoacyl glycerol lipases, lipoprotein lipases, e.g. steapsin, erepsin, pepsin, other mammalian, botanical, bacterial lipases and purified ones. Natural papain is preferred as said enzyme. Further, stimulating hormones, e.g. insulin, can be used together with these enzymes to boost the effectiveness of them.

[083] The pharmaceutically active ingredient may also be a sunscreen agent. The Sunscreen agent can be selected from any Sunscreen agent known in the art to protect skin from the harmful effects of exposure to sunlight. The sunscreen compound is typically chosen from an organic compound, an inorganic compound, or mixtures thereof that absorbs ultraviolet (UV) light. Thus, representative non limiting examples that can be used as the sunscreen agent include; aminobenzoic acid, cinoxate, diethanolamine methoxycinnamate, digalloyl trioleate, dioxybenzone, ethyl 4-bis(Hydroxypropyl) aminobenzoate, glyceryl aminobenzoate, homosalate, lawsone with dihydroxyacetone, menthyl anthranilate, octocrylene, octyl methoxycinnamate, octyl salicylate, oxybenzone, padimate O, phenylbenzimidazole sulfonic acid, red petrolatum, sulisobenzone, titanium dioxide, trolamine salicylate, cetarninosalol, allatoin, PABA, benzalphthalide, benzophenone, benzophenone 1-12, 3-benzylidene camphor, benzylidenecamphor hydrolyzed collagen sulfonamide, benzylidene camphor sulfonic acid, benzyl salicylate, bomelone, bumetriozole, butyl methoxydibenzoylmethane, butyl PABA, ceria/silica, ceria/silica talc, cinoxate, DEA-methoxycinnamate, dibenzoxazol naphthalene, di-t-butyl hydroxybenzylidene camphor, digalloyl trioleate, diisopropyl methyl cinnamate, dimethyl PABA ethyl cetearyldimonium tosylate, dioctyl butamido triazone, diphenyl carbomethoxy acetoxy naphthopyran, disodium bisethylphenyl tiamminotriazine stilbenedisulfonate, disodium sistyrylbiphenyl triaminotriazine stilbenedisulfonate, disodium distyrylbi phenyl disulfonate, drometrizole, drometrizole trisiloxane, ethyl dihydroxypropyl PABA, ethyl diisopropylcinnamate, ethyl methoxycinnamate, ethyl PABA, ethyl urocanate, etrocrylene ferulic acid, glyceryl octanoate dimethoxycinnamate, glyceryl PABA, glycol salicylate, homosalate, isoamyl p-methoxycinnamate, isopropylbenzyl salicylate, isopropyl

dibenzolylmethane, isopropyl methoxycinnamate, menthyl anthranilate, menthyl salicylate, 4-methylbenzylidene, camphor, octocrylene, octrizole, octyl dimethyl PABA, octyl methoxycinnamate, octyl salicylate, octyl triazone, PABA, PEG-25 PABA, pentyl dimethyl, PABA, phenylbenzimidazole sulfonic acid, polyacrylamidomethyl benzylidene camphor, potassium methoxycinnamate, potassium phenylbenzimidazole sulfonate, red petrolatum, sodium phenylbenzimidazole sulfonate, sodium urocanate, TEA-phenylbenzimidazole sulfonate, TEA-salicylate, terephthalylidene dicamphor sulfonic acid, titanium dioxide, zinc dioxide, serium dioxide, TriPABA panthenol, urocanic acid, and VA/crotonates/ methacryloxybenzophenone-1 copolymer.

[084] The sunscreen agent can be a single one or combination of more than one. Alternatively, the sunscreen agent is a cinnamate based organic compound, or alternatively, the sunscreen agent is octyl methoxycinnamate, such as Uvinul R. MC 80 (an ester of para-methoxycinnamic acid and 2-ethyl hexanol).

[085] Component (E) may also be a fragrance or perfume. The perfume can be any perfume or fragrance active ingredient commonly used in the perfume industry. These compositions typically belong to a variety of chemical classes, as varied as alcohols, aldehydes, ketones, esters, ethers, acetates, nitrites, terpenic hydrocarbons, heterocyclic nitrogen or sulfur containing compounds, as well as essential oils of natural or synthetic origin. Many of these perfume ingredients are described in detail in standard textbook references such as Perfume and Flavour Chemicals, 1969, S. Arctander, Montclair, N.J.

[086] Fragrances may be exemplified by, but not limited to, perfume ketones and perfume aldehydes. Illustrative of the perfume ketones are buccoxime, isojasmone, methyl beta naphthyl ketone, musk indanone, tonalid/musk plus, Alpha Damascone, Beta-Damascone, Delta-Damascone, Iso Damascone, Damascenone, Damarose, Methyl Dihydrojasmonate, Menthone, Carvone, Camphor, Fenchone, Alpha-lonone, Beta-lonone, Gamma-Methyl So called lonone, Fleuramone, Dihydrojasmone, Cis-Jasmone, Iso-E-Super, Methyl-Cedrenyl-ketone or Methyl-Cedrylone, Acetophenone, Methyl-Acetophenone, Para-Methoxy-Acetophenone, Methyl-Beta-Naphtyl-Ketone, Benzyl-Acetone, Benzophenone, Para-Hydroxy-Phenyl-Butanone, Celery Ketone or LiveScone, 6-Isopropyldecahydro-2-naphtone, Dimethyl-Octenone, Freskomenthe, 4-(1-Ethoxyvinyl)-3,3, 5,5,-tetramethyl-Cyclohexanone, Methyl-Heptenone, 2-(2-(4-Methyl-3-cyclohexen-1-yl)propyl)-cyclopentanone, 1-(p- Menthen-6(2)-yl)-1-propanone, 4-(4-Hydroxy-3-methoxyphenyl)-2-butanone, 2-Acetyl-3,3-Dimethyl Norbornane, 6,7-Dihydro-1,1,2,3,3-Pentamethyl-4(5H)-Indanone, 4-Damascol, Dulcinyl or Cassione, Gelsone, Hexylon, Isocyclemone E. Methyl Cyclocitrone, Methyl Lavender-Ketone, Orivon, Para-tertiary-Butyl-

Cyclohexanone, Verdone, Delphone, Muscone, Neobutenone, Plica tone, Veloutone, 2,4,4,7-Tetramethyl-oct-6-en-3-one, and Tetrameran.

[087] More preferably, the perfume ketones are selected for its odor character from Alpha Damascone, Delta Damascone, Iso Damascone, Carvone, Gamma-Methyl-lonone, Iso-E-Super, 2.4.4.7-Tetramethyl-oct-6-en-3-one, Benzyl Acetone, Beta Damascone, Damascenone, methyl dihydrojasmonate, methyl cedrylone, and mixtures thereof.

[088] Preferably, the perfume aldehyde is selected for its odor character from adoxal, anisic aldehyde, cymal, ethylvanillin, florhydral, helional, heliotropin, hydroxycitronellal, koavone, lauric aldehyde, lyral, methyl nonyl acetaldehyde, P. T. bucinal, phenyl acetaldehyde, undecylenic aldehyde, vanillin, 2,6,10-trimethyl-9-undecenal, 3-dodecen-1-al, alpha-n-amyl cinnamic aldehyde, 4-methoxybenzaldehyde, benzaldehyde, 3-(4-tert-butylphenyl)-propanal, 2-methyl-3-(para-methoxyphenyl propanal, 2-methyl-4-(2,6,6-trim ethyl-2(1)-cyclohexen-1-yl) butanal, 3-phenyl-2-propenal, cis-/trans-3,7-dimethyl-2,6-octadien-1-al, 3,7-dimethyl-6-octen-1-al. (3,7-dimethyl-6-octenyl)oxyacetaldehyde, 4-isopropylbenzyaldehyde, 1,2,3,4,5,6,7,8-octahydro-8.8-dimethyl-2-naphthaldehyde, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, 2-methyl-3-(isopropylphenyl)propanal, 1-decanal; decyl aldehyde, 2,6-dimethyl-5-heptenal, 4-(tri cyclo[5.2.1.0(2,6)-decylidene-8)-butanal, octahydro-4,7-methano-1H-indenecarboxaldehyde, 3-ethoxy-4-hydroxy benzaldehyde, para-ethyl-alpha,alpha-dimethyl hydrocinnamaldehyde, alpha-methyl-3,4-(methylenedioxy)-hydrocinnamaldehyde, 3,4-methylenedioxybenzaldehyde, alpha-nhexyl cinnamic aldehyde, m-cymene-7-carboxaldehyde, alpha-methyl phenyl acetaldehyde, 7-hydroxy-3,7-dimethyl octanal, undecenal, 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde, 4-(3)(4-methyl-3-pentenyl)-3-cyclohexen-carboxaldehyde, 1-dodecanal, 2,4-dimethyl cyclohexene-3-carboxaldehyde, 4-(4-hydroxy-4-methylpentyl)-3-cylohexene 1-carboxaldehyde, 7-methoxy-3,7-dimethyloctan-1-al, 2-methyl undecanal, 2-methyl decanal, 1-nonanal, 1-octanal, 2,6,10-trimethyl-5.9-undecadienal, 2-methyl-3-(4-tertbutyl)propanal, dihydrocinnamic aldehyde, 1-methyl-4-(4-methyl 3-pentenyl)-3-cyclohexene-1-carboxaldehyde, 5(or 6)-methoxy hexahydro-4,7-methanoindan-1(or 2)-carboxaldehyde, 3,7-dimethyloctan-1-al, 1-undecanal, 10-undecen-1-al, 4-hydroxy-3-methoxybenzaldehyde, 1-methyl-3-(4-methylpentyl)-3-cyclhexenecarboxaldehyde, 7-hydroxy-3,7-dimethyloctanal, trans-4-decenal, 2,6-nonadienal, paratolylacetaldehyde, 4-methylphenylacetaldehyde, 2-me thyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butenal, ortho-methoxycinnamic aldehyde, 3,5,6-trimethyl-3-cyclohexene carboxaldehyde, 3,7-dimethyl-2-methylene-6-octenal, phenoxyacetaldehyde, 5,9-dimethyl-4,8-decadienal, peony aldehyde (6,10-dimethyl-3-oxa-5.9-undecadien-1-al), hexahydro-4,7-methanoindan-1-carboxaldehyde, 2-methyloctanal, alpha-methyl-4-(1-methylethyl)benzene acetaldehyde, 6,6-dimethyl-2-norpinene-2-propionaldehyde, para methyl phenoxyacetaldehyde,

2-methyl-3-phenyl-2-propen-1-al, 3.5.5-trimethylhexanal, Hexahydro-8,8-dimethyl-2-naphthaldehyde, 3-propyl-bicyclo[2.2.1-hept-5-ene-2-carbaldehyde, 9-decenal, 3-methyl-5-phenyl-1-pentanal, methylnonyl acetaldehyde, hexanal, trans-2-hexenal, 1-p-menthene-q-carboxaldehyde and mixtures thereof. More preferred aldehydes are selected for their odor character from 1-decanal, benzaldehyde, florhydral, 2,4-dim ethyl-3-cyclohexen-1-carboxaldehyde, cis/trans-3,7-dim ethyl-2,6-octadien-1-al, heliotropin, 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde, 2,6-nonadienal, alpha-amyl-cinnamic aldehyde, alpha-n-hexyl-cinnamic aldehyde, P.T. Bucinal, lyral, cymal, methylnonyl acetaldehyde, hexanal, trans-2-hexenal, and mixture thereof. In the above list of perfume ingredients, some are commercial names conventionally known to one skilled in the art, and also includes isomers. Such isomers are also suitable for use in the present invention.

[089] Component (E) may also be one or more plant extracts. Examples of these components are as follows: Ashitaba extract, avocado extract, hydrangea extract, Althea extract, Arnica extract, aloe extract, apricot extract, apricot kernel extract, Ginkgo Biloba extract, fennel extract, turmeric Curcuma extract, oolong tea extract, rose fruit extract, Echinacea extract, Scutellaria root extract, Phellodendro bark extract, Japanese Coptis extract, Barley extract, Hyperium extract, White Nettle extract, Watercress extract, Orange extract, Dehydrated saltwater, seaweed extract, hydrolyzed elastin, hydrolyzed wheat powder, hydrolyzed silk, Chamomile extract, Carrot extract, Artemisia extract, Glycyrrhiza extract, hibiscustea extract, Pyracantha Fortuneana Fruit extract, Kiwi extract, Cinchona extract, cucumber extract, guanocine, Gardenia extract, Sasa Albo-marginata extract, Sophora root extract, Walnut extract, Grapefruit extract, Clematis extract, Chlorella extract, mulberry extract, Gentiana extract, black tea extract, yeast extract, burdock extract, rice bran ferment extract, rice germ oil, comfrey extract, collagen, cowberry extract, Gardenia extract, Asiasarum Root extract, Family of Bupleurum extract, umbilical cord extract, Salvia extract, Saponaria extract, Bamboo extract, Crataegus fruit extract, Zanthoxylum fruit extract, Shiitake extract, Rehmannia root extract, gromwell extract, Perilla extract, linden extract, Filipendula extract, peony extract, calamus root extract, white birch extract, Horsetail extract, Hedera Helix(Ivy) extract, hawthorn extract, Sambucus migra extract, Achillea millefolium extract, Mentha piperita extract, sage extract, mallow extract, Cnidium officinale Root extract, Japanese green gen tian extract, Soybean extract, jujube extract, thyme extract, tea extract, clove extract, Gramineae imperata cyrillo extract, citrus unshiu peel extract, Japanese angelica root extract, calendula extract, peach kernel extract, bitter orange peel extract, Houttuyna cordata extract, tomato extract, natto extract, ginseng extract, green tea extract (camelliea sine sis), garlic extract, wild rose extract, hibiscus extract, Ophiopogon tuber extract, Nelumbo nucifera extract, parsley extract, honey, hamamelis extract, parietaria extract, isodonis

herba extract, bisabolol extract, Loquat extract, coltsfoot extract, butterbur extract, Poria cocos wolf extract, extract of butcher's broom, grape extract, propolis extract, lufa extract, safflower extract, peppermint extract, linden tree extract, Paeonia extract, hop extract, pine tree extract, horse chestnut extract, Mizu-bashou Lysichiton camtschatcese extract, Mukurossi peel extract, Melissa extract, peach extract, corn flower extract, eucalyptus extract, saxifrage extract, citron extract, coix extract, mugwort extract, lavender extract, apple extract, lettuce extract, lemon extract, Chinese milk vetch extract, rose extract, rosemary extract, Roman Chamomile extract, and royal jelly extract.

[090] The amount of component (E) present in the polyurethane gel composition may vary, but typically range as follows: 0.05 to 50 wt %, alternatively 1 to 25 wt %, or alternatively 1 to 10 wt %, based on the amount by weight of polyurethane elastomer gel present in the composition, that is total weight of components (A), (B), (C) and (D) in the gel composition.

[091] Component (E) may be added to the polyurethane gel composition either during the making of the polyurethane elastomer (pre-load method), or added after the formation of the polyurethane elastomer gel (post load method).

[092] The pre-load method comprises: reacting: (A) polyisocyanate; (B) polyol; and (C) an optional polyurethane reaction catalyst, optionally in (D) a carrier fluid; and admixing (E) a personal care or healthcare active with the polyurethane elastomer gel to form the polyurethane elastomer gel containing active.

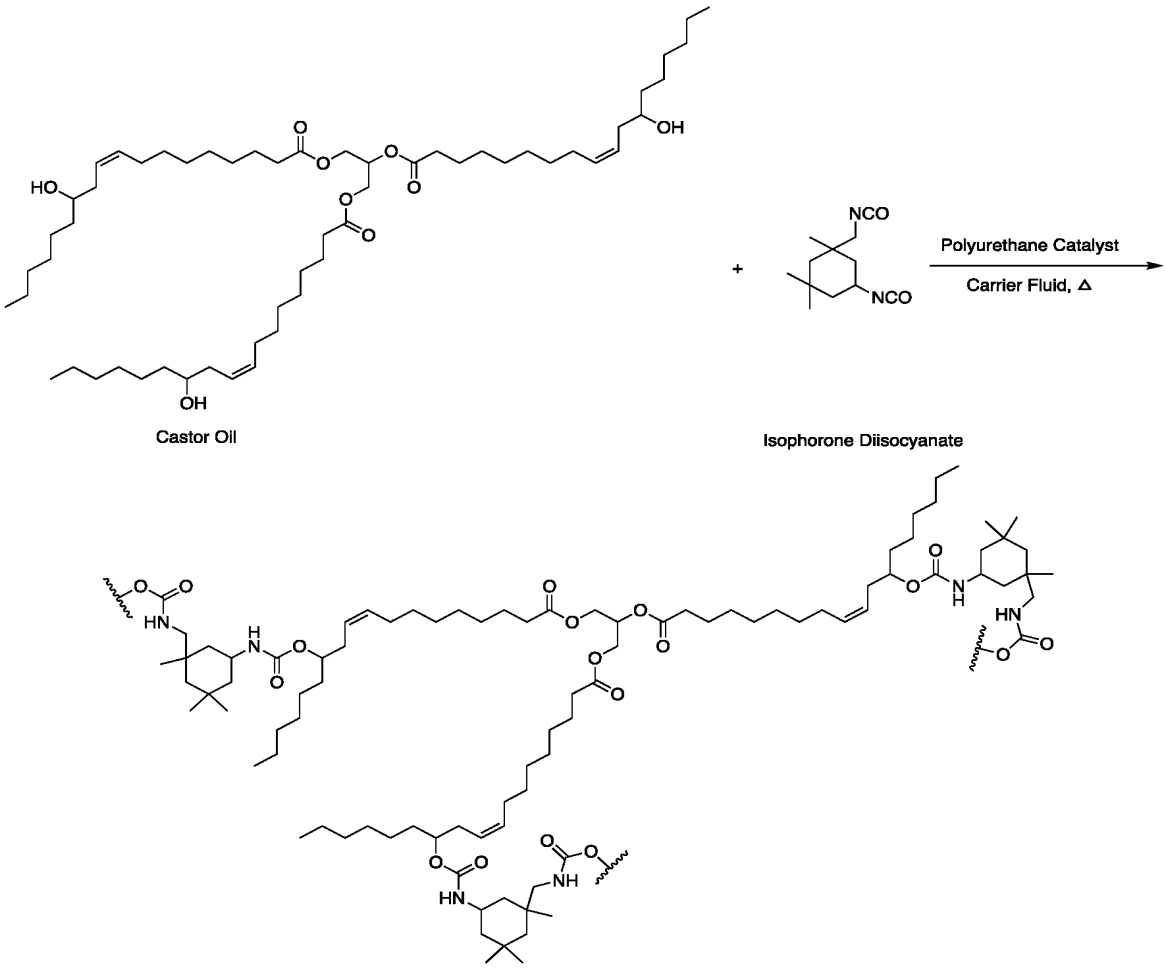
[093] The post-load method comprises: (I) reacting: (A) polyisocyanate; (B) polyol; (C) an optional polyurethane reaction catalyst, optionally in (D) a carrier fluid to form a polyurethane elastomer gel; (II) shearing the polyurethane elastomer gel into a smooth paste; and (III) admixing (E) a personal care or healthcare active ingredient with the polyurethane elastomer gel to form the polyurethane elastomer gel containing active. The personal care active may also be admixed as a component of another mixture with one or more excipients.

Polyurethane Elastomer

[094] The polyurethane elastomers of the present invention are obtainable as polyurethane reaction products of components (A) polyisocyanate, (B) polyol, and (C) an optional polyurethane reaction catalyst, optionally in (D) a carrier fluid. The term "polyurethane reaction" means the addition of a compound containing a hydroxyl group (such as component (A)) to a compound containing an isocyanate group (such as component (B)), in the presence of a catalyst (such as component (C)), wherein the molar ratio of hydroxyl groups to isocyanate groups is 1:1. Alternatively, this ratio can range from 8:1 to 0.9:1. The polyurethane reaction is

conducted in the presence of a solvent, where the solvent is the same as the carrier fluid described as component (D) and used without further purification.

[095] In a specific embodiment, the invention provides a cross-linked polyurethane elastomer network according to the following general structure and prepared by the following general scheme (the depicted structure is based on the principle triglyceride component of castor oil, ricinolein), formed from the reaction of castor oil with isophorone diisocyanate:

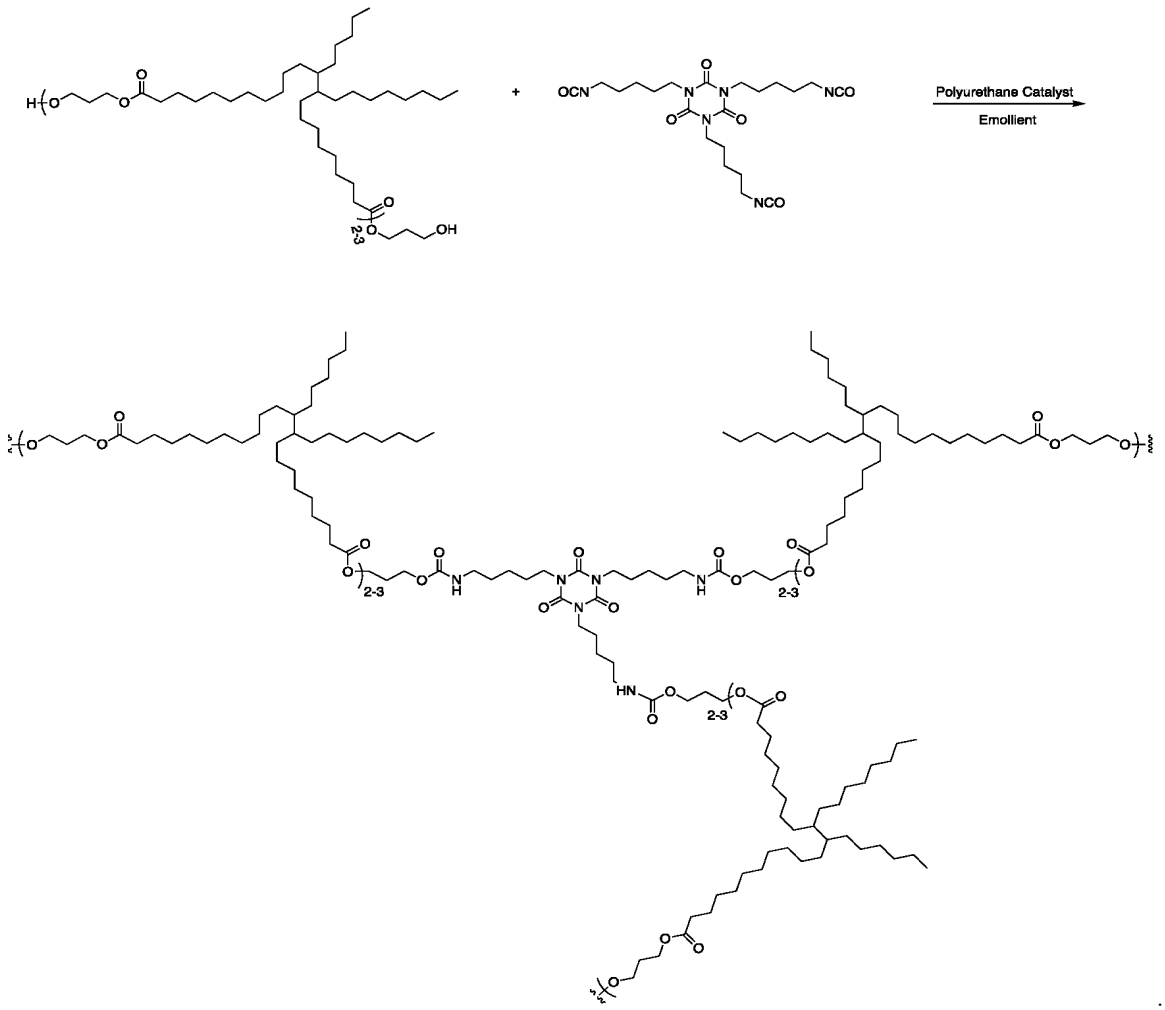


Castor Oil

Isophorone Diisocyanate

Castor Oil/Isophorone Diisocyanate Polyurethane Elastomer

[096] In a further embodiment, the structure of the polyurethane elastomer is a cross-linked polymer network of the repeat units dilinoleic acid/propane diol copolymer, alkyl carbamate, and triazine trione. A typical chemical structure for the polyurethane polymer network is represented below and formed according to the following reaction scheme:



[097] In certain embodiments, the polyurethane elastomer gel described above is prepared in a three-step process. First, dilinoleic acid/propane diol copolymer is reacted with 1,5-pentamethylene diisocyanate trimer in the presence of bismuth neodecanoate in a reaction medium of triheptanoin and coco-caprylate/caprate at elevated temperature with mixing. The molecular weight range of the dilinoleic acid/propane diol copolymer is about 1000-3000. The molar ratios of NCO of the polyisocyanate to OH of the copolymer can be between 2:1 to 1:2. The amount of bismuth neodecanoate in the reaction mixture can approximately be between 0.05-2.25% by weight. The reaction occurs between the hydroxyl groups of the copolymer and the isocyanate groups of the polyisocyanate in the presence of a catalyst to create a urethane linkage −RNHCOOR′−. The product is a cross-linked polyurethane elastomer rubber with the topically acceptable carrier fluids triheptanoin and coco-caprylate/caprate entrapped in the elastomeric matrix. The resulting off-white rubber is soft, not brittle, and slightly sticky to the touch. In the second step, the rubber is diluted with a carrier fluid such as triheptanoin and milled into a gel using a high sheer mixture, a disperser, or a homogenizer. The resulting gel

concentrate is thick and smooth, and with no granule particles. When applied to skin the gel is easily absorbed and spreads evenly with no pilling. In the third step, a carrier fluid such as undecane and/or tridecane or coconut alkanes may be added to the gel concentrate with high sheer mixer until the desired viscosity achieved.

[098] The hardness of the polyurethane elastomer rubber is an important factor that determines if it can be readily processed into a gel. If the polyurethane elastomer rubber is too hard, the rubber granules will not swell properly or grind into a smooth gel upon processing. If the polyurethane elastomer rubber is too soft, it will not easily process into a gel due to stickiness and lack of swellable particles. Five factors mainly determine the hardness of the polyurethane elastomer rubber.

[099] First, the solid content as determined by weight percent of reactants in the synthesis of the polyurethane elastomer rubber is a critical factor that determines the polyurethane elastomer rubbers hardness and gelation capacity. If the solid content is to high the rubber will be hard and brittle. If the solid content is too low the rubber will be sticky and soft. In practice, the total weight percent of reactants in the rubber formation can be between 70-95%.

[0100] Second, the identity of the topically acceptable carrier fluid(s) affects polyurethane hardness and processing. If coco-caprylate/caprate is used as the only carrier fluid, the polyurethane elastomer rubber may be too hard and brittle and therefore will not process into a smooth gel. Using triheptanoin or a mixture of triheptanoin and coco-caprylate/caprate in ratios of 4:1 to 1:1 can produce a polyurethane elastomer rubber with appropriate hardness. Preferably a ratio of 3:1 is used.

[0101] Third, the ratios of polyol to polyisocyanate based polyisocyanate affects the polyurethane elastomer rubber hardness. If the molar ratios of hydroxyl groups to isocyanates is too large or small, sufficient cross-linking will not occur and a soft and sticky product will be formed, which cannot be processed into a gel. The molar ratios of NCO of said isocyanate to OH of said polyol can be between 2:1 to 1:2.

[0102] Fourth, the amount of bismuth catalyst used in the synthesis of the polyurethane elastomer rubber is another factor that determines its ability to be processed into a gel. If too much catalyst is used the rubber will over-cure while heating and will be too hard to be processed into a gel. If too little catalyst is used the rubber will not form. In practice, the amount of bismuth catalyst can be about 0.05-2.25% by weight.

[0103] Fifth, the reaction temperature should not exceed 80 °C or the elastomer rubber may over cure, resulting in a rubber that is too hard. In addition, weeping of the solvent may occur at

temperatures above 80 °C. The reaction temperature for rubber formation should be about 40-80 °C.

Methods for Measuring Viscosity of Polyurethane Elastomer Gel Paste

[0104] The Brookfield HELIPATH™ Stand, when used with a suitable Brookfield Viscometer fitted with a special T-bar type spindle, will permit viscosity/consistency measurements in centipoise values for materials having characteristics similar to paste, putty, cream, gelatin, or wax. The viscosity of polyurethane elastomer blends was determined using a Brookfield Model DV-II+Pro Viscometer with HELIPATH™ stand (Brookfield Model D) and T-Bar spindles (Brookfield HELIPATH™ Spindle Set). All were purchased from Brookfield Engineering Laboratories, Inc. (11 Commerce Boulevard Middleboro, Mass., USA). A sample size of 50 g in a 4-ounce round jar was required. The following preparation procedure was used before measurement: air bubbles were removed from samples first via centrifuge and then under vacuum for two hours. After de-airing, the sample was conditioned for a minimum of 4 hours at 25 °C. The measurement was taken according to the typical procedure for a HELIPATH™ spindle. In general, spindle 93 (T-bar spindle E) is used and the standard setting for rpm was 6.5. The spindle speed is maintained at constant 6.5 rpm.

Topical Formulations

[0105] Topical formulations comprising the gel compositions or gel pastes are also provided herein. In such formulations, the gel compositions or gel pastes are suitably used as thickeners or stabilizers for the topical formulations. Other components of the topical formulations are known in the art, and can include for example, various components such as emulsion stabilizers, emulsifiers skin conditioners, suspending agents etc. The amounts of these additional components can be on the order of about 0.01% to about 50% by weight.

[0106] As used herein, an "emulsion stabilizer" refers to a composition that aids in keeping an emulsion from separating into its oil and aqueous components. In embodiments, the emulsion stabilizer utilized in the formulations described herein is a naturally derived gum or a modified gum or natural mineral. Exemplary emulsion stabilizers include, but are not limited to, acacia, cellulose, crystalline cellulose, gellan, guar, locust (carob) bean, xanthan, magnesium aluminum silicate, bentonite or hectorite clays and the like, including combinations thereof.

[0107] As used herein, a "skin conditioner" refers to a composition that acts as a lubricant on the surface of the skin or a composition that increases the water content of the surface of the skin. Exemplary skin conditioners for use in the formulations include, but are not limited to, adipate esters, alkyl benzoates, fatty acid esters of C8 or greater, esterified erucates, laurates,

neopentanoates, salicylates, stearates, triglycerides, carbonates, glycols, glycerin, mineral oils and the like, including combinations thereof.

[0108] As used herein, an "emulsifier" refers to a composition that aids in the formation of an oil in water, or a water in oil, emulsion. Exemplary emulsifiers for use in the formulations include, but are not limited to, polysorbates, ethoxylated fatty acids, fatty acids neutralized with sodium hydroxide, potassium hydroxide or amines, substituted glucosides, sodium lauryl and lauryl ether sulfates, ethoxylated esters, lecithin and lecithin derivatives and the like, including combinations thereof.

[0109] As used herein, a "suspending agent" refers to a composition that modifies the interface between solid particles and a liquid medium to improve the particles' resistance to coming together and falling out of solution. Exemplary suspending agents for use in the formulations include, but are not limited to, hydroxy stearic acid, polyhydroxystearic acid, sodium polyacrylate polymers, methyl methacrylate crosspolymers and the like, including combinations thereof.

[0110] In additional embodiments, the polyurethane elastomers can be utilized in solid-based formats, including for example, as a foot conforming shoe insert or shoe sole.

Exemplary Embodiments

Embodiment 1: A gel composition comprising a polyurethane elastomer gel prepared from the reaction of:

(A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups;

(B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups;

(C) an optional polyurethane reaction catalyst; and

(D) an optional topically acceptable carrier fluid.

Embodiment 2: The gel composition of embodiment 1, wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, oils, and combinations thereof.

Embodiment 3: The gel composition of embodiment 1, wherein the topically acceptable carrier fluid is selected from the group consisting of diisooctyl succinate, heptyl undecylenate, neopentyl glycol diheptanoate, coco-caprylate/caprate, triheptanoin, caprylic/capric triglyceride, dodecane, tridecane, C13-15 alkane, squalene, squalene, isoamyl laurate, isopentyl laurate, caprylic/capric/myristic/stearic triglyceride, caprylic/capric/succinic triglyceride, isopropyl myristate, jojoba esters, tricaprylin, and palm oil.

Embodiment 4: The gel composition of embodiment 1, further comprising a pharmaceutically active ingredient dissolved in the topically acceptable carrier fluid.

Embodiment 5: The gel composition of embodiment 1 wherein the polyisocyanate or mixture of polyisocyanates is a low molecular weight polyisocyanate or mixture of polyisocyanates and wherein the polyol or mixture of polyols contains two or more hydroxyl, amine, thiol, or carboxylic acid groups.

Embodiment 6: A gel composition comprising a polyurethane elastomer from the reaction of:

(A) castor oil;

(B) isophorone diisocyanate, wherein the molar ratio of isocyanate groups to hydroxyl groups is between 1:1 and 1:2;

(C) an optional polyurethane reaction catalyst; and

(D) a topically acceptable carrier fluid at a concentration of 60% (w/w) to 99.9% (w/w) of the gel composition;

wherein a personal care or healthcare active ingredient is optionally incorporated into the polyurethane elastomer gel by dissolving the personal care or healthcare active ingredient in the topically acceptable solvent during the formation of the polyurethane elastomer gel, or by admixing the personal care or healthcare active ingredient with a formed polyurethane elastomer gel.

Embodiment 7: The gel composition of embodiment 6, wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof.

Embodiment 8: The gel composition of embodiment 6, wherein the topically acceptable carrier fluid is selected from the group consisting of diisooctyl succinate, heptyl undecylenate, neopentyl glycol diheptanoate, and coco-caprylate/caprate.

Embodiment 9: The gel composition of embodiment 6, further comprising a pharmaceutically active ingredient dissolved in the topically acceptable carrier fluid.

Embodiment 10: The gel composition of embodiment 1, wherein the polyurethane catalyst is a bismuth group containing catalyst.

Embodiment 11: The gel composition of embodiment 6, wherein the polyurethane catalyst is a bismuth group containing catalyst.

Embodiment 12: The gel composition of embodiment 1, wherein greater than 50% of the carbon content of the topically acceptable solvent is derived from plant sources.

Embodiment 13: The gel composition of embodiment 6, wherein greater than 50% of the carbon content of the topically acceptable solvent is derived from plant sources.

Embodiment 14: A process for preparing the gel composition of embodiment 1, comprising reacting:

(A) a polyol;

(B) isophorone diisocyanate; and

(C) an optional polyurethane reaction catalyst;

optionally in the presence of

(D) a topically acceptable carrier fluid.

Embodiment 15: A process for preparing the gel composition of embodiment 6, comprising reacting:

(A) castor oil;

(B) isophorone diisocyanate; and

(C) an optional polyurethane reaction catalyst;

optionally in the presence of

(D) a topically acceptable carrier fluid.

Embodiment 16: A gel composition prepared according to the process of embodiment 14.

Embodiment 17: A gel composition prepared according to the process of embodiment 15.

Embodiment 18: A process for preparing a gel paste composition, comprising:

(I) shearing the gel composition of embodiment 1, and

(II) combining the sheared polyurethane elastomer gel with an additional quantity of the carrier fluid to form a gel paste composition.

Embodiment 19: A process for preparing a gel paste composition comprising:

(I) shearing the gel composition of embodiment 1, and

(II) combining the sheared polyurethane elastomer gel with an active ingredient.

Embodiment 20: A process for preparing a gel paste composition, comprising:

(I) shearing the gel composition of embodiment 6, and

(II) combining the sheared polyurethane elastomer gel with an additional quantity of the carrier fluid to form a gel paste composition.

Embodiment 21: A process for preparing a gel paste composition comprising:

(I) shearing the gel composition of embodiment 6, and

(II) combining the sheared polyurethane elastomer gel with an active ingredient.

Embodiment 22: A method of making a polyurethane elastomer comprising:

I) mixing a polyisocyanate reactant and a polyol reactant, optionally in a topically acceptable carrier fluid to form a reaction mixture with a reactant concentration of about

80% (w/w), wherein the polycisocyanate reactant comprises two or more isocyanate functional groups and the polyol reactant comprises two or hydroxyl groups;

II) optionally adding a polyurethane reaction catalyst; and

III) optionally heating the reaction mixture to about 80 °C to form the polyurethane elastomer.

Embodiment 23: The method of embodiment 22, wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combination thereof.

Embodiment 24: The method of embodiment 22, wherein the topically acceptable carrier fluid is selected from the group consisting of diisooctyl succinate, heptyl undecylenate, neopentyl glycol diheptanoate, coco-caprylate/caprate, and combination thereof.

Embodiment 25: The method of embodiment 22, further comprising dissolving a pharmaceutically active ingredient in the topically acceptable carrier fluid.

Embodiment 26: The method of embodiment 22, wherein the polyisocyanate reactant is derived from the polymerization of another polyisocyanate.

Embodiment 27: The method of embodiment 22, further comprising preparing the polyisocyanate reactant from hexamethylene diisocyanate.

Embodiment 28: The method of embodiment 22, further comprising preparing the polyisocyanate reactant from pentamethylene diisocyanate.

Embodiment 29: A polyurethane elastomer gel paste prepared by the method of embodiment 18.

Embodiment 30: A polyurethane elastomer gel paste prepared by the method of embodiment 19.

Embodiment 31: A polyurethane elastomer gel paste prepared by the method of embodiment 20.

Embodiment 32: A polyurethane elastomer gel paste prepared by the method of embodiment 21.

Embodiment 33: A topical formulation comprising:

the gel composition of embodiment 1 or embodiment 6; and a pharmaceutically active ingredient, wherein the pharmaceutically active ingredient is a personal care active ingredient or a healthcare active ingredient.

Embodiment 34: A topical formulation comprising:

the polyurethane elastomer gel paste of any of embodiments 29 to 32; and a pharmaceutically active ingredient, wherein the pharmaceutically active ingredient is a personal care active ingredient or a healthcare active ingredient.

Embodiment 35: A foot conforming shoe insert or shoe sole comprising the gel composition of embodiment 1 or embodiment 6.

Embodiment 36: A medical medically acceptable gel comprising the gel composition of embodiment 1 or embodiment 6.

Embodiment 37: A topical formulation comprising the gel composition of embodiment 1 or embodiment 6.

[0111] The disclosure is further illustrated by the following examples which are provided merely to be exemplary and do not limit the scope of the invention. Certain modifications and equivalents will be apparent to those skilled in the art and are intended to be included within the scope of the disclosure. The present disclosure provides, but is not limited to, the following formulation examples.

Example 1 - Preparation of dilinoleic acid/propane diol copolymer based polyurethane elastomer gel with triheptanoin, coco-caprylate/caprate, and undecane (and) tridecane.

[0112] To a reaction kettle was added triheptanoin, coco-caprylate/caprate, dilinoleic acid/propane diol copolymer, and pentamethylene diisocyanate trimer. This mixture was stirred at room temperature until a clear, homogeneous solution was obtained. Bismuth neodecanoate was added with stirring, and the reaction was heated to 60 °C for about 1 hour, at which point an off-white soft rubber is formed. After rubber formation the rubber is allowed to cool to room temperature.

[0113] The polyurethane elastomer rubber was then placed in a drum, triheptanoin was added with high sheer mixing. The resulting suspension was then run through a disperser and the resulting gel was allowed to cool to room temperature. Undecane and/or tridecane were then added with mixing until the desired viscosity was achieved.

Example 2 - Preparation of dilinoleic acid/propane diol copolymer based polyurethane elastomer gel with triheptanoin, coco-caprylate/caprate, and coconut alkanes.

[0114] Prepare a polyurethane elastomer rubber according to Example 1. The polyurethane elastomer gel is prepared by placing the polyurethane elastomer rubber in a drum, then triheptanoin was added with high sheer mixing. The resulting suspension was then run through a disperser and the resulting gel was allowed to cool to room temperature. Coconut alkanes were then added with mixing until the desired viscosity was achieved.

Example 3 - Preparation of dilinoleic acid/propane diol copolymer based polyurethane elastomer gel with triheptanoin, and coco-caprylate/caprate.

[0115] Prepare a polyurethane elastomer rubber according to Example 1. The polyurethane elastomer gel is prepared by placing the polyurethane elastomer rubber in a drum, then

triheptanoin was added with high sheer mixing. The resulting suspension was then run through a disperser and the resulting gel was allowed to cool to room temperature. Coco-caprylate/caprate were then added with mixing until the desired viscosity was achieved.

Example 4 - Preparation of dilinoleic acid/propane diol copolymer based polyurethane elastomer gel with triheptanoin.

[0116] Prepare a polyurethane elastomer rubber according to Example 1. The polyurethane elastomer gel is prepared by placing the polyurethane elastomer rubber in a drum, then triheptanoin was added with high sheer mixing. The resulting suspension was then run through a disperser and the resulting gel was allowed to cool to room temperature. Triheptanoin were then added with mixing until the desired viscosity was achieved.

Example 5 - Preparation of castor oil based pentamethylene diisocyanate trimer polyurethane elastomer

[0117] To a jar was added triheptanoin, castor oil, and pentamethylene diisocyanate trimer. This mixture was stirred at room temperature until a clear, homogeneous solution was obtained. Bismuth neodecanoate was added with stirring, and the reaction was heated to 60 °C for about 1 hour, at which point an off-white soft rubber is formed. After rubber formation the rubber was allowed to cool to room temperature.

[0118] The polyurethane elastomer rubber was then placed in a steel container and triheptanoin was added with high sheer mixing until the desired viscosity was achieved.

[0119] In a certain example, to a stainless steel reaction vessel was added triheptanoin (202.0 grams), castor oil (32.0 grams), pentamethylene diisocyanate trimer (15.9 grams), and bismuth neodecanoate (2.5 grams). This mixture was vigorously stirred at room temperature for about 20 minutes until a clear, homogeneous mixture was obtained. The reaction mixture was placed in an aluminum container and heated to 80 °C for 1 hour, at which point a translucent rubber was formed.

[0120] The polyurethane elastomer rubber was then broken into smaller pieces, placed in a metal container, and triheptanoin added before homogenization into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

[0121] In another example, to a 4 ounce glass jar was added triheptanoin (41.1 grams), castor oil (6.7 grams), pentamethylene diisocyanate trimer (3.31 grams), and bismuth neodecanoate (0.5 grams). This mixture was vigorously stirred at room temperature for about 10 minutes until a clear, homogeneous mixture was obtained. The reaction mixture was covered and heated to 80 °C for 19.5 hours, at which point a translucent rubber was formed. The hardness of the 50 gram

sample of gel was 1.72 N, as determined using a Stable Micro Systems Texture Analyzer with a 5 kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

Example 6 - Preparation of Castor Oil/Isophorone diisocyanate polyurethane elastomer

[0122] To a stainless steel reaction vessel was added diisooctyl succinate (440 grams), castor oil (71.1 grams) with hydroxyl value of 166.87 mg/g, isophorone diisocyanate (23.5 grams) with 37.80% isocyanate content, and bismuth neodecanoate (5.33 grams). This mixture was vigorously stirred at room temperature for about 20 minutes until a clear, homogeneous mixture was obtained and 50 grams of the mixture poured into a 4 ounce glass jar. The remainder of the reaction mixture and the 50 gram sample were heated to 75 °C for 18 hours, at which point a translucent gel formed. The hardness of the 50 gram sample of gel was 2.85 N, as determined using a Stable Micro Systems Texture Analyzer with a 5 kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

[0123] The polyurethane elastomer gel was then broken into smaller pieces, placed in a metal container, and heptyl undecylenate added before homogenization into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

[0124] In a certain example, to a glass reaction vessel was added triheptanoin (293.5 grams), castor oil (87.9 grams) with hydroxyl value of 166.87 mg/g, isophorone diisocyanate (29.0 grams) with 37.80% isocyanate content, and bismuth neodecanoate (8.9 grams). This mixture was vigorously stirred at room temperature for about 20 minutes until a clear, homogeneous mixture was obtained and 50 grams of the mixture poured into a 4 ounce glass jar. The remainder of the reaction mixture and the 50 gram sample were covered and heated to 75 °C for 19.5 hours, at which point a translucent rubber was formed. The hardness of the 50 gram sample of gel was 3.69 N, as determined using a Stable Micro Systems Texture Analyzer with a 5 kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

[0125] The polyurethane elastomer rubber was then broken into smaller pieces, placed in a metal container, and triheptanoin added before homogenization into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 7 - Preparation of dilinoleic acid/propane diol copolymer based hexamethylene diisocyanate trimer elastomer

[0126] To a plastic reaction vessel was added heptyl undecylenate (1959.2 g grams), dilinoleic acid/propane diol copolymer (410.0 grams) with hydroxyl value of 56 mg/g, hexamethylene diisocyanate trimer (70.0 grams) with 22.77% isocyanate content, and bismuth neodecanoate (10.0 grams). This mixture was vigorously stirred at room temperature for about 20 minutes until a clear, homogeneous mixture was obtained and 50 grams of the mixture poured into a 4 ounce glass jar. The remainder of the reaction mixture and the 50 gram sample were covered and left at 25 °C for 25 hours, at which point a translucent rubber was formed. The hardness of the 50 gram sample of gel was 3.14 N, as determined using a Stable Micro Systems Texture Analyzer with a 5 kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

[0127] The polyurethane elastomer rubber was then broken into smaller pieces, placed in a metal container, and heptyl undecylenate added before homogenization into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 8 - Preparation of dilinoleic acid/propane diol copolymer based pentamethylene diisocyanate trimer elastomer

[0128] To a stainless steel reaction vessel was added coco-caprylate/caprate (445.0 grams), dilinoleic acid/propane diol copolymer (87.5 grams), pentamethylene diisocyanate trimer (20.6 grams), and bismuth neodecanoate (3.2 grams). This mixture was vigorously stirred at room temperature for about 10 minutes until a clear, homogeneous mixture was obtained. The reaction mixture heated to 80 °C for 1 hour, at which point a translucent rubber was formed.

[0129] The polyurethane elastomer rubber was then broken into smaller pieces, placed in a metal container, and coco-caprylate/caprate added before homogenization into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

[0130] In a certain example, to a 4 ounce glass jar was added coco-caprylate/caprate (39.5 grams), dilinoleic acid/propane diol copolymer (7.8 grams) with hydroxyl value of 56 mg/g, pentamethylene diisocyanate trimer (1.8 grams) with 23.5% isocyanate content, and bismuth neodecanoate (0.3 grams). This mixture was vigorously stirred at room temperature for about 10 minutes until a clear, homogeneous mixture was obtained. The reaction mixture was covered and the heated to 80 °C for 19.5 hours, at which point a translucent rubber was formed. The hardness of the 50 gram sample of gel was 7.12 N, as determined using a Stable Micro Systems Texture Analyzer with a 5 kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

Example 9 - Preparation of a castor oil based hexamethylene diisocyanate trimer elastomer

[0131] To a plastic reaction vessel was added triheptanoin (2354.7 grams), castor oil (373.0 grams), hexamethylene diisocyanate trimer (188.6 grams) with 22.77% isocyanate content, and bismuth neodecanoate (27.0 grams). This mixture was vigorously stirred at room temperature for about 20 minutes until a clear, homogeneous mixture was obtained and 50 grams of the mixture poured into a 4 ounce glass jar. The remainder of the reaction mixture and the 50 gram sample were covered and left at room temperature for 20 hours, at which point a translucent rubber was formed. The hardness of the 50 gram sample of gel was 2.72 N, as determined using a Stable Micro Systems Texture Analyzer with a 5 kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

[0132] The polyurethane elastomer rubber was then broken into smaller pieces, placed in a metal container, and triheptanoin added before homogenization into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 10 - Preparation of dilinoleic acid/dilinoleic diol copolymer based hexamethylene diisocyanate trimer elastomer

[0133] To a glass reaction vessel was added coco-caprylate/caprate (826.3 g grams), dilinoleic acid/dilinoleic diol copolymer (172.8 grams) with hydroxyl value of 56 mg/g, hexamethylene diisocyanate trimer (29.5 grams) with 22.77% isocyanate content, and bismuth neodecanoate (4.23 grams). This mixture was vigorously stirred at room temperature for about 20 minutes until a clear, homogeneous mixture was obtained and 50 grams of the mixture poured into a 4 ounce glass jar. The remainder of the reaction mixture and the 50 gram sample were covered and heated to 75 °C for 17 hours, at which point a translucent rubber was formed. The hardness of the 50 gram sample of gel was 4.51 N, as determined using a Stable Micro Systems Texture Analyzer with a 5 kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

[0134] The polyurethane elastomer rubber was then broken into smaller pieces, placed in a metal container, and coco-caprylate/caprate added before homogenization into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 11 - Preparation of dilinoleic acid/dilinoleic diol copolymer based pentamethylene diisocyanate trimer elastomer

[0135] To a glass reaction vessel was added coco-caprylate/caprate (231.6 g grams), dilinoleic acid/dilinoleic diol copolymer (49.0 grams) with hydroxyl value of 56 mg/g, pentamethylene diisocyanate trimer (7.7 grams) with 23.5% isocyanate content, and bismuth neodecanoate (1.2 grams). This mixture was vigorously stirred at room temperature for about 20 minutes until a clear, homogeneous mixture was obtained and 50 grams of the mixture poured into a 4 ounce glass jar. The remainder of the reaction mixture and the 50 gram sample were covered and heated to 80 °C for 19.5 hours, at which point a translucent rubber was formed. The hardness of the 50 gram sample of gel was 0.49 N, as determined using a Stable Micro Systems Texture Analyzer with a 5 kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

[0136] The polyurethane elastomer rubber was then broken into smaller pieces, placed in a metal container, and coco-caprylate/caprate added before homogenization into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 12 - Formulation of Polyurethane Elastomers

[0137] To explore the ability to formulate the polyurethane elastomers described herein as topical formulations, the following experiments were performed.

[0138] Table 1 below provides exemplary polyurethane elastomers of the present specification ("biolastomers"), along with comparison elastomers. The compositions in Table 1 omit the isocyanate cross-linking agent for Biolastomers A and C, which is hexamethylene diisocyanate trimer. For Biolastomers D, IPDI is isophorone diisocyanate.

Table 1: Elastomers Examined

	Name	Composition
Disclosed Herein	Biolastomer A	Dilinoleic Acid/Propane Diol Copolymer Crosspolymer (and) Heptyl Undecylenate (and) C13-15 Alkane
	Biolastomer C	Dilinoleic Acid/Dilionoleic Diol Copolymer Crosspolymer (and) Coco-caprylate/Caprate
	Biolastomer D	Castor Oil/IPDI Copolymer (and) Diisooctyl Succinate (and) Heptyl Undecylenate
Comparison	Velvesil* DM	Dimethicone (and) Cetearyl Dimethicone Crosspolymer
	Dowsil 9040	Cyclopentasiloxane (and) Dimethicone Crosspolymer

[0139] The biolastomers described above were added to the following common topical carriers to determine their ability to be formulated as a topical formulation.

[0140] In FIG. 1, a scoring system of 5 to 1 was utilized, with a score of "5" indicating a hard gel, a score of "1" indicating a flowable gel. At the amounts studied, the Biolastomers described herein showed good compatibility with: Fatty alcohol > Triglyceride > Ester; Less compatibility with hydrocarbon; and NO compatibility with silicone.

[0141] The three Biolastomers were then combined with different sunscreen agents to examine their compatibility with an active agent, and their ability for use as a formulation agent. Tables 2-4 describe the results for the three Biolastomers as noted.

Table 2: Biolastomer A at 10% Solids

Ingredients	**UVA Sunscreen**	**UVB Sunscreen**		**Physical Sunscreens**	
	Avobenzone	**Octocrylene**	**Homosalate**	**ZnO**	**TiO2**
Sunscreen%	5	10	10	10	10
C12-15 alkyl benzoate%	15	10	10	10	10
Biolastomer A%	80	80	80	80	80
Observation	Light yellow Clear gel	Clear gel	Clear gel	Opaque gel	Opaque gel

Table 3: Biolastomer C at 9% Solids

Ingredients	**UVA Sunscreen**	**UVB Sunscreen**		**Physical Sunscreens**	
	Avobenzone	**Octocrylene**	**Homosalate**	**ZnO**	**TiO2**
Sunscreen%	5	10	10	10	10
C12-15 alkyl benzoate%	10	5	5	5	5
Biolastomer C%	85	85	85	85	85
Observation	Light yellow translucent gel	Translucent gel	Translucent gel	Opaque gel	Opaque spongy gel

Table 4: Biolastomer D at 10% Solids

Ingredients	UVA Sunscreen	UVB Sunscreen		Physical Sunscreens	
	Avobenzone	Octocrylene	Homosalate	ZnO	TiO2
Sunscreen%	5	10	10	10	10
C12-15 alkyl benzoate%	25	20	20	20	20
Biolastomer D%	70	70	70	70	70
Observation	Light yellow Clear gel	Clear gel	Clear gel	Opaque gel	Opaque gel

[0142] The results of these experiments indicate that the Biolastomers described herein are highly compatible with organic and physical sunscreens and do not negatively impact the clarity of final formulations.

[0143] The processability of the Biolastomers was then evaluated as follows in both oil-in-water emulsions, and water-in-oil emulsions.

Table 5: Processability of 5% Elastomer Gels in Water-in-Oil (W/O) Emulsions

Phase	Ingredient	INCI Name	q.s. (%)
A	Water	Aqua	Up to 100.0
	Glycerin	Glycerin	3.0
	Sodium Chloride	Sodium Chloride	1.0
B	**Y-20537**	**Caprylic/Capric Triglycerides (and) PEG/PPG-20/15 Dimethicone**	**4.0**
	Neossance Hemisqualane	C13-15 Alkane (emollient)	5.0
	Blooming Feel In2	Isononyl Isononanoate (emollient)	3.0
	Cetiol E	PPG-15 Stearyl Ether (emollient)	2.0
	Elastomer gel *		**5.0**
	Silsoft 034 fluid	**Caprylyl Methicone (emollient)**	**2.0**
C	Preservative	Preservative	q.s.

[0144] Each of the following elastomer gels* were investigated: Biolastomer A; Biolastomer C; Biolastomer D; Velvesil DM gel; and Dowsil 9040. All the elastomer gels were added into the formulations as premixes with Caprylyl Methicone to the oil phase (B). Premixes were homogenized before addition. Small particles of the elastomer were visible in the premixes, but were not in the products. Phase A was added very slowly to the phase B at high mixing (cold process, standard w/Si emulsion preparation). No major differences were observed during processability of any of elastomer gels in w/o emulsion, confirming that the biolastomers described herein can be readily processed in water-in-oil emulsions.

[0145] The processability of the elastomer gels in oil-in-water emulsions was investigated as follows:

Table 6: Processability of 2.5% Elastomer Gels in Oil-in-Water (O/W) Emulsions

Phase	Ingredients	Inci Name	W/W (%)
A	Water	Aqua	Up to 100.0
	Glycerin	Glycerin	3.0
	Disodium EDTA	Disodium EDTA	0.05
B	Arlacel 165	Glyceryl Stearate/PEG-100 Stearate	3.0
	Cutina GMS	Glyceryl Stearate	1.5
	Lanette O	Cetearyl Alcohol	1.5
	***Elastomer gel**		**2.5**
	Cetiol E	PPG-15 Stearyl Ether	4.0
	Blooming Feel In2	Isononyl Isononanoate	4.0
	Neossance Hemisqualane	C13-15 Alkane	4.0
C	Carbopol Ultrez 10	Carbomer	0.2
	Water	Aqua	10.0
	TEA	TEA	0.2
D	Preservative		q.s.

[0146] Each of the following elastomer gels* were investigated: Control – No elastomer; Biolastomer C; Biolastomer D; Biolastomer A; Velvesil DM 6; and DM 9040. Water (A) and oil (B) phases were heated separately up to 70 °C, then mixed and homogenized. At 50 °C the premix of Carbomer was added, mixed and neutralized. Premixing was required for biolastomers C and D, but no premix was required for Biolastomer, Velvesil DM 6, and DM 9040. Results of the experiments indicated that the ease of processability was, from greatest to least, Velvesil DM> DC 9040> Biolastomer A > Biolastomer C~ Biolastomer D.

[0147] The sensory (skin feel) characteristics of the elastomers were also evaluated. The results indicated the following: Control- "flat" sensory, no cushioning; Biolastomer C - provides smooth cushioning sensory, moisturized, and not dry. The skin is soft; Biolastomer D – a bit shiny and lubricious, after feel is smooth, elastic and cushioning; Biolastomer A – in between C and D; Velvesil DM- powdery and dry cushioning sensory, matting benefits; Dowsil 9040 – powdery but elastic cushioning, less dry than Velvesil DM, provides matting benefits.

[0148] The following are also evaluated for the elastomer formulations: Rheology: shear-thinning behavior of Biolastomers; Ease of production: Prepare a kilogram of Biolastomer in an emollient using Ross Mixer and in-line homogenizer and Evaluate shear sensitivity.

Example 13 - Fourier-Transform Infrared Spectroscopy of polyurethane elastomers

[0149] Fourier-Transform Infrared Spectroscopy (FTIR) was performed to analyze the molecular structures of the polyurethane elastomers.

[0150] The FTIR spectrograph of dilinoleic acid/propane diol copolymer based pentamethylene diisocyanate trimer elastomer is shown in FIG. 1.

[0151] The FTIR spectrograph of dilinoleic acid/propane diol copolymer based hexamethylene diisocyanate trimer elastomer is shown in FIG. 2.

[0152] The FTIR spectrograph of castor oil based pentamethylene diisocyanate trimer elastomer is shown in FIG. 3.

[0153] The FTIR spectrograph of castor oil based hexamethylene diisocyanate trimer elastomer is shown in FIG. 4.

[0154] The FTIR spectrograph of dilinoleic acid/dilinoleic diol copolymer based pentamethylene diisocyanate trimer elastomer is shown in FIG. 5.

[0155] The FTIR spectrograph of dilinoleic acid/dilinoleic diol copolymer based hexamethylene diisocyanate trimer elastomer is shown in FIG. 6.

[0156] The FTIR spectrograph of castor oil based isophorone diisocyanate trimer elastomer is shown in FIG. 7.

CLAIMS

1. A gel composition comprising a polyurethane elastomer gel prepared from the reaction of:

(A) a polyisocyanate or a mixture of polyisocyanates comprising two or more isocyanate functional groups;

(B) a polyol or mixture of polyols comprising two or more hydroxyl, amine, thiol, or carboxylic acid functional groups;

(C) an optional polyurethane reaction catalyst; and

(D) an optional topically acceptable carrier fluid.

2. The gel composition of claim 1, wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, oils, and combinations thereof.

3. The gel composition of claim 1, wherein the topically acceptable carrier fluid is selected from the group consisting of diisooctyl succinate, heptyl undecylenate, neopentyl glycol diheptanoate, coco-caprylate/caprate, triheptanoin, caprylic/capric triglyceride, dodecane, tridecane, C13-15 alkane, squalene, squalene, isoamyl laurate, isopentyl laurate, caprylic/capric/myristic/stearic triglyceride, caprylic/capric/succinic triglyceride, isopropyl myristate, jojoba esters, tricaprylin, and palm oil.

4. The gel composition of claim 1, further comprising a pharmaceutically active ingredient dissolved in the topically acceptable carrier fluid.

5. The gel composition of claim 1 wherein the polyisocyanate or mixture of polyisocyanates is a low molecular weight polyisocyanate or mixture of polyisocyanates and wherein the polyol or mixture of polyols contains two or more hydroxyl, amine, thiol, or carboxylic acid groups.

6. A gel composition comprising a polyurethane elastomer from the reaction of:

(A) castor oil;

(B) isophorone diisocyanate, wherein the molar ratio of isocyanate groups to hydroxyl groups is between 1:1 and 1:2;

(C) an optional polyurethane reaction catalyst; and

(D) an optional topically acceptable carrier fluid at a concentration of 60% (w/w) to 99.9% (w/w) of the gel composition;

wherein a personal care or healthcare active ingredient is optionally incorporated into the polyurethane elastomer gel by dissolving the personal care or healthcare active ingredient in the topically acceptable solvent during the formation of the polyurethane elastomer gel, or by admixing the personal care or healthcare active ingredient with a formed polyurethane elastomer gel.

7. The gel composition of claim 6, wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof.

8. The gel composition of claim 6, wherein the topically acceptable carrier fluid is selected from the group consisting of diisooctyl succinate, heptyl undecylenate, neopentyl glycol diheptanoate, and coco-caprylate/caprate.

9. The gel composition of claim 6, further comprising a pharmaceutically active ingredient dissolved in the topically acceptable carrier fluid.

10. The gel composition of claim 1, wherein the polyurethane catalyst is a bismuth group containing catalyst.

11. The gel composition of claim 6, wherein the polyurethane catalyst is a bismuth group containing catalyst.

12. The gel composition of claim 1, wherein greater than 50% of the carbon content of the topically acceptable solvent is derived from plant sources.

13. The gel composition of claim 6, wherein greater than 50% of the carbon content of the topically acceptable solvent is derived from plant sources.

14. A process for preparing the gel composition of claim 1, comprising reacting:

(A) a polyol;

(B) isophorone diisocyanate; and

(C) an optional polyurethane reaction catalyst;

optionally in the presence of

(D) a topically acceptable carrier fluid.

15. A process for preparing the gel composition of claim 6, comprising reacting:

(A) castor oil;

(B) isophorone diisocyanate; and

(C) an optional polyurethane reaction catalyst;

optionally in the presence of

(D) a topically acceptable carrier fluid.

16. A gel composition prepared according to the process of claim 14.

17. A gel composition prepared according to the process of claim 15.

18. A process for preparing a gel paste composition, comprising:

I) shearing the gel composition of claim 1, and

II) combining the sheared polyurethane elastomer gel with an additional quantity of the carrier fluid to form a gel paste composition.

19. A process for preparing a gel paste composition comprising:

I) shearing the gel composition of claim 1, and

II) combining the sheared polyurethane elastomer gel with an active ingredient.

20. A process for preparing a gel paste composition, comprising:

I) shearing the gel composition of claim 6, and

II) combining the sheared polyurethane elastomer gel with an additional quantity of the carrier fluid to form a gel paste composition.

21. A process for preparing a gel paste composition comprising:

I) shearing the gel composition of claim 6, and

II) combining the sheared polyurethane elastomer gel with an active ingredient.

22. A method of making a polyurethane elastomer comprising:

I) mixing a polyisocyanate reactant and a polyol reactant, optionally in a topically acceptable carrier fluid to form a reaction mixture with a reactant concentration of about 80% (w/w), wherein the polycisocyanate reactant comprises two or more isocyanate functional groups and the polyol reactant comprises two or hydroxyl groups;

II) optionally adding a polyurethane reaction catalyst; and

III) optionally heating the reaction mixture to about 80 °C to form the polyurethane elastomer.

23. The method of claim 22, wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combination thereof.

24. The method of claim 22, wherein the topically acceptable carrier fluid is selected from the group consisting of diisooctyl succinate, heptyl undecylenate, neopentyl glycol diheptanoate, coco-caprylate/caprate, and combination thereof.

25. The method of claim 22, further comprising dissolving a pharmaceutically active ingredient in the topically acceptable carrier fluid.

26. The method of claim 22, wherein the polyisocyanate reactant is derived from the polymerization of another polyisocyanate.

27. The method of claim 22, further comprising preparing the polyisocyanate reactant from hexamethylene diisocyanate.

28. The method of claim 22, further comprising preparing the polyisocyanate reactant from pentamethylene diisocyanate.

29. A polyurethane elastomer gel paste prepared by the method of claim 18.

30. A polyurethane elastomer gel paste prepared by the method of claim 19.

31. A polyurethane elastomer gel paste prepared by the method of claim 20.

32. A polyurethane elastomer gel paste prepared by the method of claim 21.

33. A topical formulation comprising:

the gel composition of claim 1 or claim 6; and a pharmaceutically active ingredient, wherein the pharmaceutically active ingredient is a personal care active ingredient or a healthcare active ingredient.

34. A topical formulation comprising:

the polyurethane elastomer gel paste of any of claims 29 to 32; and a pharmaceutically active ingredient, wherein the pharmaceutically active ingredient is a personal care active ingredient or a healthcare active ingredient.

35. A foot conforming shoe insert or shoe sole comprising the gel composition of claim 1 or claim 6.

36. A medical medically acceptable gel comprising the gel composition of claim 1 or claim 6.

37. A topical formulation comprising the gel composition of claim 1 or claim 6.

Biolastomer Compatibility with Common Carriers

	Biolastomer A (12.5%)		Biolastomer C (11%)		Biolastomer D (14%)		Velvesil DM (17.5%)		DOWSIL 9040 (12%)	
Wt% emollients	**20%**	**30%**	**20%**	**30%**	**20%**	**30%**	**10%**	**20%**	**20%**	**30%**
Triglycerides	Clarity Gel strength	Clarity Gel strength	Clarity Gel strength	Clarity Gel strength	Clarity Gel strength	Clarity Gel strength	Clarity Gel strength	Clarity Gel strength	Clarity Gel strength	Clarity Gel strength
Caprylic/capric triglyceride	Translucent 5	Hazy 1	Hazy 3	Hazy 1	Hazy 3	Hazy 3	Not Compatible	Not Compatible	Clear 1	Compatible
Esters										
Isopropyl palmitate	Hazy 3	Hazy 1	Hazy 2	Hazy 2	Hazy 1	Not Compatible	Not Compatible	Not Compatible	Clear 3	Not Compatible
Fatty alcohol										
Octyl dodecanol	Translucent 5	Hazy 1	Translucent 5	Hazy 1	Translucent 5	Translucent 5	Not Compatible	Not Compatible	Not Compatible	Not Compatible
Hydrophilics										
EtOH	Translucent 5	Hazy 2	Translucent 5	Hazy 3	Translucent 5	Translucent 5	TBD	Not Compatible	TBD	TBD
Hydrocarbons										
Hemisqualane	Hazy 1	Hazy 1	Hazy 1	Not Compatible	Not Compatible	Not Compatible	Not Compatible	Not Compatible	Clear 3	Not Compatible
Silicones										
Dimethicone 350 cst	Not Compatible	Not Compatible	Not Compatible	Not Compatible	Not Compatible	Not Compatible	Not Compatible	Not Compatible	Clear 1	Compatible

FIG. 1

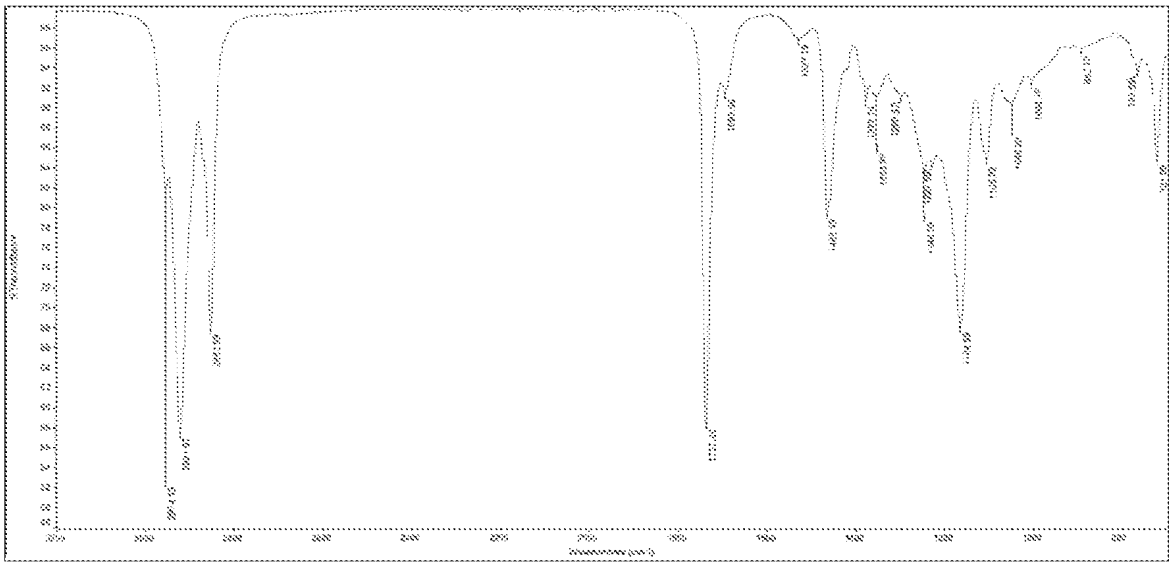


FIG. 2

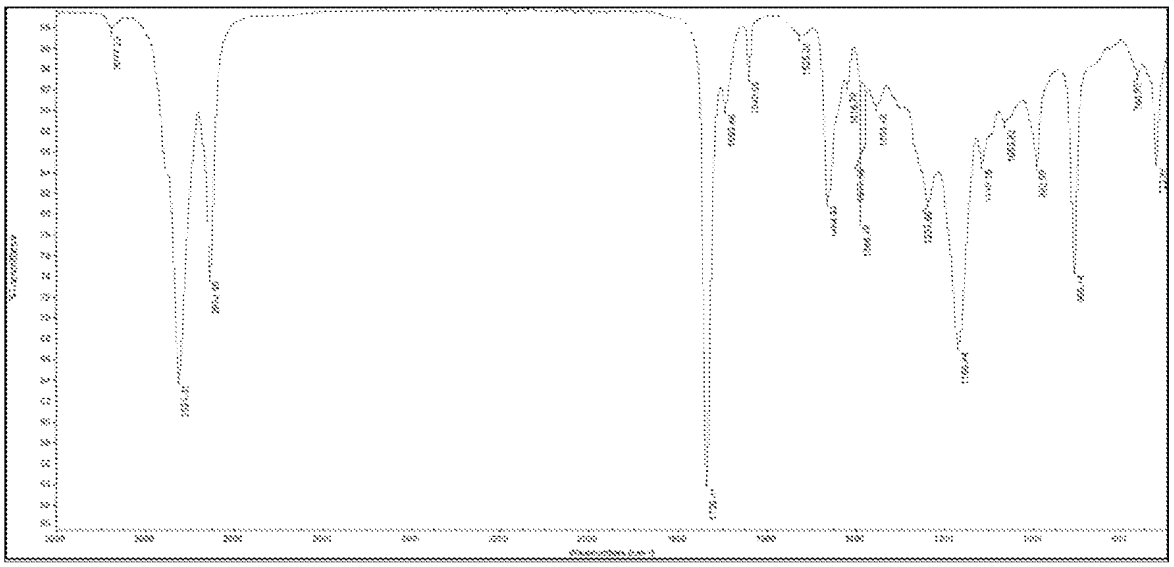


FIG. 3

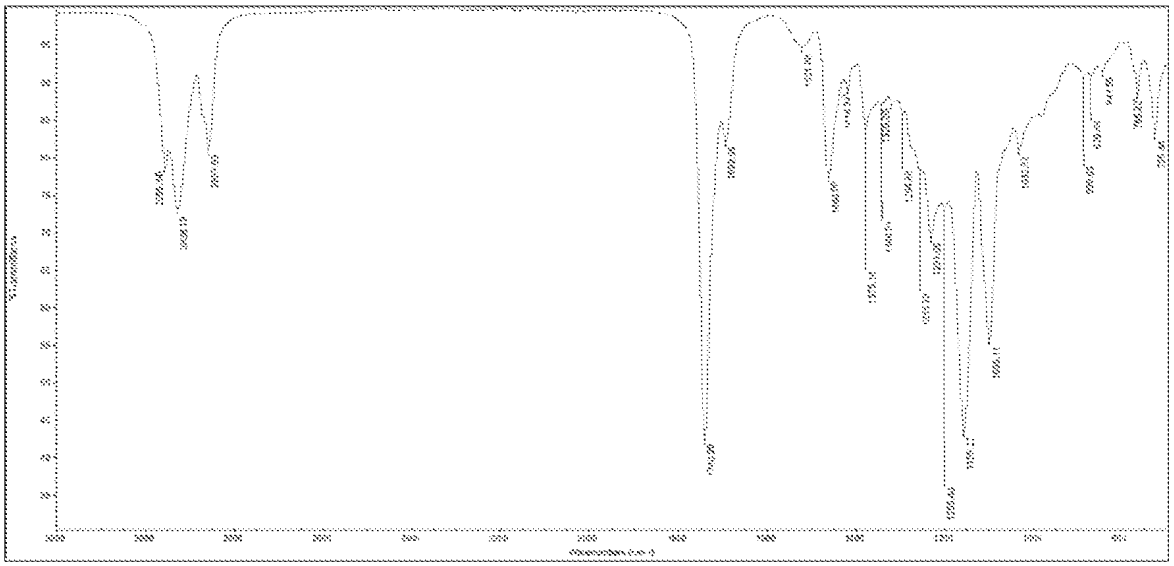


FIG. 4

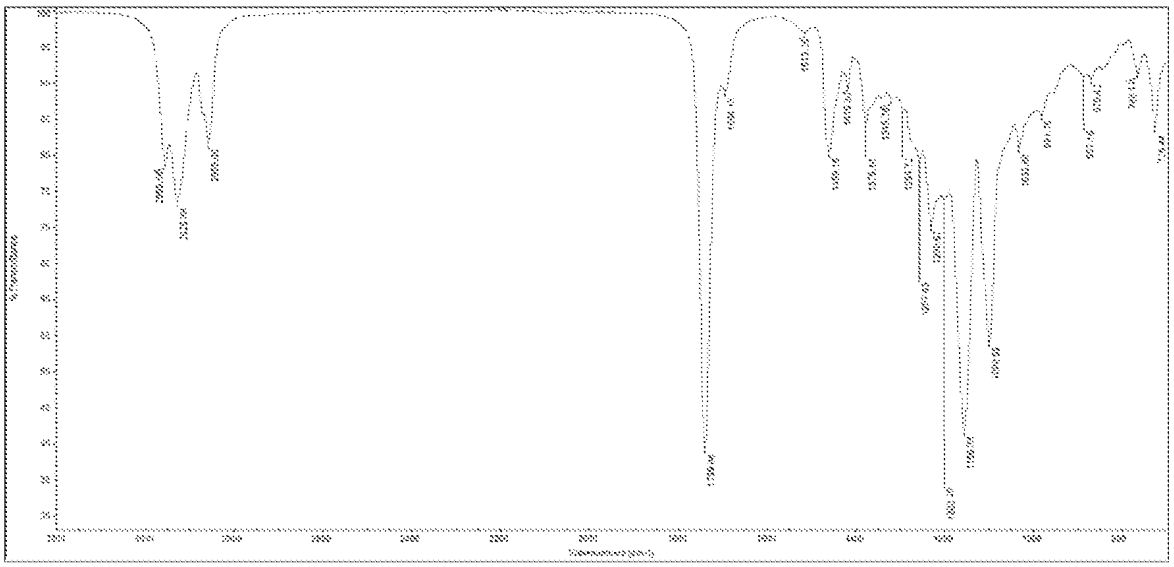


FIG. 5

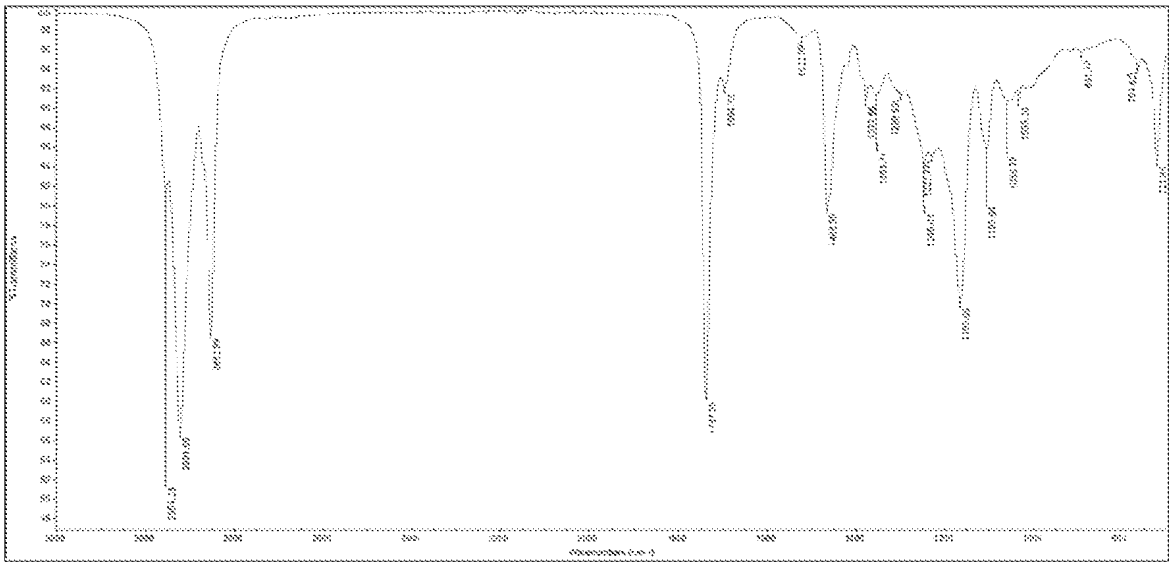


FIG. 6

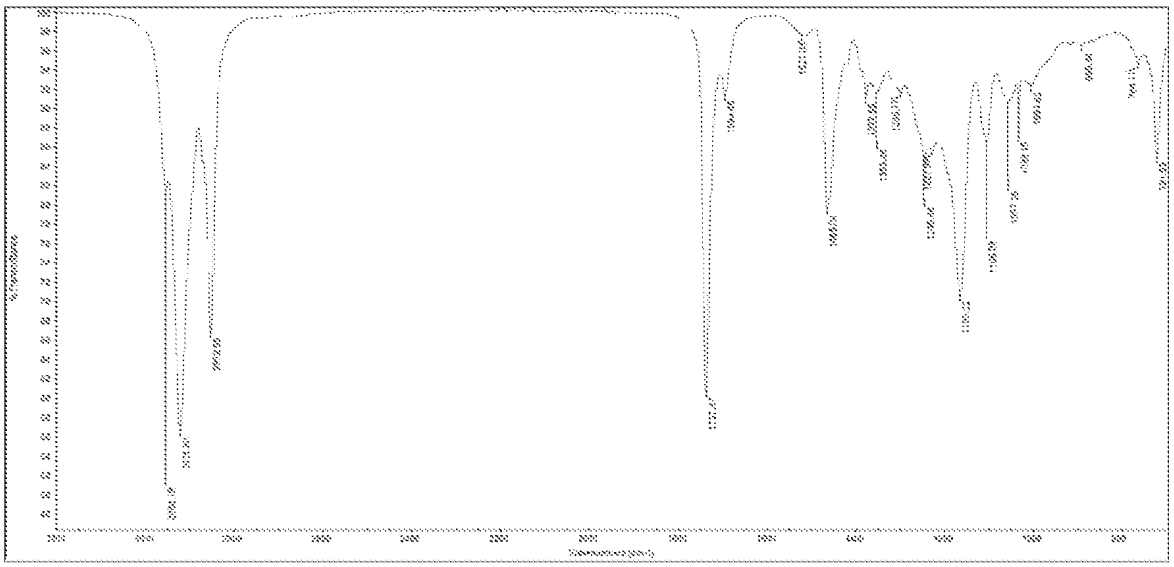


FIG. 7

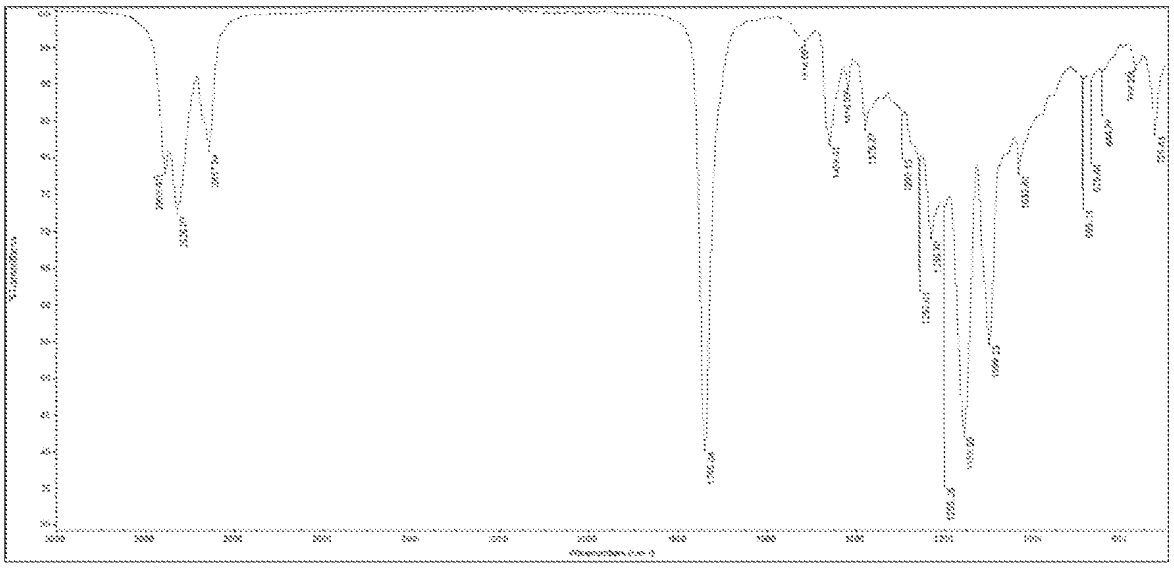


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 20/41540

A. CLASSIFICATION OF SUBJECT MATTER

IPC - A61K 8/87; A61Q 19/00; C08G 18/72 (2020.01)

CPC - A61K 8/87; A61Q 19/00; C08G 18/72; C08G 18/32; C08G 2220/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,661,099 A (von Bittera et al.) 28 April 1987 (28.04.1987); entire document, but especially: col 1 lines 7-16, col 6 lines 42-44, col 7 lines 39-41, col 7 lines 44-45, col 7 line 57, example 1, example 5	1, 5, 22, 27, 33/(1), 36/(1), 37/(1)
X	US 2018/0208720 A1 (Mitsui Chemicals, Inc.) 26 July 2018 (26.07.2018); para [0013], entire document, but especially: para [0013], para [0014], para [0084], para [0111], para [0112], para [0114], para [0129], para [0204], para [0255]- para [0259], para [0353], table 1, production example 3, example 6	1, 6, 10-11, 22, 26, 28, 35
X --- Y	EP 1 142 959 A1 (Dai-Ichi Kogyo Seiyaku Co., Ltd.) 10 October 2001 (10.10.2001); entire document, but especially: para [0002], para [0013], para [0017], para [0023], para [0024], para [0026], table 1	1, 5-6, 14-17, 22, 33/(6), 37/(6) --- 2-4, 7-9, 12-13, 18-21, 23-25, 29-32, 34
Y	JP 3631542 B2 (Dai-Ichi Kogyo Seiyaku Co., Ltd.) 24 December 2004 (24.12.2004); entire document, but especially: para [0001], para [0006], para [0014]	2-4, 7-9, 12-13, 23-25

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 September 2020	16 OCT 2020
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Lee Young Telephone No. PCT Helpdesk: 571-272-4300

Form PCT/ISA/210 (second sheet) (July 2019)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 20/41540

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2011/0014139 A1 (Viala et al.) 20 January 2011 (20.01.2011); entire document, but especially: para [0001], para [0031]- para [0035], para [0048], para [0113], para [0133], para [0140], para [0227]	18-21, 29-32, 34
Y	US 2012/0046358 A1 (Cheng et al.) 23 February 2012 (23.02.2012); para [0020], para [0021], para [0024], para [0034]	8, 24
A	Jones, Charla. "What Is Coco-Caprylate Doing In My Natural Skin Care Products?" Eu2Be (08 May 2015): pages 1-2 <https://eu2be.com/blogs/discover/19389252-what-is-coco-caprylate-doing-in-my-natural-skin-care-products>; page 2	8, 24
A	US 2009/0232752 A1 (Carson et al.) 17 September 2009 (17.09.2009); entire document	1-37
A	US 2019/0169390 A1 (Peterson Chemical Technology LLC) 06 June 2019 (06.07.2019); entire document	1-37
A	JP 2018-90662 A2 (Mitsui Chemicals, Inc.) 14 June 2018 (14.06.2018); entire document	1-37

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING
TRANSMITTAL OF COPY OF INTERNATIONAL
PRELIMINARY REPORT ON PATENTABILITY
(CHAPTER I OF THE PATENT COOPERATION TREATY)

(PCT Rule 44bis.1(c))

To:

MERCANTI, Michael N.
Lucas & Mercanti, LLP
30 Broad Street, 21 Floor
New York, New York 10004
ÉTATS-UNIS D'AMÉRIQUE

Date of mailing *(day/month/year)*	
10 March 2022 (10.03.2022)	
Applicant's or agent's file reference	**IMPORTANT NOTICE**
GRAN-1012-W	

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2020/046170	13 August 2020 (13.08.2020)	30 August 2019 (30.08.2019)

Applicant

GRANT INDUSTRIES, INC.

The International Bureau transmits herewith a copy of the international preliminary report on patentability (Chapter I of the Patent Cooperation Treaty)

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Simin Baharlou e-mail pct.team9@wipo.int Telephone No. +41 22 338 74 09

Form PCT/IB/326 (revised January 2020)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY
(Chapter I of the Patent Cooperation Treaty)

(PCT Rule 44*bis*)

Applicant's or agent's file reference GRAN-1012-W	**FOR FURTHER ACTION**	See item 4 below
International application No. PCT/US2020/046170	International filing date *(day/month/year)* 13 August 2020 (13.08.2020)	Priority date *(day/month/year)* 30 August 2019 (30.08.2019)
International Patent Classification (8th edition unless older edition indicated) See relevant information in Form PCT/ISA/237		
Applicant GRANT INDUSTRIES, INC.		

1. This international preliminary report on patentability (Chapter I) is issued by the International Bureau on behalf of the International Searching Authority under Rule 44 *bis*.1(a).

2. This REPORT consists of a total of 8 sheets, including this cover sheet.

   In the attached sheets, any reference to the written opinion of the International Searching Authority should be read as a reference to the international preliminary report on patentability (Chapter I) instead.

3. This report contains indications relating to the following items:

☒	Box No. I	Basis of the report
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

4. The International Bureau will communicate this report to designated Offices in accordance with Rules 44*bis*.3(c) and 93*bis*.1 but not, except where the applicant makes an express request under Article 23(2), before the expiration of 30 months from the priority date (Rule 44*bis* .2).

	Date of issuance of this report 01 March 2022 (01.03.2022)
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Simin Baharlou e-mail pct.team9@wipo.int

Form PCT/IB/373 (revised January 2020)

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To: MICHAEL N. MERCANTI
LUCAS & MERCANTI, LLP
30 BROAD STREET, 21 FLOOR
NEW YORK, NY 10004

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing *(day/month/year)*	18 NOV 2020
Applicant's or agent's file reference GRAN-1012-W	FOR FURTHER ACTION See paragraph 2 below

International application No.	International filing date *(day month year)*	Priority date *(day/month/year)*
PCT/US 20/46170	13 August 2020 (13.08.2020)	30 August 2019 (30.08.2019)

International Patent Classification (IPC) or both national classification and IPC

IPC - A61K 8/02; A61K 8/06; A61K 8/19 (2020.01)

CPC - A61K 8/0241; A61K 8/062; A61K 8/19

Applicant GRANT INDUSTRIES, INC.

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA/US	Date of completion of this opinion	Authorized officer
Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	25 October 2020	Lee Young PCT Help Desk Telephone No. 571-272-4300

Form PCT/ISA/237 (cover sheet) (revised January 2019)

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/46170

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of:

☒ the international application in the language in which it was filed.

☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

2. ☐ This opinion has been established taking into account the **rectification** of **an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(b)).

3. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing:

a. ☐ forming part of the international application as filed:

☐ in the form of an Annex C/ST.25 text file.

☐ on paper or in the form of an image file.

b. ☐ furnished together with the international application under PCT Rule 13*ter*.1(a) for the purposes of international search only in the form of an Annex C/ST.25 text file.

c. ☐ furnished subsequent to the international filing date for the purposes of international search only:

☐ in the form of an Annex C/ST.25 text file (Rule 13*ter*.1(a)).

☐ on paper or in the form of an image file (Rule 13*ter*.1(b) and Administrative Instructions, Section 713).

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that forming part of the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/46170

Box No. V **Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Claims	2, 5-6, 8-9, 11, 13-15, and 19-34	YES
	Claims	1, 3-4, 7, 10, 12, and 16-18	NO
Inventive step (IS)	Claims	none	YES
	Claims	1-34	NO
Industrial applicability (IA)	Claims	1-34	YES
	Claims	none	NO

2. Citations and explanations:

Claims 1,3-4, 7, 10, 12, 16-18 lack novelty under PCT Article 33(2) as being anticipated by US 2015/0128335 A1 to Dehni (hereinafter Dehni).

Regarding claim 1, Dehni discloses a cross-linked polyurethane elastomer rubber composition (Para [0042] In the hard foam, the hydrophilic silicone elastomer is cross-linked with another polymeric silicone and with polyurethane polymer. In the case of a Si-OH group reaction with an electrophilic group on a polyurethane compound...will result in a cross-linked elastomer-polyurethane composition), comprising a cross-linked polyurethane elastomer rubber (Para [0032] Flexible polyurethane foam is manufactured as a product of a reaction of two raw materials, a polyol and a diisocyanate. The general reaction is shown below. Each R1 group has multiple isocyanate groups; thus, there is a high degree of cross-linking in the polyurethane); a cosmetic emollient (Para [0087] In one embodiment, the polyurethane foam can include an emollient or humectant. Example emollients or humectants, include, but are not limited to include: hyaluronic acid); and a urethanation catalyst (Para [0033]-[0034] However, suitable catalysts that can be used include: a-tertiary amines such as N-methylimidazole; See instant specification Pg. 15 In 10-27 Preferred urethanation catalysts with reduced toxicity include...tertiary amines) wherein the cosmetic emollient forms a solvent matrix substantially surrounds the cross-linked polyurethane elastomer rubber (Para [0087] hyaluronic acid may be used to improve the tactile response and feel on surfaces of a final product. As a general guideline humectants can comprise from about 0.05% to about 4% by volume of the polyurethane).

Regarding claim 3, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the cross-linked polyurethane rubber is formed with a pre-polymer having at least two free hydroxyl groups (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol both of which contain an average two or more functional groups per molecule. By reacting two or more isocy anate groups per molecule (R(N=C=O)n) with a polyol containing on average two or more hydroxyl groups).

Regarding claim 4, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the solvent matrix comprises one or more cosmetic emollient (Para [0087] In one embodiment, the polyurethane foam can include an emollient or humectant. Example emollients or humectants, include, but are not limited to include: hyaluronic acid).

Regarding claim 7, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 3, wherein the prepolymer (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol) is a polyester reaction product of a diol and a dimer acid (Para [0004] Polyols can be polyether polyols or polyester polyols).

Regarding claim 10, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the urethanation catalyst is a bismuth, zinc, or amine catalyst (Para [0033]-[0034] However, suitable catalysts that can be used include: a-tertiary amines such as N-methylimidazole).

Regarding claim 12, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 6, wherein the overall molar ratio between the NCO in the polyisocyanate and the OH groups in the prepolymer is from 2:1 to 1:2 (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol both of which contain an average two or more functional groups per molecule).

Regarding claim 16, Dehni discloses a process (Para [0030] Any steps recited in any method or process claims may be executed in any order) for preparing a cross-linked polyurethane elastomer rubber composition (Para [0042] In the hard foam, the hydrophilic silicone elastomer is cross-linked with another polymeric silicone and with polyurethane polymer. In the case of a Si-OH group reaction with an electrophilic group on a polyurethane compound...will result in a cross-linked elastomer-polyurethane composition), comprising: reacting a polyisocyanate with a prepolymer having at least two free hydroxyl groups (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol both of which contain an average two or more functional groups per molecule. By reacting two or more isocyanate groups per molecule (R(N=C=O)n) with a polyol containing on average two or more hydroxyl groups) in the presence of a urethanation catalyst (Para [0033]-[0034] However, suitable catalysts that can be used include: a-tertiary amines such as N-methylimidazole; See instant specification Pg. 15 In 10-27 Preferred urethanation catalysts with reduced toxicity include...tertiary amines) and a cosmetic emollient (Para [0087] In one embodiment, the polyurethane foam can include an emollient or humectant. Example emollients or humectants, include, but are not limited to include: hyaluronic acid) under conditions sufficient to form a cross-linked polyurethane rubber (Para [0032] Flexible polyurethane foam is manufactured as a product of a reaction of two raw materials, a polyol and a diisocyanate. The general reaction is shown below. Each R1 group has multiple isocyanate groups; thus, there is a high degree of cross-linking in the polyurethane).

********CONTINUED ON SUPPLEMENTAL PAGE********

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/46170

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:
Box V(2): Citations and Explanations

Regarding claim 17, Dehni discloses the process of claim 16, wherein said conditions include reacting the prepolymer having at least two free hydroxyl groups (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol both of which contain an average two or more functional groups per molecule. By reacting two or more isocyanate groups per molecule (R((N=C=O)n) with a polyol containing on average two or more hydroxyl groups) the urethanation catalyst (Para [0033]-[0034] However, suitable catalysts that can be used include: a-tertiary amines such as N-methylimidazole; See instant specification Pg. 15 ln 10-27 Preferred urethanation catalysts with reduced toxicity include...tertiary amines) and cosmetic emollient (Para [0087] In one embodiment, the polyurethane foam can include an emollient or humectant. Example emollients or humectants, include, but are not limited to include: hyaluronic acid) at a temperature of from about 20 to about 100 degrees Celsius (Para [0031] unique composition of polyurethane formed from an isocyanate and a polyol...The initiator, and accelerator along with the optional gelling agent, surfactant, and reinforcement filler are added at room temperature).

Regarding claim 18, Dehni discloses the process of claim 16, wherein the urethanation catalyst is a bismuth, zinc, or amine catalyst (Para [0033]-[0034] However, suitable catalysts that can be used include: a-tertiary amines such as N-methylimidazole).

Claims 2, 5-6, 8-9 lack an inventive step under PCT Article 33(3) as being obvious over Dehni.

Regarding claim 2, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the polyurethane elastomer rubber composition has a hardness value from 15 to about 40A (Para [0038] This foam can have a shore hardness value from 15 to about 40A, and most often about 30) and high resilience (Para [0068] Reinforcement fillers are capable of cross-linking and contribute to the increased resilience, toughness, and comprehensive strength of the material) but does not disclose wherein the polyurethane elastomer rubber composition has a hardness force greater than 200 g as measured by a texture analyzer prior to any milling or dilution and that it has a resilience greater than or equal to 70%. However, it would have been obvious to one of ordinary skill in the art to change the hardness and resilience of the elastomer through routine experimentation (Para [0110] in conjunction with polyurethane, polysulfide polymers, natural and synthetic rubber and silk fibroin can be used to affect cell size, hardness, resiliency and toughness).

Regarding claim 5, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the polyurethane elastomer rubber is formed with from a prepolymer having at least two free hydroxyl group (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol both of which contain an average two or more functional groups per molecule. By reacting two or more isocyanate groups per molecule (R((N=C=O)n) with a polyol containing on average two or more hydroxyl groups) but does not disclose wherein the prepolymer comprises from about 5 to about 25 weight percent. However, it would have been obvious to one of ordinary skill in the art to change the amount of prepolymer in the polyurethane through routine experimentation.

Regarding claim 6, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the polyurethane elastomer rubber is formed with from an isocyanate functionalized molecule and a prepolymer having OH-groups (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol both of which contain an average two or more functional groups per molecule. By reacting two or more isocyanate groups per molecule (R((N=C=O)n) with a polyol containing on average two or more hydroxyl groups) but does not disclose wherein polyurethane elastomer rubber is formed with from about 1 to about 20 weight percent of an isocyanate functionalized molecule and a prepolymer having OH-groups. However, it would have been obvious to change the weight percentages of isocyanate and prepolymer in the composition through routine experimentation.

Regarding claim 8, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the polyurethane elastomer rubber is formed with a polyisocyanate (Para [0036] In one embodiment of the present disclosure, a methylene bisphenyl isocyanate (MDI) solution and a mixture of polyether polyol can be mixed...to form polyurethane) containing NCO (Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol both of which contain an average two or more functional groups per molecule. By reacting two or more isocyanate groups per molecule (R((N=C=O)n)) but does not disclose wherein the polyisocyanate contains from about 15 to about 38 weight% NCO. However, it would have been obvious to one of ordinary skill in the art to change the weight percent of NCO through routine experimentation.

Regarding claim 9, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, wherein the amount of urethanation catalyst (Para [0033]-[0034] suitable catalysts that can be used include: a-tertiary amines such as N-methylimidazole; See Instant Specification Pg. 15 ln 10-27 urethanation catalysts with reduced toxicity include...tertiary amines) is about 10% by volume (Para [0039] the catalyst can compose about 10% by volume) but does not disclose wherein the catalyst is from about 0.1 to about 2.5 weight%. However, it would have been obvious to one of skill in the art to change the amount of the catalyst through routine experimentation.

Claim 11 lacks an inventive step under PCT Article 33(3) as being obvious over Dehni in view of US 2003/0092932 A1 to Tong et al. (hereinafter Tong)

Regarding claim 11, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, but does not disclose the composition further comprising an amount of a finisher containing an alcohol or an amine sufficient to quench unreacted isocyanate groups. However, Tong discloses a polyurethane (Para [0011] invention provides a method of reducing the amount of unreacted polyisocyanate from a polyurethane prepolymer) further comprising an amount of a finisher containing an alcohol or an amine (Para [0012] the process comprising reacting the composition with a quenching agent, the quenching agent comprising an arylalkyl alcohol and an alkoxysilane) sufficient to quench unreacted isocyanate groups (Para [0001] invention relates to a process for reducing residual monomeric polyisocyanate in a composition comprising a polymer or oligomer bearing isocyanate groups). It would have been obvious to one of ordinary skill in the art to combine these references to include a finisher in order to reduce isocyanate groups (Tong Para [0025] Reaction of the mixture of the arylalkyl alcohol and alkoxysilane with residual monomeric polyisocyanate eliminates at least one of the isocyanate groups of the residual monomeric polyisocyanate).

*********CONTINUED ON SUPPLEMENTAL PAGE*********

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/46170

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:
Box V(2): Citations and Explanations

Claims 13-14 and 19-20 lack an inventive step under PCT Article 33(3) as being obvious over Dehni in view of US 2018/0371149 A1 to Massachusetts Institute of Technology (hereinafter Massachusetts)

Regarding claim 13, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1, but does not disclose wherein the cross-linked polyurethane elastomer rubber is formed with a bio-based and biodegradable prepolymer. However, Massachusetts discloses a cross-linked polyurethane elastomer rubber (title; Para [0004] present disclosure provides elastomeric materials In particular, the present invention provides compositions comprising a polyester material together with and/or crosslinked by a polyisocyanate crosslinker. The present invention therefore provides elastomeric materials that include at least one urethane crosslink) is formed with a bio-based and biodegradable prepolymer (Para [0035] A pre-polymer, in some embodiments, is biodegradable and/or biocompatible). It would have been obvious to one of ordinary skill in the art to combine these references to use a bio-based and biodegradable prepolymer and so the polyurethane can be broken down (Para [0019] biodegradable materials are enzymatically broken down. Alternatively or additionally, in some embodiments, biodegradable materials are broken down by hydrolysis).

Regarding claim 14, Dehni in view of Massachusetts discloses the cross-linked polyurethane elastomer rubber composition of claim 13. Dehni discloses wherein the cosmetic emollient are bio-based and biodegradable (Para [0087] Example emollients or humectants, include, ...glycerin; See Instant Specification Pg. 12 In 17-41 Appropriate emollients or solvents include but are not limited to...glycerin) but does not disclose wherein the prepolymer and the polyisocyanate are bio-based and biodegradable and wherein the cross-linked polyurethane elastomer rubber composition is comprised of greater than about 85%, preferably greater than about 95% or, greater than about 99% renewable, bio-based feedstocks. However, Massachusetts discloses a cross-linked polyurethane elastomer rubber (Para [0004] disclosure provides elastomeric materials In particular, the present invention provides compositions comprising a polyester material together with and/or crosslinked by a polyisocyanate crosslinker. The present invention therefore provides elastomeric materials that include at least one urethane crosslink) wherein the prepolymer is bio-based and biodegradable (Para [0035] A pre-polymer, in some embodiments, is biodegradable and/or biocompatible) and the polyisocyanate is bio-based and biodegradable (Para [0077] In some embodiments, polyisocyanates for use in the present invention include...4,4'-dicyclohexylmethane diisocyanate; See Instant Specification Pg. 13 Para 3 to Pg. 14 Para 1 Appropriate functionalized isocyanates include but are not limited to....4,4'-dicyclohexylmethane diisocyanate) but does not disclose wherein the cross-linked polyurethane elastomer rubber composition is comprised of greater than about 85%, preferably greater than about 95% or, greater than about 99% renewable, bio-based feedstocks. However, it would have been obvious to one of skill in the art to change the weight percentage of renewable, bio-based feedstock through routine experimentation. It would have also been obvious to one of ordinary skill in the art to combine these references to use a bio-based and biodegradable prepolymer and polyisocyante so the polyurethane can be broken down (Massachusetts Para [0019] biodegradable materials are enzymatically broken down. Alternatively or additionally, in some embodiments, biodegradable materials are broken down by hydrolysis).

Regarding claim 19, Dehni discloses the process of claim 16 wherein the cosmetic is bio-based and biodegradable (Para [0087] Example emollients or humectants, include, but are not limited to include...glycerin; See Instant Specification Pg. 12 In 17-41 Appropriate emollients or solvents include but are not limited to...glycerin) but does not disclose wherein the prepolymer and the polyisocyanate are bio-based and biodegradable. However, Massachusetts discloses a cross-linked polyurethane elastomer rubber (title; Para [0004] present disclosure provides elastomeric materials In particular, the present invention provides compositions comprising a polyester material together with and/or crosslinked by a polyisocyanate crosslinker. The present invention therefore provides elastomeric materials that include at least one urethane crosslink) wherein the prepolymer is bio-based and biodegradable (Para [0035] A pre-polymer, in some embodiments, is biodegradable and/or biocompatible) and the polyisocyanate is bio-based and biodegradable (Para [0077] In some embodiments, polyisocyanates for use in the present invention include...4,4'-dicyclohexylmethane diisocyanate; See Instant Specification Pg. 13 Para 3 to Pg. 14 Para 1 Appropriate functionalized isocyanates include but are not limited to....4,4'-dicyclohexylmethane diisocyanate). It would have also been obvious to one of ordinary skill in the art to combine these references to use a bio-based and biodegradable prepolymer and polyisocyante so the polyurethane can be broken down (Massachusetts Para [0019] biodegradable materials are enzymatically broken down. Alternatively or additionally, in some embodiments, biodegradable materials are broken down by hydrolysis).

Regarding claim 20, Dehni in view of Massachusetts discloses the process of claim 19, but does not disclose wherein the cross-linked polyurethane elastomer rubber composition is comprised of greater than about 85%, preferably greater than about 95% or, greater than about 99%, bio-based feedstock. However, it would have been obvious to one of ordinary skill in the art to change the weight percentage of renewable, bio-based feedstock through routine experimentation.

Claims 21-34 lack an inventive step under PCT Article 33(3) as being obvious over Dehni in view of US 2011/0045983 A1 to Healy et al. (hereinafter Healy)

Regarding claim 21, Dehni discloses the cross-linked polyurethane elastomer rubber composition of claim 1 in micronized form (Para [0093] polymer polyols formed by the polymer ization process increase the load bearing capacity of the low density and high resiliency of the flexible polyure thane and add toughness to the microcellular foam structure) and at least one cosmetic emollient (Para [0087] Example emollients or humectants, include, but are not limited to include: hyaluronic acid, glyc erin) but does not disclose a gel composition composition comprising a mixture of the cross-linked polyurethane elastomer rubber. However, Healy discloses a polyurethane (Para [0026] Numerous commercially available block copoly mers may be used in embodiments of the invention. For example...polyes ter/polyurethane) elastomer rubber (Para [0021] In some embodiments of the invention, a block copolymer capable of forming a three-dimensional network through physical cross-linking...Upon cooling, removal of shear, or solvent evaporation, the rigid domains reform and harden, locking the elastomeric network in place) in a gel composition (Para [0006] the invention relates to a gel composition that includes an ester compound and a polymer compound). It would have been obvious to one of ordinary skill in the art to combine these references to include a geling agent to form a gel composition (Healy Para [0005] A gel composition typically is made by mixing one or more compounds to be gelled with a gelling agent).

********CONTINUED ON SUPPLEMENTAL PAGE*********

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/46170

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:
Box V(2): Citations and Explanations

Regarding claim 22, Dehni in view of Healy discloses the gel composition of claim 21. Dehni further discloses wherein the amount of the micronized (Para [0093] polyurethane/polyorganosiloxane foam and add toughness to the microcellular foam structure) cross-linked polyurethane elastomer rubber composition (Para [0042] In the case of a Si-OH group reaction with an electrophilic group on a polyurethane compound...will result in a cross-linked elastomer-polyurethane composition; Para [0032] Flexible polyurethane foam is manufactured as a product of a reaction a polyol and a diisocyanate. Each R1 group has multiple isocyanate groups thus, there is a high degree of cross-linking in the polyurethane) is from about 66 to 87% by volume(Para [0036] the present disclosure, a methylene bisphenyl isocyanate (MDI) solution and a mixture of polyether polyol can be mixed to form polyurethane. Although other proportions can be suitable, this mixture can often comprise about 66% to about 87% by volume) but does not disclose wherein the polyurethane elastomer rubber composition is from about 30 to about 5 weight. However, it would have been obvious to one of ordinary skill in the art to change the weight percentage of polyurethane elastomer rubber through routine experimentation.

Regarding claim 23, Dehni in view of Healy discloses the gel composition of claim 22. Dehni further discloses wherein the amount of the micronized (Para [0093]] polyurethane/polyorganosiloxane foam and add toughness to the microcellular foam structure) cross-linked polyurethane elastomer rubber composition (Para [0042] In the case of a Si-OH group reaction with an electrophilic group on a polyurethane compound...will result in a cross-linked elastomer-polyurethane composition; Para [0032] Flexible polyurethane foam is manufactured as a product of a reaction a polyol and a diisocyanate. Each R1 group has multiple isocyanate groups thus, there is a high degree of cross-linking in the polyurethane) is from about 66 to 87% by volume(Para [0036] the present disclosure, a methylene bisphenyl isocyanate (MDI) solution and a mixture of polyether polyol can be mixed to form polyurethane. Although other proportions can be suitable, this mixture can often comprise about 66% to about 87% by volume) but does not disclose wherein the polyurethane elastomer rubber composition is from about 5 to about 17 weight %. However, it would have been obvious to one of ordinary skill in the art to change the weight percentage of polyurethane elastomer rubber through routine experimentation.

Regarding claim 24, Dehni in view of Healy discloses the gel composition of claim 21. Dehni further discloses wherein the amount of the cosmetic emollient is from about 0.05% to about 4% by volume (Para [0087] Example emollients or humectants, include, but are not limited to include...glycerin. As a general guideline humectants can comprise from about 0.05% to about 4% by volume) but does not disclose wherein the amount of the cosmetic emollient is from about 70 to about 95 weight %. However, it would have been obvious to one of ordinary skill in the art to change the weight percentage of humectant through routine experimentation.

Regarding claim 25, Dehni in view of Healy discloses the gel composition of claim 22. Dehni further discloses wherein the amount of the cosmetic emollient is from about 0.05% to about 4% by volume (Para [0087] Example emollients or humectants, include, but are not limited to include...glycerin. As a general guideline humectants can comprise from about 0.05% to about 4% by volume) but does not disclose wherein the amount of the cosmetic emollient is from about 83 to about 95 weight %. However, it would have been obvious to one of ordinary skill in the art to change the weight percentage of humectant through routine experimentation.

Regarding claim 26, Dehni in view of Healy discloses the gel composition of claim 21. Healy further discloses the composition comprising a secondary solvent (Para [0043] Examples of the suitable naturally-occurring fats and oils include, but are not limited to...triheptanoin; See Instant Specification 27 the secondary solvent is selected from the group consisting of triheptanoin).

Regarding claim 27, Dehni in view of Healy discloses the gel composition of claim 21. Healy further discloses wherein the secondary solvent is selected from the group consisting of triheptanoin; undecane; tridecane; or wherein the secondary solvents are naturally derived alkanes or naturally derived esters (Para [0043] Examples of the suitable naturally-occurring fats and oils include, but are not limited to...triheptanoin).

Regarding claim 28, Dehni in view of Healy discloses the gel composition of claim 21. Healy further discloses the composition comprising an active composition, optionally selected from the group consisting of selected from vitamins, sunscreens, plant extracts fragrances and mixtures thereof (Para [0066] The gel compositions in accordance with embodiments of the invention also have a wide spectrum of cosmetic applications when the gel compositions include an effective amount of one or more...fragrance oils).

Regarding claim 29, Dehni in view of Healy discloses the gel composition of claim 21. Healy further discloses the composition comprising a member of the group consisting of fragrances, colorants, preservatives, active compositions, and mixtures thereof (Para [0066] The gel compositions in accordance with embodiments of the invention also have a wide spectrum of cosmetic applications when the gel compositions include an effective amount of one or more...fragrance oils).

Regarding claim 30, Dehni in view of Healy discloses the gel composition of claim 21, but does not disclose wherein the micronized cross-linked polyurethane elastomer rubber composition has a cross-sectional diameter of from about 1 to about 61 microns. However, it would have been obvious to one of ordinary skill in the art to change the diameter of the polyurethane elastomer rubber through routine experimentation.

Regarding claim 31, Dehni in view of Healy discloses the gel composition of claim 21, but does not disclose the composition having a viscosity ranging from about 15,000 cP to about 1,000,000 cP, preferably from about 40,000 to about 1,000,000 cP. However, it would have been obvious to one of ordinary skill in the art to change the viscosity of the gel through routine experimentation.

Regarding claim 32, Dehni in view of Healy discloses the gel composition of claim 21. Healy further discloses wherein the gel is a non-Newtonian fluid or a thixotropic fluid (Para [0021] The physical cross-linking via these rigid domains yields a continuous three-dimensional network. In the presence of heat, shear, or solvent, the rigid domains soften and permit flow. Upon cooling, removal of shear, or solvent evaporation, the rigid domains reform and harden).

*********CONTINUED ON SUPPLEMENTAL PAGE*********

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/46170

Supplemental Box

In case **the space in any of the preceding boxes is not sufficient.**
Continuation of:
Box V(2): Citations and Explanations

Regarding claim 33, Dehni discloses a method (Para [0030] Any steps recited in any method or process claims may be executed in any order and are not limited to the order presented) comprising: a) micronizing (Para [0093] novel polymer polyols formed by the polymerization process above, increase the load bearing capacity of the low density and high resiliency of the flexible polyurethane and add toughness to the microcellular foam structure) the cross-linked polyurethane elastomer rubber composition of claim 1 (Para [0042] In the case of a Si-OH group reaction with an electrophilic group on a polyurethane compound...will result in a cross-linked elastomer-polyurethane composition; Para [0032] Flexible polyurethane foam is manufactured as a product of a reaction a polyol and a diisocyanate. Each R1 group has multiple isocyanate groups thus, there is a high degree of cross-linking in the polyurethane) in the presence of a cosmetic emollient (Para [0087] Example emollients or humectants, include, but are not limited to include...glycerin) but does not disclose a method of preparing a gel composition and optionally, b) combining the mixture resulting from step a) with a secondary solvent. However, Healy discloses a polyurethane (Para [0026] Numerous commercially available block copoly mers may be used in embodiments of the invention. For example...polyes ter/polyurethane) elastomer rubber (Para [0021] In some embodiments of the invention, a block copolymer capable of forming a three-dimensional network through physical cross-linking...Upon cooling, removal of shear, or solvent evaporation, the rigid domains reform and harden, locking the elastomeric network in place) in a gel composition (Para [0006] the invention relates to a gel composition that includes an ester compound and a polymer compound) and optionally, b) combining the mixture resulting from step a) with a secondary solvent (Para [0043] Examples of the suitable naturally-occurring fats and oils include, but are not limited to...triheptanoin). It would have been obvious to one of ordinary skill in the art to combine these references to include a geling agent to form a gel composition (Healy Para [0005] A gel composition typically is made by mixing one or more compounds to be gelled with a gelling agent).

Regarding claim 34, Dehni in view of Healy discloses the process of claim 33. Healy further discloses wherein the secondary solvent is the secondary solvent is selected from the group consisting of triheptanoin; undecane; tridecane; or wherein the secondary solvents are naturally derived alkanes or naturally derived esters (Para [0043] Examples of the suitable naturally-occurring fats and oils include, but are not limited to...triheptanoin).

Claim 15 lack an inventive step under PCT Article 33(3) as being obvious over Dehni in view of Massachusetts and further in view of US 2013/0079486 A1 to Hidesaki et al. (hereinafter Hidesaki)

Regarding claim 15, Dehni in view of Massachusetts discloses the cross-linked polyurethane elastomer rubber composition of claim 14, but does not disclose wherein the bio-based and biodegradable polyisocyanate is 1,5-pentamethylene diisocyanate trimer. However, Hidesaki discloses a polyurethane (Para [0017] a polyurethane resin obtained by using 1,5-pentamethylene diisocyanate and the polyisocyanate composition) wherein the bio-based and biodegradable polyisocyanate is 1,5-pentamethylene diisocyanate trimer (Para [0017] a polyurethane resin obtained by using 1,5-pentamethylene diisocyanate and the polyisocyanate composition). It would have been obvious to one of ordinary skill in the art to combine these references to use 1,5-pentamethylene diisocyanate trimer to form polyurethane because the isocyante groups also for crosslinking (Dehni Para [0025] Polyurethanes are formed by reacting an isocyanate with a polyol...By reacting two or more isocy anate groups with a polyol a flexible polyurethane foam is produced).

Claims 1-34 have industrial applicability as defined by PCT Article 33(4) because the subject matter can be made or used in industry.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
16 October 2014 (16.10.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/167518 A1

(51) International Patent Classification:
C08L 77/02 (2006.01) *C08G 69/14* (2006.01)
C08J 3/20 (2006.01) *C08L 101/16* (2006.01)

(21) International Application Number:
PCT/IB2014/060594

(22) International Filing Date:
10 April 2014 (10.04.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2013204225 12 April 2013 (12.04.2013) AU

(71) Applicant: **STERIPAK PTY LTD** [AU/AU]; Level 9, 5 Elizabeth Street, Sydney, New South Wales 2000 (AU).

(72) Inventor: **LEFEBVRE, Michel**; PO Box 152, Kurrajong, New South Wales 2758 (AU).

(74) Agent: **ASHBY, Kevin**; PO Box 900, 1 Victor Russell Dr, Samford, Queensland 4520 (AU).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to the identity of the inventor (Rule 4.17(i))*

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

— *of inventorship (Rule 4.17(iv))*

[Continued on next page]

(54) Title: DEGRADABLE AND BIODEGRADABLE PLASTIC MATERIAL AND A METHOD FOR MAKING IT

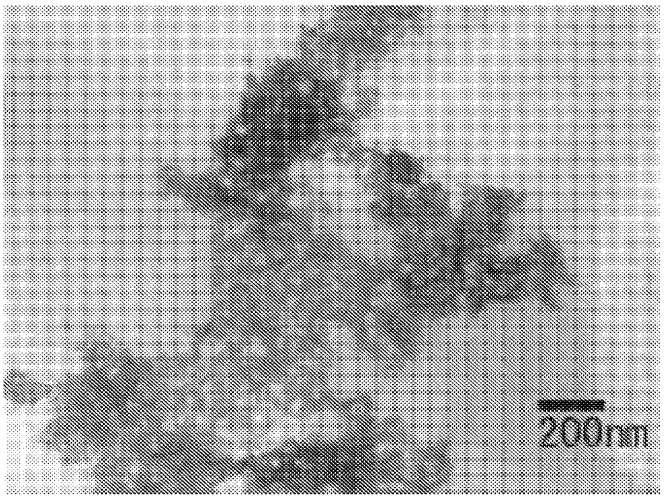


FIG. 1

(57) Abstract: There is disclosed herein a degradable or biodegradable plastic material containing a first polymer and at least one fractal polymer. There is also disclosed herein a method of making a degradable or biodegradable plastic material comprising mixing a first polymer with a fractal polymer to form a mixture thereof. There is also disclosed herein a degradable plastic material containing a first polymer and a pro-degradation additive with fractal local concentration repartition. There is also disclosed herein a biodegradable plastic material containing a first polymer and a biodegradable additive with fractal local concentration repartition. There is also disclosed herein a method of making a degradable or biodegradable plastic material comprising the step of creating inside the plastic material a fractal repartition of a pro-degradation additive and/or a biodegradation additive.

WO 2014/167518 A1

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

DEGRADABLE AND BIODEGRADABLE PLASTIC MATERIAL AND A METHOD FOR MAKING IT

Technical Field

[001] The present invention relates to a degradable or biodegradable plastic material and a method of making it.

Background of the Invention

[002] The information provided herein and references cited are provided solely to assist the understanding of the reader, and do not constitute an admission that any of the references or information is prior art to the present invention.

[003] The use of plastics in society has the downside that they are difficult to decompose. The addition of additives to plastic materials to achieve various types of degradation such as photo-degradation, oxo-degradation or biodegradation has been well documented. Reference is made to "An Overview of degradable and biodegradable polyolefins", A. Amala *et al*., Progress in Polymer Science, 36, 2011 p 1015-1049. However the poor performance of many additives, particularly for biodegradation under various conditions, has also been noted. Reference is made to "Fundamental principles and concepts of biodegradability – sorting through the facts, hypes, and claims of biodegradable plastics in the marketplace" R. Narayan, Bioplastics Magazine 01/09 vol 4.

[004] Degradation of plastics by living microorganisms is achieved when the polymer is used as a nutrient source for the production of by-products such as biogas and the multiplication and organisation of the microorganism in colonies.

[005] The effects of most pro-degradation additives (including biodegradation additives) are concentration dependant but their use is limited not only by cost considerations but by the imperative to maintain physical performance in first use and recycled products.

[006] It would be desirable to provide a plastic material which is degradable or biodegradable, but still maintains its physical performance. It would also be desirable to provide a plastics material which contains an additive which is concentrated locally in a

manner such as to lower its overall use but still maintain the degradation or biodegradation performance.

Summary of the Invention

[007] According to a first aspect of the present invention, there is provided a degradable or biodegradable plastic material containing a first polymer and at least one fractal polymer.

[008] According to a second aspect of the present invention, there is provided a method of making a degradable or biodegradable plastic material comprising mixing a first polymer with at least one fractal polymer to form a mixture thereof.

[009] According to a third aspect of the present invention, there is provided a degradable plastic material containing a first polymer and a pro-degradation additive with fractal local concentration repartition.

[0010] According to a fourth aspect of the present invention, there is provided a biodegradable plastic material containing a first polymer and a biodegradable additive with fractal local concentration repartition.

[0011] According to a fifth aspect of the present invention, there is provided a method of making a degradable or biodegradable plastic material comprising the step of creating inside the plastic material a fractal repartition of a pro-degradation additive and/or a biodegradation additive.

Definitions

[0012] The following are some definitions that may be helpful in understanding the description of the present invention. These are intended as general definitions and should in no way limit the scope of the present invention to those terms alone, but are put forth for a better understanding of the following description.

[0013] Unless the context requires otherwise or specifically stated to the contrary, integers, steps or elements of the invention recited herein as singular integers, steps or elements clearly encompass both singular and plural forms of the recited integers, steps or elements.

[0014] Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated step or element or integer or group of steps or elements or integers, but not the exclusion of any other step or element or integer or group of elements or integers. Thus, in the context of this specification, the term "comprising" means "including principally, but not necessarily solely".

[0015] By "degradable" is meant that the plastic material is capable of being weakened by outside agents such as atmospheric oxygen or UV light.

[0016] By "biodegradable" is meant that the plastic material is capable of being at least partially consumed by microorganisms. This may occur under composting conditions, under soil conditions, under aerobic condition, under anaerobic conditions or under marine conditions.

[0017] By "fractal polymer" is a polymer having a fractal configuration of structure which is substantially self-similar or is scale invariant at different scales. The polymer has a constructed or in-built reticulated structure.

[0018] By "fractal local concentration repartition" is meant that localised concentration zones of an additive in a polymer are shaped in a fractal form.

Brief Description of the Drawings

[0019] FIG. 1 is a scanning electron microscope image of pure fractal poly ε caprolactam embedded in a polymer matrix showing the fractal structure at micrometre scale;

[0020] FIG. 2 is a scanning electron microscope image of fractal poly ε caprolactam composite within a polymer matrix after staining with phospho-tungstenic acid and shows the fractal repartition of amine radical concentration used as a pro-degradation additive.

Detailed Description of Preferred Embodiments of the Invention

[0021] There is disclosed herein a degradable or biodegradable plastic material containing a first polymer and at least one fractal polymer.

[0022] There is also disclosed herein a method of making a degradable or biodegradable plastic material comprising mixing a first polymer with at least one fractal polymer.

[0023] In some embodiments the first polymer may be in the form of a melt or may be melted with the at least one fractal polymer which is retained as a solid in the mixture.

[0024] There is also disclosed herein a degradable plastic material containing a first polymer and a pro-degradation additive with fractal local concentration repartition.

[0025] There is also disclosed herein a biodegradable plastic material containing a first polymer and a biodegradable additive with fractal local concentration repartition.

[0026] Suitably the fractal polymer is present in a concentration of about 2% w/w or lower. For example the fractal polymer may be present in a range of about 0.01% to about 1% w/w or about 0.01 to about 0.1% w/w, or about 0.1 to about 1% w/w or about 1 to about 2% w/w or about 0.05 to about 0.5% w/w. Suitable amounts include 0.01% w/w, 0.02% w/w, 0.03% w/w, 0.04% w/w, 0.05% w/w, 0.06% w/w, 0.07% w/w, 0.08% w/w, 0.09% w/w, 0.1% w/w, 0.2% w/w, 0.3% w/w, 0.4% w/w, 0.5% w/w, 0.6% w/w, 0.7% w/w, 0.8% w/w, 0.9% w/w, 1% w/w, 1.1% w/w, 1.2% w/w, 1.3% w/w, 1.4% w/w, 1.5% w/w, 1.6% w/w, 1.7% w/w, 1.8% w/w, 1.9% w/w or 2% w/w.

[0027] The first polymer may be a polyolefin such as polyethylene or polypropylene, a polystyrene such as high impact polystyrene (HIPS) or oriented polystyrene (OPS), a polyester such as PET, a polyamide and/or an imide such as nylon or MXD6. A mixture of polymers may be used.

[0028] The plastic material may additionally include one or more of a pro-degradation additive and a biodegradable additive. In some embodiments, the additive is localised in the plastics material with fractal local concentration repartition.

[0029] In some embodiments, the pro-degradation additive may be a carbon containing copolymer such as carbon monoxide copolymer. One suitable carbon containing copolymer is poly(ethylene-co-carbon monoxide copolymer). In some embodiments, the pro-degradation additive may be a vinyl ketone copolymer. A vinyl

ketone copolymer may be used when photodegradation is desired. One suitable pro-degradation additive is polyamide-12.

[0030] One suitable biodegradable additive is EcoPure® polystyrene based biodegradation additive. Another suitable biodegradable additive is a polypeptide such as a keratin. In some embodiments if biodegradation is required, the biodegradable additive may be a polyamide starch mix or a polymer derivative, for example, from corn starch such as polylactic acid. One suitable biodegradable additive is amylase.

[0031] The fractal polymer may be single polymer or may be mix of polymers. The fractal polymer or mix of fractal polymers may be obtained by phase inversion or coagulation of a polymer or mix of polymers dissolved in a solvent with a gas producing reagent according to U.S. Patent No. 6,001,889 and Australian Patent 696330 entitled "Polymers with fractal structure", both of which are incorporated herein by reference. As set out in U.S. Patent No. 6,001,889, for general preparation of fractal structure polymers the procedure may be as follows:

(a) Preparations of the original base polymers for reaction.

(1) Polymerization, extrusion and chip manufacture, followed by purification (to remove unreacted monomer) and drying.

(2) Spinning and drawing of the polymer at very high drawing ratio to obtain a highly crystalline structure in the base polymer.

(b) Preparation of the liquid phase and controlled depolymerization (produces cut segments).

(3) Mixing of the base crystalline polymer with a liquid reagent breaking cohesion bonds (e.g., the hydrogen bonds) to unfold the polymer micelle in a slow controlled reaction (i.e., step-by-step unfolding).

(4) Addition to the reagent, if necessary, of a depolymerization agent (to cut the structure).

(5) Addition to the reagent, if necessary, of a complementary reagent to permit lateral grafting.

(6) Controlled maturation (controlled parameters being time and temperature).

(c) Phase Inversion

(7) Preparation of a mixture of a non-solvent liquid for the polymer and a foaming/expanding reagent, soluble in this mixture, and capable of producing a gas by reaction with the dissolution reagent of the base polymer.

(8) Coagulation reaction of (b) in (c) by mixing, film forming of (b) and immersion in (c), or extrusion of (b) and (c).

[0032] In some embodiments, the process includes polymerising a polymer solution with or without the addition of one or more of a pro-degradation additive or biodegradable additive; phase inversion and the expansion of the polymer within a solvent containing an expanding reagent; and washing, drying and optionally mixing with one or more of a pro-degradation additive, or biodegradable additive in powder form, to form the fractal polymer or mix of fractal polymers. In some embodiments, in the phase inversion step, a solvent is used which is suitably non-solvent for the polymer, but is a solvent for the expanding reagent. In some embodiments, the washing stage may include the use of a solvent miscible with the previous solvents used.

[0033] When compatible with the solvent used in the polymerisation step, the pro-degradation additives or biodegradable additives can be added at that stage. If not they may be added during a later washing step or alternatively added to a master-batch for forming the final product. The pro-degradation additives and biodegradable additives may be added in solid powder form or in some other form.

[0034] In some embodiments, the fractal polymer or mix of fractal polymers can be made from one or more of polyamides (e.g., polyamide 6, polyamide 6,6, polyamide 4, polyamide 11, polyamide 12 or others), polyesters, cellulosic materials or other polymers. These may be suitable for the manufacture of synthetic semi-permeable membranes by phase inversion. The solvent used may be chosen from the list of solvents for each

polymer as established in techniques used for preparation of samples for analysis, as cited in H. Cantow, "Polymer Fractionation," Academic Press: New York, 1967 or in H. Morawetz, "Macromolecules in Solution," John Wiley & Sons, Interscience: New York, 1966. Suitable solvents include 1,2-propylene carbonate, ethylene carbonate, m-cresol, formic acid, dimethyl sulfoxide. The non-solvent may be selected from the above sources. Suitable non-solvents include hexane, methylene chloride and water. In some embodiments, the non-solvent is water.

[0035] Suitable combinations of polymers and solvents which may be used include vinyl polymers (such as polyacrylonitrile) with a 1,2-propylene carbonate (solvent) and hexane (non-solvent) or ethylene carbonate (solvent) and methylene chloride (non-solvent); polyesters such as crystalline polyethyleneteraphthalate with m-cresol (solvent) and hexane (non-solvent), or poly Ɛ caprolactam with ethylene carbonate (solvent) and water(non-solvent) or with formic acid (solvent) and hexane (non-solvent); or polyhexamethylene (such as adipamide) with dimethyl sulfoxide (solvent) and water (non-solvent) or with formic acid (solvent) and hexane (non-solvent).

[0036] The fractal polymer or mix of fractal polymers may be in the form of a powder or film. It may have an active surface area greater than about 20,000m^2/kg.

[0037] In some embodiments the present invention relates to a master batch comprising a carrier compatible with the first polymer and the fractal polymer or mix of fractal polymers. In some embodiments, the present invention provides a method for mixing and melting the fractal polymer or mix of fractal polymers with a carrier compatible with the first polymer to prepare a master-batch.

[0038] In some embodiments, the present invention provides a method of making a plastic material including mixing the fractal polymer or mix of fractal polymers or the master-batch with a first polymer followed by extrusion, injection moulding, blow moulding or thermoforming to form a product. Suitable products include plastic cups, lids, plates, films, packaging materials and more generally all products obtained by extrusion, injection moulding, blow moulding or thermoforming.

[0039] In some embodiments, the present invention provides a method of making a plastic material, suitably of improved degradation and/or biodegradation capability, by creating inside the plastic material a fractal repartition of a pro-degradation additive and/or the biodegradation additive. In these embodiments, the fractal polymer is thought to act as a carrier to create concentration zones of the pro-degradation or biodegradable additive shaped in a fractal form (such as shown in Figure 2). This may permit a faster and more complete degradation using a low average concentration and without changing other properties significantly during first use or recycling. During recycling, this geometric effect of fractal repartition will typically disappear during melting and the low concentration of additive ensures that the mechanical properties are maintained.

[0040] In some embodiments, the present invention provides the use of a polymer or polymers with fractal structure to ensure a fractal repartition of one or more commonly used pro-degradation additives or biodegradation additives to improve degradation performance. In some embodiments, this may be achieved by inserting the pro-degradation additive or biodegradable additive into the fractal polymer structure during manufacturing.

[0041] In some embodiments, the present invention provides a method of dispersion of a pro-degradation or biodegradable additive inside a plastic material to achieve a fractal repartition of the additive concentration within the plastic material by use of a fractal polymer or a mix of fractal polymers.

[0042] In some embodiments, the present invention provides a method of making a mix of fractal polymer and a pro-degradation and/or biodegradable additive and a master-batch containing this mix and addition of the mix to a first polymer to achieve a fractal repartition of the additive concentration within the first polymer and the plastic material produced thereby.

[0043] In some embodiments, the present invention provides a method of making a mix of a fractal polymer, one or more of a pro-degradation additive or a biodegradable additive, and a master-batch containing this mix and addition of this mix or master-batch to a first polymer to achieve a fractal repartition of the mix within the first polymer, and

the plastics material produced thereby. This may provide a better degradation or biodegradation performance in anaerobic conditions.

[0044] In some embodiments, the present invention provides a method of making a mix of a fractal polymers, one or more of a pro-degradation additive or a biodegradable additive, and a master-batch containing this mix and addition of this mix or master-batch to a first polymer to achieve a fractal repartition of the mix within the first polymer, and the plastics material produced thereby. This may provide a better degradation or biodegradation performance in aerobic conditions.

[0045] The present inventor has found that by providing a fractal polymer within the first polymer, the growth characteristics and colony formation of microorganism may be replicated and as a result faster degradation may occur as in the diffusion limited aggregated growth process characteristic of polymer degradation, colonies grow in a fractal pattern with a very often measurable fractal dimension. Reference is made to "Colony Formation in Bacteria: Experiments and modelling", M. Matsushita et al, Biofilms (2004), 1, pp 305-317.

[0046] The invention will now be described by way of example only having regard to the following examples.

EXAMPLE 1 - NON-LIMITING EXAMPLE OF APPLICATION TO THE PRODUCTION OF BIODEGRADABLE HIGH IMPACT POLYSTYRENE.

[0047] A fractal polymer in the form of poly-epsilon caprolactam was prepared in accordance with the technique described in Australian patent 696330 (see Figure 1). The fractal polymer was then mixed with 4 times its weight of polyamide-12 powder (as a pro-degradation additive) calibrated at 20 microns and 4 times its weight of amylase powder (as a biodegradable additive) calibrated at 20 microns. An EcoPure® polystyrene based biodegradation additive was then added to the mix and the mix added to High Impact polystyrene before extrusion at a rate of 0.175% mix with 0.7% EcoPure® additive. The mix was extruded to form a film which was used in thermoforming of lids for polystyrene disposable cups. Tests performed under ASTM D5511-11 method on the finished product showed that anaerobic biodegradation occurred at a rate more than four times the rate

shown by the same product containing the same 0.7% concentration of EcoPure® additive but without any fractal polymer, with the biogas producing period more than doubled before a plateau is observed.

EXAMPLE 2 - NON-LIMITING EXAMPLE OF APPLICATION OF THE PRODUCTION OF BIODEGRADABLE POLYETHYLENE

[0048] A fractal polymer in the form of a poly-epsilon caprolactam/keratin composite was prepared in accordance with the technique described in Australian Patent 696330 by slow dissolution and depolymerisation of a highly crystalline polyamide 6 fibre (polycaprolactam) mixed with a polypeptide as a biodegradable additive (for example a keratin natural product such as a fine micron wool (or another polypeptide)) with continued mixing in the solvent for 24 hours. After phase inversion, washing and drying the fractal polymer composite (illustrated in Figure 2) was mixed with four times its weight of fine denier viscose fibres and the product then micronized by cryo-crushing. The powder obtained was used at 1% in polyethylene to obtain a biodegradable resin to be used in extrusion or injection moulding.

EXAMPLE 3 – TESTING THE ANAEROBIC BIODEGRADABILITY OF MODIFIED HIGH IMPACT POLYSTYRENE CONTAINING FRACTAL POLYMER

[0049] A modified high-impact polystyrene (HIPS) beverage container lid containing 0.02% (200ppm) embedded fractal polymer with 0.7% EcoPure® additive was subjected to anaerobic biodegradation testing in accordance with ASTM D5511-11 “Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under High-Solids Anaerobic-Digestion Conditions”.

[0050] A sample of about 30 kg of compost (inoculum) was obtained. The moisture content of the inoculum was about 72% dry solids.

[0051] The lid was cut into pieces of about 1.5cm x 1.5cm to obtain a sample mass of 12g. A blank sample containing only compost was also prepared and tested to obtain a baseline of biogas production from the inoculum. For comparison, a lid containing a commercial EcoPure® additive (0.7%) without fractal polymer was also tested.

[0052] Testing was performed in a laboratory oven using 2L (2 litre) glass flasks as the incubation vessel. The temperature of the incubation was maintained at a constant 52°C with an ambient temperature ranging from 15-22°C. Temperature measurement throughout the testing indicated a constant temperature was maintained in all sections of the oven for the duration of the test. During incubation, the biogas generated by the process was collected in sealed oxygen proof polyethylene bags and the volume of gas produced was measured by water displacement.

[0053] Over time it was found that the high impact polystyrene container lid containing the fractal polymer produced biogas. The biogas production was relatively constant for the first 30 days; this was followed by a decreased production rate until after 50 days where the production rate increased again. This cycle was repeated after day 100 and the test was terminated after 216 days. The biogas production profile was consistent with the growth cycles of anaerobic bacterial responsible for biogas production. Using data from the amount of biogas obtained from a blank sample, the volume of biogas produced in the test vessel was 4.3L over the test period for the polystyrene lid containing the fractal polymer. This was significantly more than the 1.9L biogas produced over the test period for the lid containing the commercial EcoPure® additive.

[0054] The percentage biodegradation was calculated based on the total production of biogas (methane and carbon dioxide) relative to the carbon content of the sample. In HIPS, the total carbon content was approximately 91% based on the components, polystyrene (67%) and butadiene rubber (33%). Since 22.4mL of biogas contains 1mmol of carbon, the amount of carbon in the produced biogas can be determined and the subsequent percentage biodegradation can be calculated based on the equation:

$$\%\text{biodegradation} = (C_s - C_b)/C_t \times 100$$

where C_s and C_b are the carbon contents generated by the samples and the blank respectively, and C_t is the total mass of the original test specimens.

[0055] The percent biodegradation of the test samples was found to be 24.2% for the lid containing the embedded fractal polymer and 10.2% for the lid containing the EcoPure® additive.

[0056] A Scanning Electron Microscope (SEM) image determined using a JOEL NeoScope (JCM-5000) of a sample, dried overnight and coated with 2nm of gold using a NeoCoater (MP19020NCTR) prior to imaging showed significant microbial growth on the surface of the lid containing the fractal polymer. The growth of bacterial populations appeared to anchor securely on the HIPS surface. The image clearly showed evidence of *cocci archaea* linked at the surface by a fractal network. The microbial growth was also not restricted to the surface of the HIPS surface but extended to the interior of the polymer suggesting that although the microbial growth originated on the surface, the bacteria were able to penetrate the material to establish growth inside and could ultimately lead to total biodegradation of the material. The microbial growth appeared to follow a fractal pattern which is consistent with the fractal additive promoting fractal growth.

[0057] The foregoing description of preferred embodiments and best mode of the invention known to the applicant at the time of filing the application have been presented for the purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed. Many modifications and variations are possible in the light of the above teaching. The embodiments were chosen and described in order to best explain the principles of the invention and its practical application to thereby enable others skilled in the art to best utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.

CLAIMS

1. A degradable or biodegradable plastic material containing a first polymer and at least one fractal polymer.

2. The plastic material according to claim 1 wherein the at least one fractal polymer is present in a concentration of 2% w/w or lower.

3. The plastic material according to claim 2 wherein the at least one fractal polymer is present in a range of 0.01% to 1% w/w.

4. The plastic material according to any one of claims 1 to 3 wherein the first polymer is a polyolefin, a polystyrene, a polyester, a polyamide, an imide or a mixture of any two or more of these.

5. The plastic material according to any one of claims 1 to 4 further comprising a pro-degradation additive and/or a biodegradable additive.

6. The plastic material according to claim 5 wherein the additive is localised in the plastic material with fractal local concentration repartition.

7. The plastic material according to any one of claims 1 to 6 wherein the at least one fractal polymer is a polyamide, polyester, cellulosic material, polyhexamethylene or a vinyl polymer.

8. The plastic material according to any one of claims 1 to 7 wherein the fractal polymer is poly ε caprolactam.

9. A method of making a degradable or biodegradable plastic material comprising mixing a first polymer with a fractal polymer to form a mixture thereof.

10. The method of claim 9 wherein the fractal polymer includes a pro-degradation additive and/or a biodegradable additive within its structure or a pro-degradation and/or a biodegradable additive is added to the mixture.

11. The method of claim 9 or 10 further comprising extruding, injection moulding, blow moulding or thermoforming the mixture.

12. The method of claim 11 wherein the product is selected from a cup, lid, plate, film or packaging material.

13. A degradable plastic material containing a first polymer and a pro-degradation additive with fractal local concentration repartition.

14. A biodegradable plastic material containing a first polymer and a biodegradable additive with fractal local concentration repartition.

15. A method of making a degradable or biodegradable plastic material comprising the step of creating inside a plastic material, a fractal repartition of a pro-degradation additive and/or a biodegradation additive.

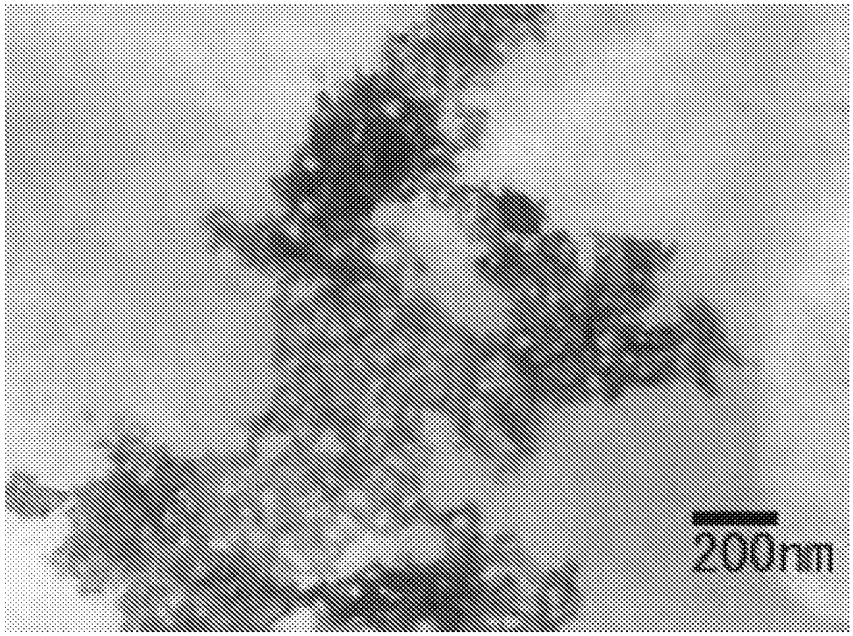


FIG. 1

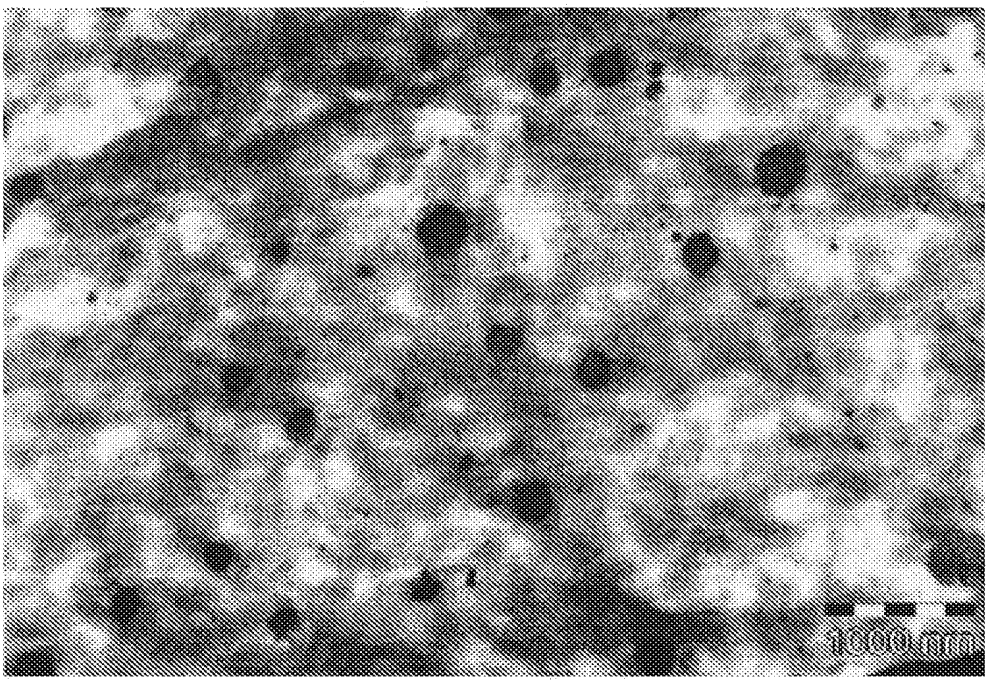


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2014/060594

A. CLASSIFICATION OF SUBJECT MATTER

C08L 77/02 (2006.01) C08J 3/20 (2006.01) C08G 69/14 (2006.01) C08L 101/16 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI, MEDLINE,, TXTE, CAPLUS, REGISTRY, FULLTEXT, GOOGLE SCHOLAR, GOOGLE PATENT, Espacenet.

IPC-C08L, FRACTAL, POLYMER, PLASTIC, DEGRADE, BIODEGRADE, POLY-EPSILON CAPROLACTONE, POLYAMIDE-6, NYLON-6, POLYAMIDE, POLYESTER, CAPROLACTAM, POLYHEXAMETHYLENE, VINYL POLYMER, POLYSTYRENE, RETICULATED, DENDRIMER, MATERIAL, CUP, FILM LOCAL CONCENTRATION REPARTITION, PARTICLE, Steripak, Lefebvre M. AND LIKE TERMS.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 August 2014	04 August 2014
Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Karl Heys AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832725

Form PCT/ISA/210 (fifth sheet) (July 2009)

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5493000 A (AHARONI) 20 February 1996 Whole of document but especially the abstract, col 18, line 12-line 40, col 29 lines 14-18 , examples, claims.	1-4, 7, 9, and 11-12
X	US 6872800 B1 (BOUQUEREL et al.) 29 March 2005 Whole of document but especially the abstract, whole of col 8, col 10 lines 61-67 , examples, claims.	1-4, 7, 9, and 11-12
X	US 5480944 A (AHARONI) 02 January 1996 Whole of document but especially the abstract, col 12 line 41-col 13 line 19, col 20 lines 63-67, examples, claims.	1-4, 7, 9, and 11-12
X	US 6001889 A (LEFEBVRE) 14 December 1999 Whole of document but especially the abstract, col 7 line 53-col 9 line 3, table middle of columns 7 and 8, examples, claims.	1, 4-5 and 7-12

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/IB2014/060594**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
US 5493000 A	20 February 1996	WO 9317062 A1	02 Sep 1993
		WO 9506081 A1	02 Mar 1995
US 6872800 B1	29 March 2005	AU 4414000 A	21 Nov 2000
		BR 0011196 A	19 Feb 2002
		BR 0011196 B1	09 Mar 2010
		CA 2373024 A1	16 Nov 2000
		CN 1354767 A	19 Jun 2002
		EP 1183301 A1	06 Mar 2002
		EP 1183301 B1	05 Nov 2003
		FR 2793252 A1	10 Nov 2000
		FR 2793252 B1	20 Jul 2001
		HU 0201073 A2	29 Jul 2002
		IL 146295 A	31 May 2010
		JP 2002544307 A	24 Dec 2002
		JP 3766595 B2	12 Apr 2006
		PL 351817 A1	16 Jun 2003
		RU 2001132726 A	20 Feb 2004
		TW I251002 B	11 Mar 2006
		WO 0068298 A1	16 Nov 2000
US 5480944 A	02 January 1996	None	
US 6001889 A	14 December 1999	AU 696330 B2	10 Sep 1998
		AU 6781896 A	27 Mar 1997
		EP 0850263 A2	01 Jul 1998
		EP 0850263 B1	07 Dec 2005
		NZ 315984 A	29 Nov 1999
		WO 9709352 A1	13 Mar 1997

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 December 2021 (23.12.2021)

WIPO | PCT

(10) International Publication Number
WO 2021/257937 A1

(51) International Patent Classification:
A61K 8/87 (2006.01) *C08G 18/72* (2006.01)
A61Q 19/00 (2006.01)

(21) International Application Number:
PCT/US2021/037992

(22) International Filing Date:
18 June 2021 (18.06.2021)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/040,571 18 June 2020 (18.06.2020) US

(71) Applicant: **NANOMETICS LLC (D.B.A. PHD BIOSCIENCES)** [US/US]; 180 Varick Street, 6th Floor, New York, New York 10014 (US).

(72) Inventors: **MAHON, Andrew Bernard**; 217 West 106 Street, Apartment 2A, New York, New York 10025 (US). **ISAACMAN, Michael Joseph**; 50 East 8th Street, Apartment 4U, New York, New York 10003 (US). **ISAACMAN, Steven**; 248 Oak Beach Road, Oak Beach, New York, New York 11702 (US).

(74) Agent: **RAO, Minxi**; MEDLER FERRO WOODHOUSE & MILLS PLLC, 8201 Greensboro Dr., Ste. 1060, McLean, Virginia 22102 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: CHEMICALLY CROSS-LINKED ELASTOMERS FORMED BY MICHAEL ADDITION AND COMPOSITIONS COMPRISING SUCH ELASTOMERS

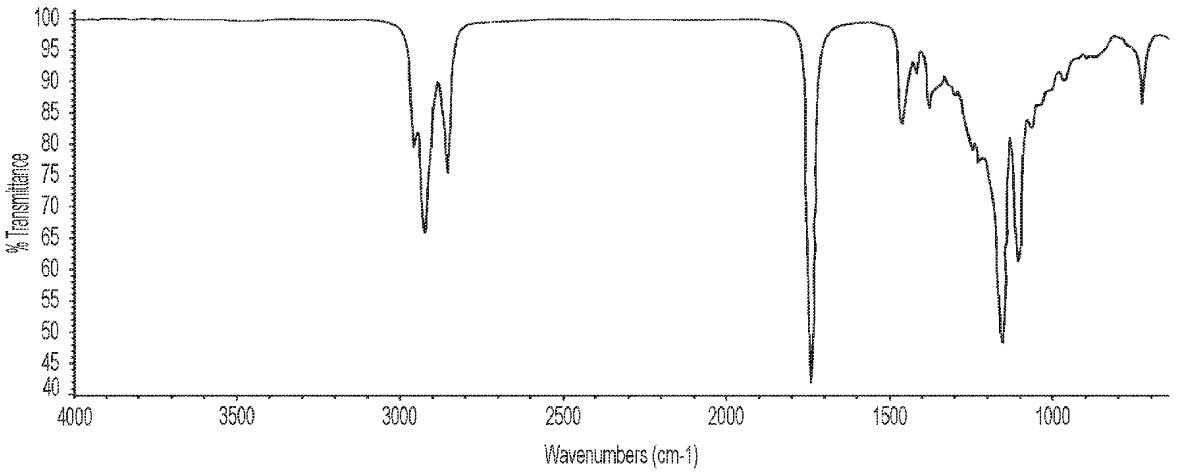


FIG. 1

(57) Abstract: Gel compositions containing a Michael addition elastomer formed from the reaction of a reactant molecule containing two or more Michael acceptor groups and a molecule containing one or Michael donor group with two or more active hydrogens in its molecule and capable of forming 1,4-addition products with the Michael acceptor reactants, in a topically acceptable carrier fluid. The gelled compositions may further contain a personal or healthcare active. The actives may be incorporated into the gel via either a pre or post load method.

[Continued on next page]

WO 2021/257937 A1

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

CHEMICALLY CROSS-LINKED ELASTOMERS FORMED BY MICHAEL ADDITION AND COMPOSITIONS COMPRISING SUCH ELASTOMERS

Technical Field

This invention relates to cross-linked elastomers from the reaction of a molecule comprising two or more Michael acceptor groups and a molecule comprising a single primary amine functional group to form 1,4-additon products, and gel compositions thereof. This invention also relates to gel compositions containing a chemically cross-linked elastomer formed from the reaction of a molecule comprising two or more Michael acceptor groups and a molecule comprising two or more Michael donor groups capable of reacting with the Michael acceptor groups to form 1,4-additon products. A catalyst may be optionally used to increase the rate of formation of the Michael addition elastomer. The gel compositions may contain a personal or healthcare active. The actives may be incorporated into the gel via either a pre or post load method. Gel compositions may be further used as components in personal care, over-the-counter drug, or pharmaceutical compositions.

Background

Silicone elastomers have been used extensively in personal care applications for their thickening and gelling efficiency, and unique silky and powdery sensory profile. Silicone elastomers are compatible with silicone-based fluids, however, silicone-based fluids for topical use are being phased out of the personal care industry due to health and environmental concerns. There is a need to develop alternatives to silicone elastomers which demonstrate efficient thickening and gelling capabilities with topically acceptable solvents (e.g., esters, triglycerides, and hydrocarbons) while imparting a favorable skin feel. Michael addition elastomers and gel compositions described herein can potentially provide desirable alternatives to silicone elastomers.

Summary

This disclosure relates to a chemically cross-linked elastomer and gel compositions of a chemically cross-linked elastomer formed by conjugate addition of a first reactant comprising one or more molecules, wherein each of the one or more molecules comprises two or more Michael acceptor functional groups, with a second reactant comprising one or more molecules, wherein each of the one or more molecules comprises one primary amine or a carbon bonded to two Michael donor hydrogen

atoms. The primary amine, which contains two Michael donor hydrogen atoms, or the carbon bonded to two Michael donor hydrogen atoms, can react with two Michael acceptor functional groups.

The disclosure also relates to gel compositions comprising a Michael addition elastomer prepared from the reaction of:

A) a first reactant comprising one or more molecules, wherein each of the one or more molecules comprises two or more Michael acceptor functional groups and optionally contains an OH, SH or NH functional group at a vicinal position to each of the Michael acceptor functional groups;

B) a second reactant comprising one or more molecules, wherein each of the one or more molecules comprises a Michael donor functional group with two or more Michael active hydrogen atoms to provide two or more nucleophilic reaction sites, such that the Michael donor functional group is capable of reacting with two Michael acceptor functional groups to form a 1,4-addition product, such as an amine, malonate, or both;

C) an optional reaction catalyst;

D) a topically acceptable carrier fluid.

A personal care or healthcare active (E) may be incorporated into the cross-linked elastomer gel by dissolving it in the topically acceptable solvent during the formation of the elastomer gel (pre-load method) or admixing it with a formed elastomer gel (post-load method).

The invention is further directed to the following:

A gel composition comprising an elastomer prepared by Michael addition reaction from:

A) a first reactant comprising one or more molecules, wherein each of the one or more molecules comprises two or more Michael acceptor functional groups;

B) a second reactant comprising one or more molecules, wherein each of the one or more molecules comprises one or more Michael donor functional groups, wherein each Michael donor functional group comprises two or more Michael active hydrogen atoms;

C) an optional reaction catalyst; and

D) a topically acceptable carrier fluid, at a concentration of 0% (w/w) to 99.9% (w/w) of the gel composition, preferably 20% (w/w) to 99.9% (w/w) of the gel composition.

Brief Description of the Drawings

FIG. 1 shows an exemplary FTIR spectrograph of propoxylate triacrylate/Priamine™ 1075 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1, as described in embodiments herein.

FIG. 2 shows an exemplary FTIR spectrograph of glycerol propoxylate triacrylate/Priamine™ 1075 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5, as described in embodiments herein.

FIG. 3 shows an exemplary FTIR spectrograph of glycerol propoxylate triacrylate/JEFFAMINE® T-403 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1, as described in embodiments herein.

FIG. 4 shows an exemplary FTIR spectrograph of glycerol propoxylate triacrylate/JEFFAMINE® T-403 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5, as described in embodiments herein.

FIG. 5 shows an exemplary FTIR spectrograph glycerol Propoxylate triacrylate/poly(dimethylsiloxane), bis(3-aminopropyl) terminated aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1, as described in embodiments herein.

FIG. 6 shows an exemplary FTIR spectrograph glycerol Propoxylate triacrylate/poly(dimethylsiloxane), bis(3-aminopropyl) terminated aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5, as described in embodiments herein.

FIG. 7 shows an exemplary FTIR spectrograph acrylated epoxidized soybean oil/Priamine™ 1074 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1, as described in embodiments herein.

FIG. 8 shows an exemplary FTIR spectrograph acrylated epoxidized soybean oil/Priamine™ 1074 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5, as described in embodiments herein.

FIG. 9 shows an exemplary FTIR spectrograph of acrylated epoxidized soybean oil/poly(dimethylsiloxane), bis(3-aminopropyl) terminated aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1, as described in embodiments herein.

FIG. 10 shows an exemplary FTIR spectrograph of acrylated epoxidized soybean oil/poly(dimethylsiloxane), bis(3-aminopropyl) terminated aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5, as described in embodiments herein.

Detailed Description

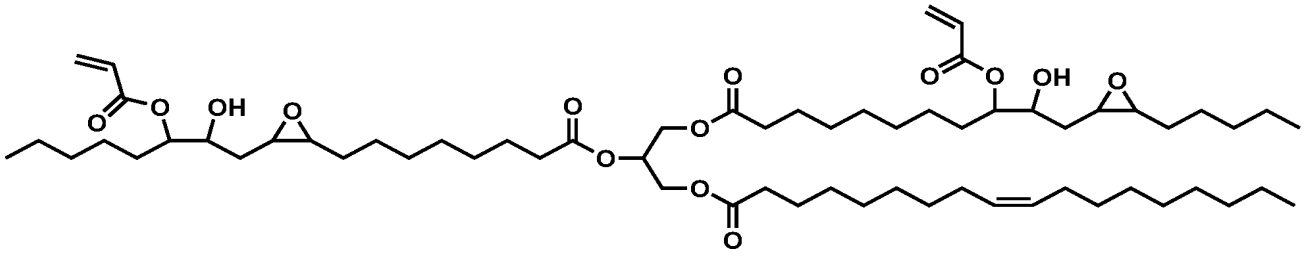
This disclosure relates to a gel composition comprising a "Michael addition elastomer," which is a polymer with elastomeric properties that is chemically cross-linked by 1,4-addition products formed from the reaction between low molecular weight molecules comprising Michael acceptor functional groups and low molecular weight molecules comprising Michael donor functional groups, requiring no purification, and formed in a topically acceptable solvent from the reaction of:

A molecule comprising a Michael acceptor functional group, (A).

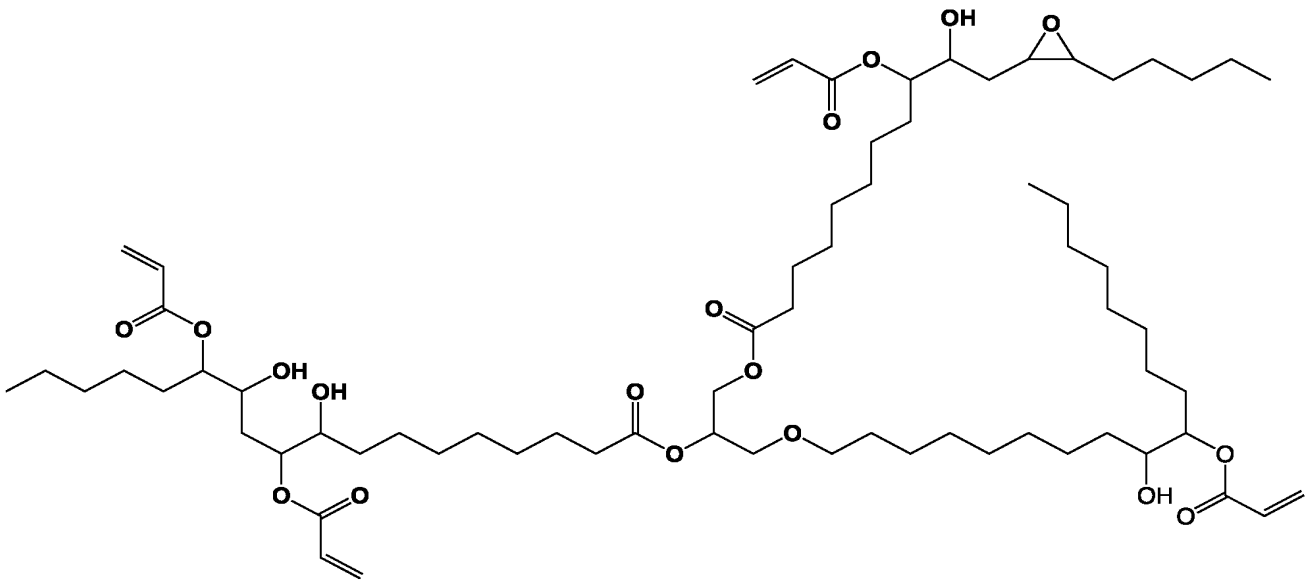
In some embodiments, a first reactant for making the Michael addition elastomer described herein comprises one or more molecules comprising a Michael acceptor functional group, wherein the Michael acceptor functional group comprises two or more electrophilic reaction sites capable of reacting with a Michael donor functional group to form 1,4-addition products.

As used herein, a "Michael acceptor" is a functional group having the structure (I): $R^1R^2C=CR^3$-C(O)-, where R^1, R^2, and R^3 are, independently, hydrogen or organic radicals such as for example, alkyl (linear, branched, or cyclic), aryl, alkaryl, including derivatives and substituted versions thereof. R^1, R^2, and R^3 may or may not, independently, contain ether linkages, carboxyl groups, further carbonyl groups, mercapto groups (also called thiol groups) or analogs thereof, nitrogen containing groups such as amines, hydroxyl groups, or combinations thereof. In one aspect, Component (A) includes one or more siloxane functional groups in its molecular or polymeric structure e.g., in the polymer backbone. In one aspect, Component (A) comprises two or more Michael acceptor functional groups. In a further aspect, Component (A) comprises an OH, SH, or NH functional group at a vicinal position to each of the Michael acceptor functional groups.

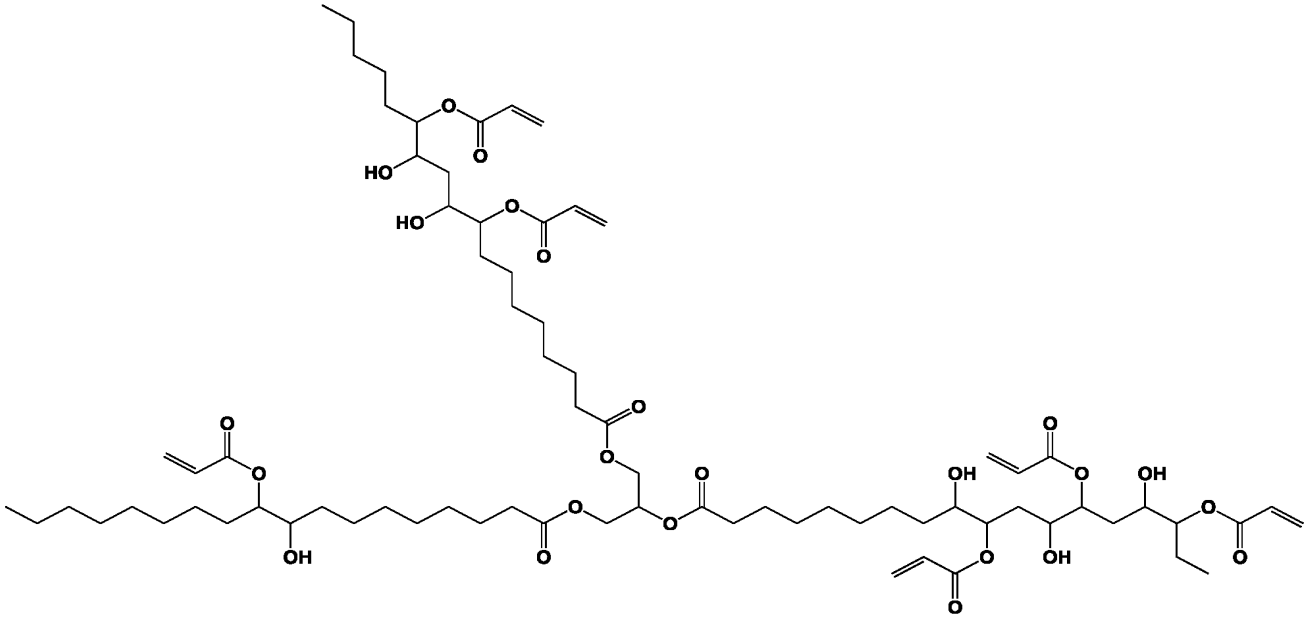
One preferred example of Component (A) is based on soybean oil, linseed oil, or other vegetable oils and has the following representative structure:



A further preferred example of Component (A) is based on soybean oil, linseed oil, or other vegetable oils and has the following representative structure:

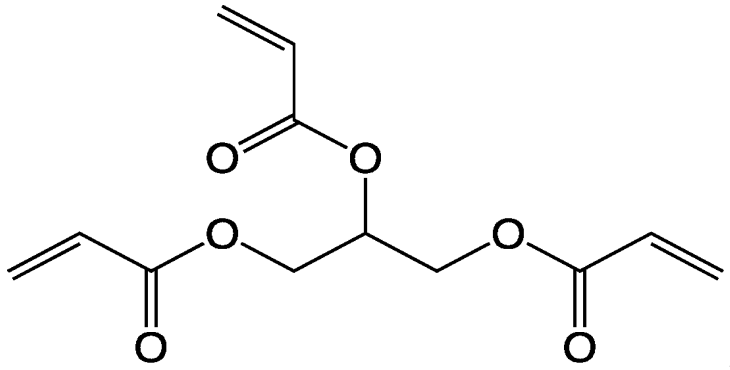


Another preferred example of a Component (A) is based on soybean oil, linseed oil, or other vegetable oils and has the following representative structure:

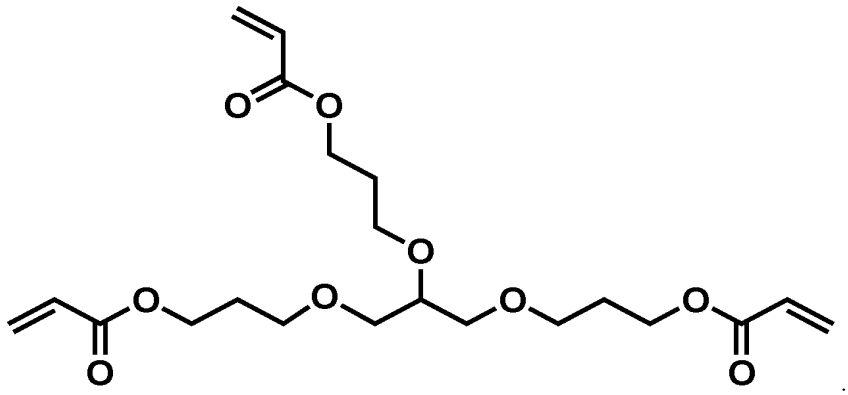


In certain embodiments, Component (A) comprises acrylated epoxidized soybean oil. In some embodiments, Component (A) is prepared from a vegetable oil or mixture thereof, wherein the vegetable oil comprises two or more hydroxyl groups or epoxides. In further embodiments, Component (A) is prepared from linseed oil or soybean oil.

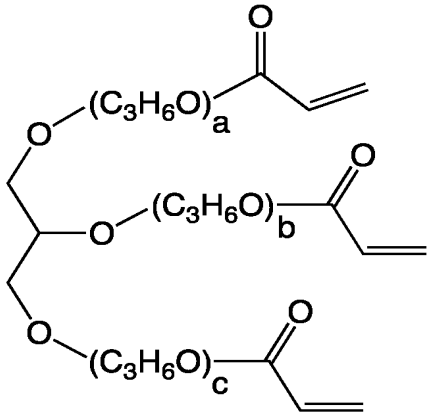
Another preferred example of a Component (A) is trimethylolpropane triacrylate and has the following structure:



Another preferred example of a Component (A) is glyceryl propoxy triacrylate (also referred to as glycerol propoxylate triacrylate) and has the following structure:

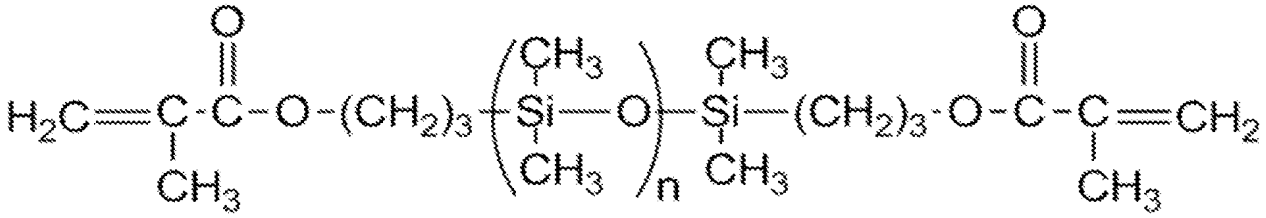


Another preferred example of a Component (A) is a polyether polyol triacrylate and has the following structure:



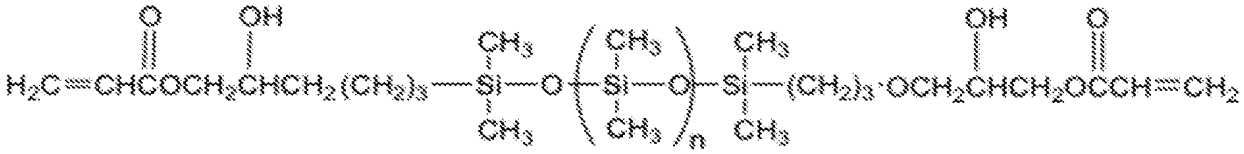
wherein a = an integer from 1 to 30, b = an integer from 1 to 30, and c = an integer from 1 to 30.

Another preferred example of component (A) is methacryloxypropyl terminated polydimethylsiloxane and has the following structure:



wherein n = an integer between 1 and about 10,000.

Another preferred example of component (A) is (3-acryloxy-2-hydroxypropoxypropyl) terminated polydimethylsiloxane and has the following structure:



wherein n = an integer between 1 and about 10,000.

In further embodiments, component (A) comprises a metal. Suitably, the metal can serve as a catalyst for the reaction between a Michael acceptor functional group and Michael donor functional group as described herein. In such embodiments, the metal is coordinated by one or more Michael acceptor functional groups of Component (A). In certain embodiments, the metal comprises a zinc ion. In some embodiments, component (A) comprises a coordinated zinc complex. In one embodiment, component (A) comprises zinc acrylate.

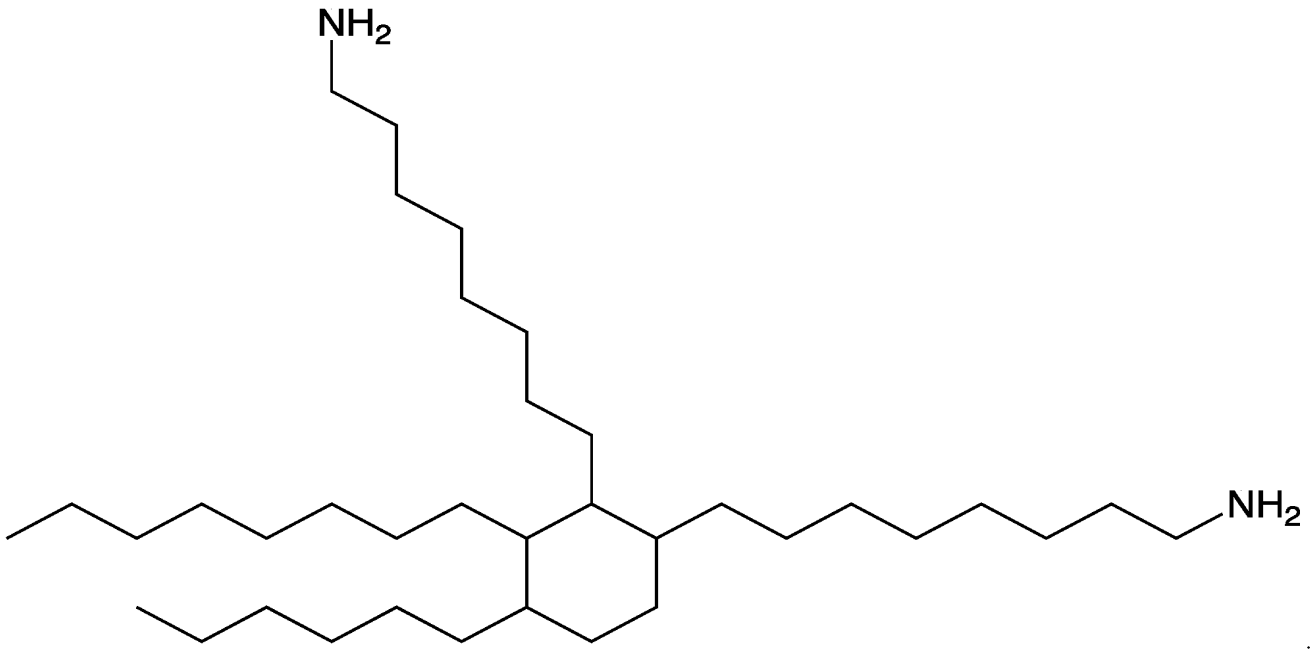
A molecule comprising a Michael donor functional group, (B).

In some embodiments, a second reactant for making the Michael addition elastomer described herein comprises one or more molecules comprising a Michael donor functional group, wherein the Michael donor functional group comprises one or more Michael active hydrogen atoms in its molecule and is capable of reacting with a Michael acceptor functional group to form a 1,4-addition product. As used herein "one or more molecules" is one or more compounds.

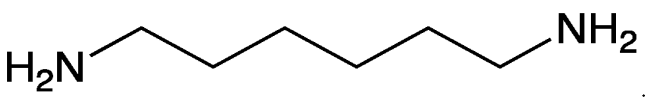
As used herein, a "Michael donor" is a functional group containing at least one Michael active hydrogen atom, which is a hydrogen atom attached to: a carbon atom that is located between two electron-withdrawing groups such as C=O and/or C=N; an oxygen atom; a nitrogen atom; or a sulfur atom. Examples of Michael donor functional groups are malonate esters, acetoacetate esters, malonamides, and acetoacetamides (in which the Michael active hydrogens are attached to the carbon atom between two carbonyl groups); and cyanoacetate esters and cyanoacetamides (in which the Michael active hydrogens are attached to the carbon atom between the carbonyl group and the cyano group); hydroxyl groups; thiol groups; and primary and secondary amines. In some embodiments, the molecule comprises a primary amine. In some embodiments, the molecule comprises a secondary amine. In some embodiments, the molecule comprises a thiol. In some embodiments, the molecule comprises a hydroxyl group. In further embodiments, the molecule comprises a carbon bonded to two Michael donor hydrogen atoms.

One preferred example of component (B) is PRIAMINE™ 1074 from Croda International. Another preferred example of component (B) is PRIAMINE™ 1075 from Croda International. A further preferred example of component (B) is PRIPLAST™ 1074 from Croda International.

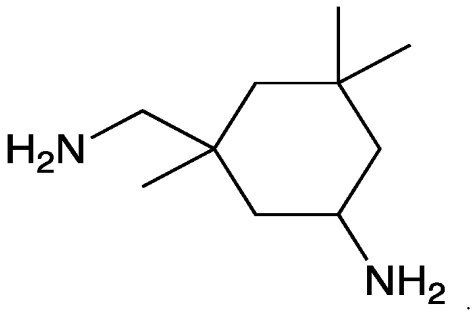
Another preferred example of component (B) is PRIPLAST™ 1075 from Croda International and has the representative molecular structure:



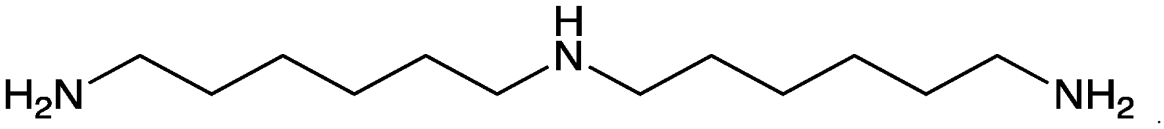
Another preferred example of component (B) is the aliphatic polyamine hexamethylenediamine and has the structure:



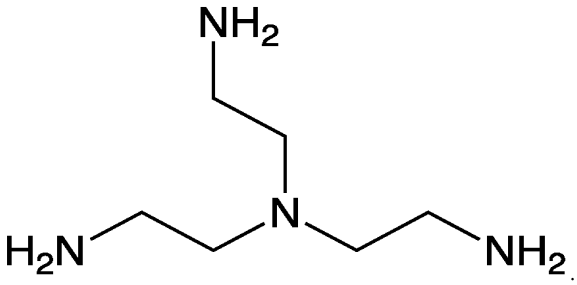
Another preferred example of component (B) is isophorone diamine and has the structure:



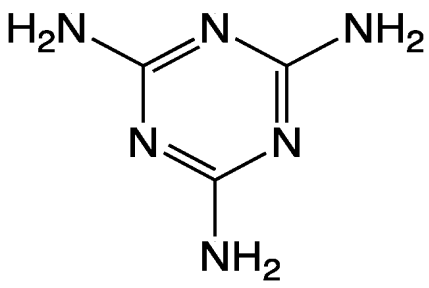
Another preferred example of component (B) is bis(hexamethylene)triamine and has the structure:



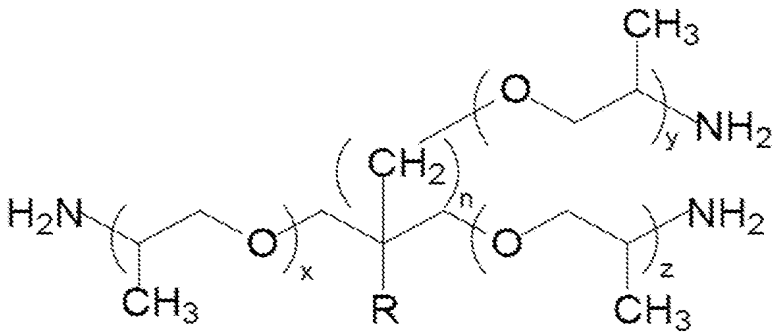
Another preferred example of component (B) is tris(aminoethyl)amine and has the structure:



Another preferred example of component (B) is melamine and has the structure:

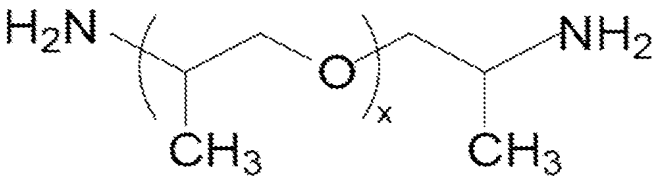


Another preferred example of component (B) is glyceryl poly(oxypropylene) triamine, supplied by Huntsman Corporation as JEFFAMINE® T-403, JEFFAMINE® T-3000, and JEFFAMINE® T-5000 and has the structure:

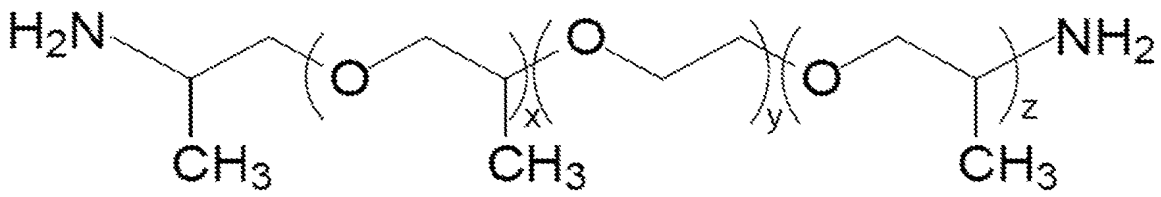


wherein x = an integer from 1 to 30, y = an integer from 1 to 30, and z = an integer from 1 to 30.

Another preferred example of component (B) are polyether diamines supplied by Huntsman Corporation as JEFFAMINE® D Series Diamines and has the following structure:



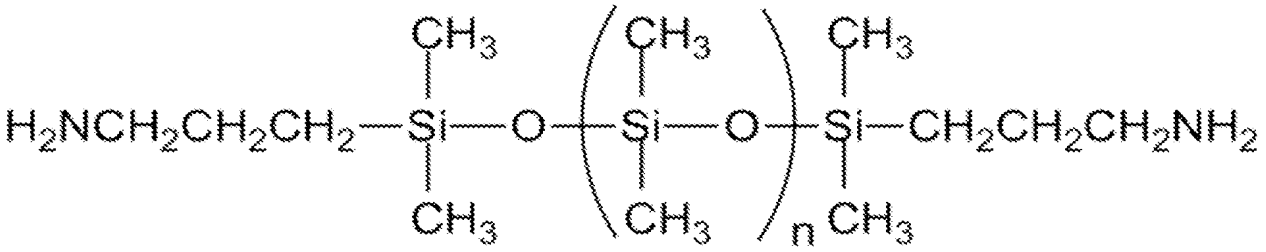
Another preferred example of component (B) are polyether diamines supplied by Huntsman Corporation as JEFFAMINE® ED Series Diamines and has the following structure:



Another preferred example of component (B) is JEFFAMINE® EDR Diamine supplies by Huntsman Corporation has the following structure:

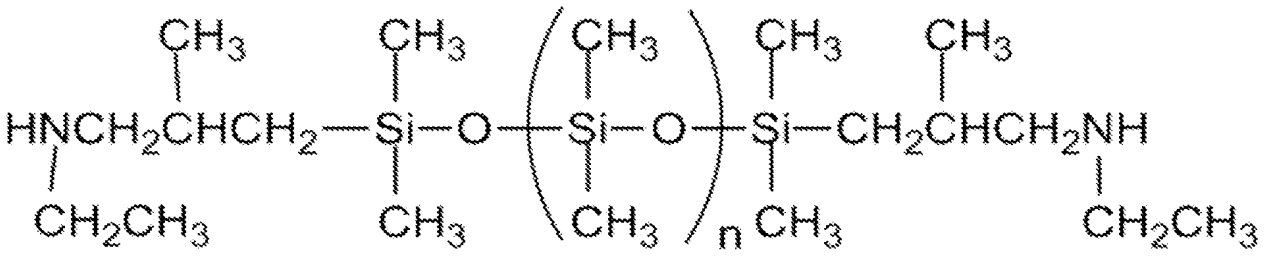


Another preferred example of component (B) is poly(dimethylsiloxane), bis(3-aminopropyl) terminated and has the following structure:

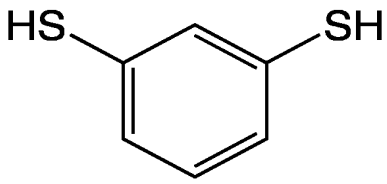


wherein n = is an integer between 1 and about 10,000.

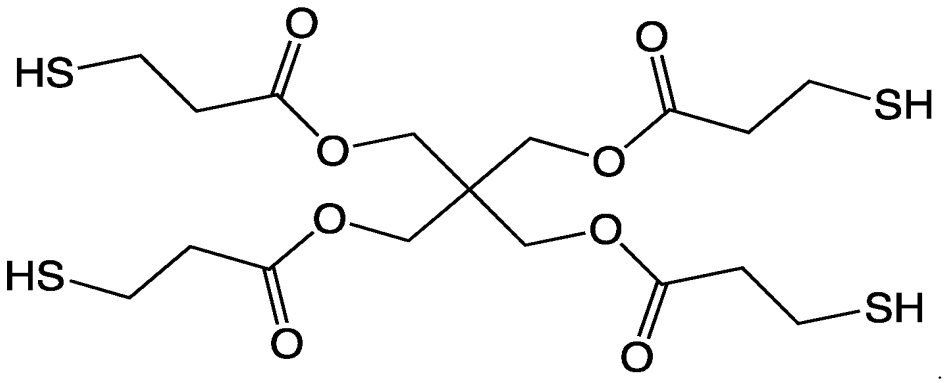
Another preferred example of component (B) is N-ethylaminoisobutyl terminated polydimethylsiloxane and has the following structure:



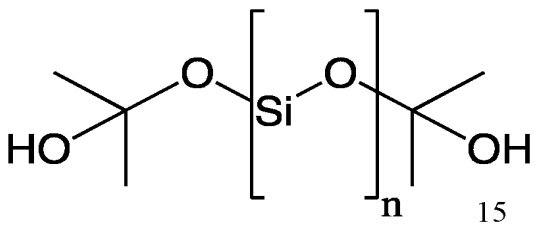
Another preferred example of component (B) is 1,3-benzenedithiol and has the structure:



Another preferred example of component (B) is pentaerythritol tetra(3-mercaptopropionate) and has the structure:

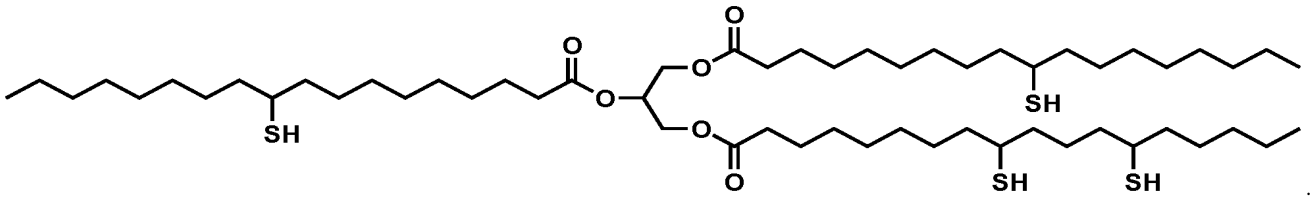


Another preferred example of component (B) is dimethiconol and has the structure:

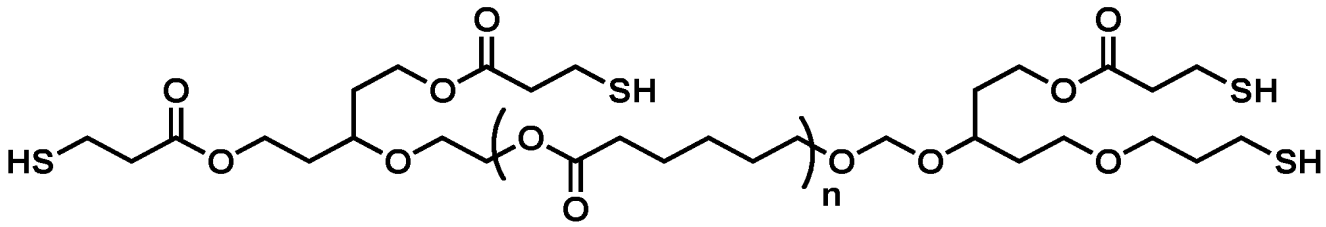


wherein is an integer from n= is an integer from 1 to 100.

Another preferred example of component (B) is mercaptanized soybean oil and has the structure:

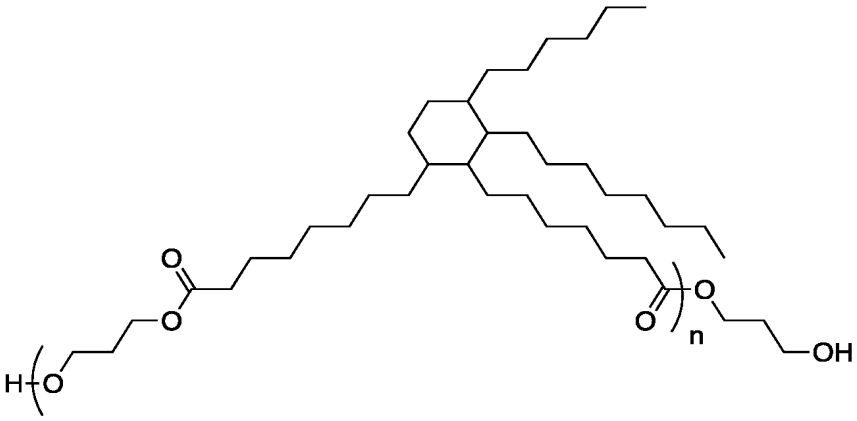


Another preferred example of component (B) is polycaprolactone tetra(3-mercaptopropionate) and has the structure:



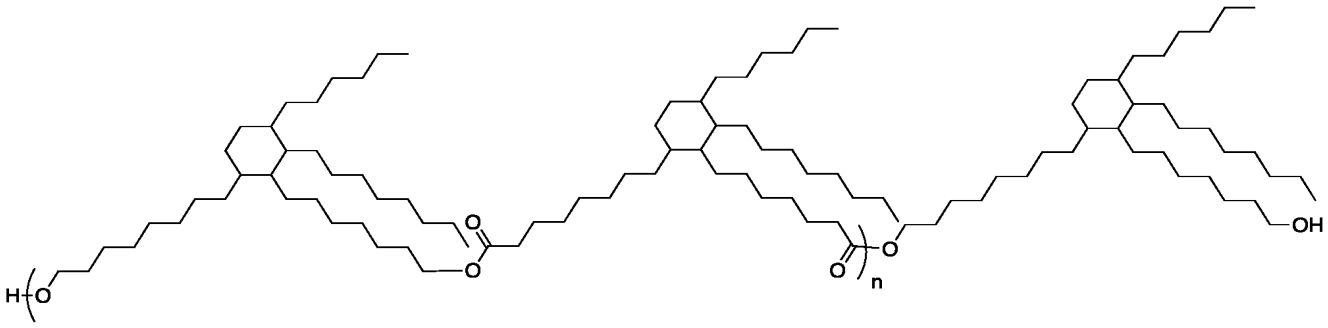
wherein n = is an integer from 1 to 30.

Another preferred example of component (B) is dilinoleic acid /propanediol copolymer and has the representative molecular structure:



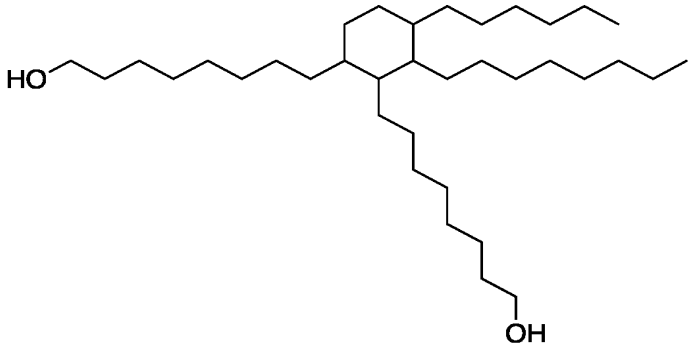
where n = is an integer from 1 to 20.

Another preferred example of component (B) is dilinoleic acid / dilinoleic diol copolymer and has the representative molecular structure:

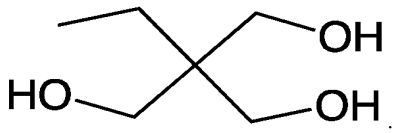


wherein n = is an integer from 1 to 20.

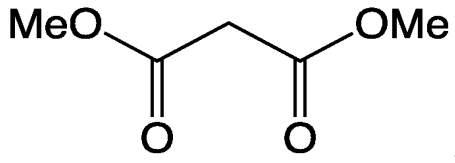
Another preferred example of component (B) is dilinoleic diol and has the representative molecular structure:



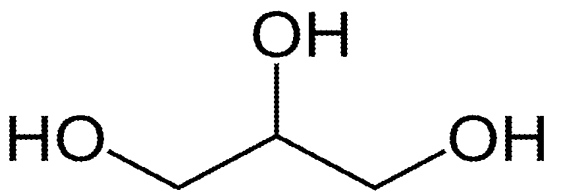
Another preferred example of component (B) is trimethylolpropane and has the structure:



Another preferred example of component (B) is dimethyl malonate and has the structure:



Another preferred example of component (B) is glycerol and has the structure:



An optional reaction catalyst, (C).

Component (C) can be optionally used to increase the rate of elastomer formation. Amine based nucleophilic catalysts are preferred catalysts for the synthesis of Michael addition elastomer gels due to their favorable reactivity profile. Preferably, 1-methylimidazole is used as the Michael addition catalyst. Base and acid catalysis can also be used, depending on the nature of the reactants. Appropriate Michael addition catalysts include but are not limited to:

- Butylamine
- Hexylamine
- Triethylamine
- Triethylenediamine
- p-Toluenesulfonic acid
- N,N,N',N",N"-Pentamethyldiethylenetriamine
- 1,2-Dimethylimidazole
- N,N,N',N'-Tetramethyl-1,6-hexanediamine
- N,N',N'-Trimethylaminoethylpiperazine
- 1,1'-[[3-(dimethylamino)propyl]imino]bispropan-2-ol
- N,N,N'-Trimethylaminoethylethanolamine
- N,N',N"-Tris(3-dimethylaminopropyl)-hexahydro-s-triazine
- 1,4-diazabicyclo[2.2.2]octane
- 1,5,7-Triazabicyclo[4.4.0]dec-5-ene
- Stannous octoate
- Stannous oxalate
- Stannous oxide
- Stannous chloride
- Dioctyltin di(2-hexylhexanoate)-solution
- Dioctyltin dithioglycolate

- Dioctyltin dilaurate
- Dioctyltin oxide blend
- Dibutyltin dilaurate
- Monobutyl tin tris-(2-ethylhexanoate)
- Dioctyltin diketanoate
- Dioctyltin diacetate
- Dioctyltin oxide
- Dibutyltin diacetate
- Modified dibutyltin diacetate
- Dibutyltin oxide
- Monobutyltin dihydroxychloride
- Organotin oxide
- Monobutyltin oxide
- Dioctyltin dicarboxylate
- Dioctyltin carboxylate
- Dioctyltin stannoxane
- Zinc neodecanoate
- Zinc octoate
- Zinc acetylacetonate
- Zinc oxalate
- Zinc acetate
- Bismuth carboxylates
- $Bi(OTf)_3$
- Zinc neodecanoate

A Carrier Fluid, (D).

The Michael addition elastomer may be contained in an optional carrier fluid (D). Carrier fluids include any suitable solvent that can be used to prepare the Michael addition elastomer. In exemplary embodiments, the carrier fluid is a "topically acceptable carrier fluid" which is a solvent for topical use on cutaneous surfaces i.e. skin, lips, mucous membranes, etc. Although it is not required, typically the carrier fluid may be the same as the solvent used for conducting the elastomer reaction as described above. The carrier fluid used for the synthesis of the Michael addition elastomer

gel and gel paste can be fully, partially, or not bio-based. The carrier fluid, including a topically acceptable carrier fluid, preferably has a viscosity between 1-65 mPas at 20 °C. The spreading value of the carrier fluid, including the topically acceptable carrier fluid, is preferably between 500-2500 mm^2/10 min. Appropriate topically acceptable carrier fluids for the synthesis of the Michael addition elastomer gel and processing of the Michael addition elastomer gel include but are not limited to esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof, and include:

- Bis-Diglyceryl Polyacyladipate-1
- Bis-Diglyceryl Polyacyladipate-2
- Butylene Glycol Dicaprylate/Dicaprate
- Butyrospermum Parkii Butter
- Caprylic/Capric Glycerides
- Caprylic/Capric Triglyceride
- Caprylic/Capric/Myristic/Stearic Triglyceride
- Caprylic/Capric/Succinic Triglyceride
- Caprylyl Methicone
- Coco-Caprylate/Caprate
- Cyclotetrasiloxane
- Decamethylcyclopentasiloxane
- Decyl Oleate
- Dimethiconol
- Diphenylsilanediol
- Dodecamethylcyclohexasiloxane
- Ethyl trisiloxane
- Glyceryl Caprylate
- Glyceryl Citrate/Lactate/Linoleate/Oleate
- Glyceryl Cocoate
- Glyceryl Isostearate
- Glyceryl Oleate
- Glyceryl Ricinoleate
- Glyceryl Ricinoleate, Tocopherol
- Glyceryl Stearate

- Glyceryl Stearate Citrate
- Hexamethyldisilazane
- Hexamethyldisiloxane
- Hydrogenated Coco-Glycerides
- Hydrogenated Palm Oil
- Hydroxytrimethylsilane
- Isopropoxytrimethylsilane
- Methylheptyl Isostearate
- Octamethylcyclotetrasiloxane
- Oleyl Erucate
- Olus Oil
- Organo-modified Siloxanes
- Organosilicone Fluids
- PCA Glyceryl Oleate
- PEG-6 Caprylic/Capric Glycerides
- Phenyltrichlorosilane
- Poly(dimethyl siloxane)
- Poly(ethylene glycol)-containing siloxanes
- Polydimethylsiloxane
- Polyglyceryl-2 Caprate
- Polyglyceryl-3 Caprate
- Polyglyceryl-3 Diisostearate
- Polyglyceryl-3 Polyricinoleate
- Polyglyceryl-4 Cocoate
- Propylene Carbonate
- Propylene Glycol Dicaprylate/Dicaprate
- Silicone oil
- Stearalkonium Bentonite
- Stearalkonium Hectorite
- Triheptanoin
- Trimethyl(bromodifluoromethyl)silane

- Trimyristin
- Tristearin

In some embodiments, the topically acceptable carrier fluid is at a concentration of 0% (w/w) to 99.9% (w/w) of the gel composition. In further embodiments, the topically acceptable carrier fluid is 20% (w/w) to 99.9% (w/w) of the gel composition. In additional embodiments, the topically acceptable carrier fluid is 60% (w/w) to 99.9% (w/w) of the gel composition.

In some embodiments, the topically acceptable carrier fluid comprises triheptanoin, diisooctyl succinate, caprylic/capric triglyceride, heptyl undecylenate, neopentyl glycol diheptanoate, coco-caprylate/caprate, diisopropyl adipate, isoamyl laurate, isopropyl myristate, jojoba esters, methylheptyl Isostearate, neopentyl glycol diheptanoate, dicaprylin caprylic/capric/myristic/stearic triglyceride, caprylic/capric/succinic triglyceride, ethyl hexyl olivate, C15-C16 branched alkanes, C17-C18 branched alkanes, dodecane, hexadecane, squalene, hemisqualane, tetradecane, undecane, tridecane, coconut alkanes, C9-12 alkane, or combinations thereof. In some embodiments, the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

The Active, (E).

Component (E) is a "pharmaceutically active ingredient," and suitably an active selected from any personal active ingredient or health care active ingredient. As used herein, a "personal care active ingredient" means any compound or mixtures of compounds that are known in the art as additives in the personal care formulations that are typically added for the purpose of treating skin, lips or to provide a cosmetic and/or aesthetic benefit. A "healthcare active ingredient" means any compound or mixtures of compounds that are known in the art to provide a pharmaceutical or medical benefit. Thus, "healthcare active ingredient" includes materials considered as active ingredient or active drug ingredient as generally used and defined by the United States Department of Health & Human Services Food and Drug Administration, contained in Title 21, Chapter I, of the Code of Federal Regulations, Parts 200-299 and Parts 300-499. Thus, pharmaceutically active ingredient can include any component that is intended to furnish pharmacological activity or other direct effect in the diagnosis, cure, mitigation, treatment, or prevention of disease, or to affect the structure or any function of the body of a human or other animals. The phrase can include those components that may undergo chemical change in the manufacture of drug products and be present in drug products in a modified form intended to furnish the specified activity or effect.

Some representative examples of pharmaceutically active ingredients include; drugs, vitamins, minerals; hormones; topical antimicrobial agents such as antibiotic active ingredients, antifungal active ingredients for the treatment of athlete's foot, jockitch, or ringworm, and acne active ingredients; astringent active ingredients; deodorant active ingredients; wart remover active ingredients; corn and callus remover active ingredients; pediculicide active ingredients for the treatment of head, pubic (crab), and body lice; active ingredients for the control of dandruff, seborrheic dermatitis, or psoriasis; and Sunburn prevention and treatment agents.

Useful pharmaceutically active ingredients for use in processes according to the invention include Vitamins and their derivatives, including "pro-vitamins". Vitamins useful herein include, but are not limited to, Vitamin A, retinol, C-C esters of retinol, Vitamin E, tocopherol, esters of vitamin E, and mixtures thereof. Retinol includes trans-retinol, 1.3-cis-retinol, 11-cis-retinol, 9-cis-retinol, and 3,4-didehydro-retinol, Vitamin C and its derivatives, Vitamin B, Vitamin B. Pro Vitamin B5, panthenol, Vitamin B. Vitamin B2, niacin, folic acid, biotin, and pantothenic acid. Other suitable vitamins and the INCI names for the vitamins considered included herein are ascorbyl dipalmitate, ascorbyl methylsilanol pectinate, ascorbyl palmitate, ascorbyl Stearate, ascorbyl glucoside, sodium ascorbyl phosphate, sodium ascorbate, disodium ascorbyl sulfate, potassium (ascorbyl/tocopheryl)phosphate.

Retinol, it should be noted, is an International Nomenclature Cosmetic Ingredient Name (INCI) designated by The Cosmetic, Toiletry, and Fragrance Association (CTFA), Washington D.C., for vitamin A. Other suitable vitamins and the INCI names for the vitamins considered included herein are retinylacetate, retinyl palmitate, retinyl propionate, o-tocopherol tocophersolan, tocopheryl acetate, tocopheryl linoleate, tocopheryl nicotinate, and tocopheryl succinate.

The pharmaceutically active ingredient used in processes according to the invention can be an active drug ingredient. Representative examples of some suitable active drug ingredients which can be used are hydrocortisone, ketoprofen, timolol, pilocarpine, adriamycin, mitomycin C, morphine, hydromorphone, diltiazem, theophylline, doxorubicin, daunorubicin, heparin, penicillin G, carbenicillin, cephalothin, cefoxitin, cefotaxime, 5-fluorouracil, cytarabine, 6-azauridine, 6-thioguanine, vinblastine, Vincristine, bleomycin sulfate, aurothioglucose, suramin, mebendazole; clonidine, scopolamine, propranolol, phenylpropanolamine hydrochloride, ouabain, atropine, haloperidol, isosorbide, nitroglycerin, ibuprofen, ubiquinones, indomethacin, prostaglandins, naproxen, Salbutamol, guanaben Z, labetalol, pheniramine, metrifonate, and steroids.

Considered to be included herein as active drug ingredients for purposes of the present invention are antiacne agents such as benzoyl peroxide and tretinoin; antibacterial agents such as

chlorohexadiene gluconate; antifungal agents such as miconazole nitrate; anti-inflammatory agents; corticosteroidal drugs; non-steroidal anti-inflammatory agents such as diclofenac; antipsoriasis agents such as clobetasol propionate; anesthetic agents such as lidocaine; antipruritic agents; antidermatitis agents; and agents generally considered barrier films.

The active component (E) of the present invention can be a protein, such as an enzyme. The internal inclusion of enzymes in the Michael addition elastomer gel have advantages to prevent enzymes from deactivating and maintain bioactive effects of enzymes for longer time. Enzymes include, but are not limited to, commercially available types, improved types, recombinant types, wild types, variants not found in nature, and mixtures thereof. For example, suitable enzymes include hydrolases, cutinases, oxidases, transferases, reductases, hemicellulases, esterases, isomerases, pectinases, lactases, peroxidases, laccases, catalases, and mixtures thereof. Hydrolases include, but are not limited to, proteases (bacterial, fungal, acid, neutral or alkaline), amylases (alpha orbeta), lipases, mannanases, cellulases, collagenases, lisozymes, superoxide dismutase, catalase, and mixtures thereof. Said proteases include, but are not limited to, trypsin, chymotrypsin, pepsin, pancreatin and other mammalian enzymes; papain, bromelain and other botanical enzymes; subtilisin, epidermin, nisin, naringinase(L-rhammnosidase) urokinase and other bacterial enzymes. Said lipases include, but are not limited to, triacyl-glycerol lipases, monoacyl glycerol lipases, lipoprotein lipases, e.g. steapsin, erepsin, pepsin, other mammalian, botanical, bacterial lipases and purified ones. Natural papain is preferred as said enzyme. Further, stimulating hormones, e.g. insulin, can be used together with these enzymes to boost the effectiveness of them.

The pharmaceutically active ingredient may also be a sunscreen agent. The Sunscreen agent can be selected from any Sunscreen agent known in the art to protect skin from the harmful effects of exposure to sunlight. The sunscreen compound is typically chosen from an organic compound, an inorganic compound, or mixtures thereof that absorbs ultraviolet (UV) light. Thus, representative non limiting examples that can be used as the sunscreen agent include; aminobenzoic acid, cinoxate, diethanolamine methoxycinnamate, digalloyl trioleate, dioxybenzone, ethyl 4-bis(Hydroxypropyl) aminobenzoate, glyceryl aminobenzoate, homosalate, lawsone with dihydroxyacetone, menthyl anthranilate, octocrylene, octyl methoxycinnamate, octyl salicylate, oxybenzone, padimate O, phenylbenzimidazole sulfonic acid, red petrolatum, sulisobenzone, titanium dioxide, trolamine salicylate, cetarninosalol, allatoin, PABA, benzalphthalide, benzophenone, benzophenone 1-12, 3-benzylidene camphor, benzylidenecamphor hydrolyzed collagen sulfonamide, benzylidene camphor sulfonic acid, benzyl salicylate, bomelone, bumetriozole, butyl methoxydibenzoylmethane, butyl PABA, ceria/silica, ceria/silica talc, cinoxate, DEA-methoxycinnamate, dibenzoxazol naphthalene,

di-t-butyl hydroxybenzylidene camphor, digalloyl trioleate, diisopropyl methyl cinnamate, dimethyl PABA ethyl cetearyldimonium tosylate, dioctyl butamido triazone, diphenyl carbomethoxy acetoxy naphthopyran, disodium bisethylphenyl tiamminotriazine stilbenedisulfonate, disodium sistyrylbiphenyl triaminotriazine stilbenedisulfonate, disodium distyrylbi phenyl disulfonate, drometrizole, drometrizole trisiloxane, ethyl dihydroxypropyl PABA, ethyl diisopropylcinnamate, ethyl methoxycinnamate, ethyl PABA, ethyl urocanate, etrocrylene ferulic acid, glyceryl octanoate dimethoxycin namate, glyceryl PABA, glycol salicylate, homosalate, isoamyl p-methoxycinnamate, isopropylbenzyl salicylate, isopropyl dibenzolylmethane, isopropyl methoxycinnamate, menthyl anthranilate, menthyl salicylate, 4-methylbenzylidene, camphor, octocrylene, octrizole, octyl dimethyl PABA, octyl methoxycinnamate, octyl salicylate, octyl triazone, PABA, PEG-25 PABA, pentyl dimethyl, PABA, phenylbenzimidazole sulfonic acid, polyacrylamidomethyl benzylidene camphor, potassium methoxycinnamate, potassium phenylbenzimidazole sulfonate, red petrolatum, sodium phenylbenzimidazole sulfonate, sodium urocanate, TEA-phenylbenzimidazole sulfonate, TEA-salicylate, terephthalylidene dicamphor sulfonic acid, titanium dioxide, zinc dioxide, serium dioxide, TriPABA panthenol, urocanic acid, and VA/crotonates/ methacryloxybenzophenone-1 copolymer.

The Sunscreen agent can be a single one or combination of more than one. Alternatively, the Sunscreen agent is a cinnamate based organic compound, or alternatively, the Sunscreen agent is octyl methoxycinnamate, Such as Uvinul R. MC 80 an ester of para-methoxycinnamic acid and 2-ethyl hexanol.

Component (E) may also be a fragrance or perfume. The perfume can be any perfume or fragrance active ingredient commonly used in the perfume industry. These compositions typically belong to a variety of chemical classes, as varied as alcohols, aldehydes, ketones, esters, ethers, acetates, nitrites, terpenic hydrocarbons, heterocyclic nitrogen or Sulfur containing compounds, as well as essential oils of natural or synthetic origin. Many of these perfume ingredients are described in detail in standard textbook references such as Perfume and Flavour Chemicals, 1969, S. Arctander, Montclair, N.J.

Fragrances may be exemplified by, but not limited to, perfume ketones and perfume aldehydes. Illustrative of the perfume ketones are buccoxime; isojasmone; methyl beta naphthyl ketone; musk indanone; tonalid/musk plus; Alpha Damascone, Beta-Damascone, Delta-Damascone, Iso Damascone, Damascenone, Damarose, Methyl Dihydrojasmonate, Menthone, Carvone, Camphor, Fenchone, Alpha-lonone, Beta-lonone, Gamma-Methyl So called lonone, Fleuramone, Dihydrojasmone, Cis-Jasmone, Iso-E-Super, Methyl-Cedrenyl-ketone or Methyl-Cedrylone,

Acetophenone, Methyl-Acetophenone, Para-Methoxy-Acetophenone, Methyl-Beta-Naphtyl-Ketone, Benzyl-Acetone, Benzophenone, Para-Hydroxy-Phenyl-Butanone, Celery Ketone or LiveScone, 6-Isopropyldecahydro-2-naphtone, Dimethyloctenone, Freskomenthe, 4-(1-Ethoxyvinyl)-3,3, 5.5,-tetramethyl-Cyclohexanone, Methyl heptenone, 2-(2-(4-Methyl-3-cyclohexen-1-yl)propyl)-cyclopentanone, 1-(p- Menthen-6(2)-yl)-1-propanone, 4-(4-Hydroxy-3- methoxyphenyl)-2-butanone, 2-Acetyl-3,3-Dimethyl Norbornane, 6,7-Dihydro-1,1,2,3,3-Pentamethyl-4(5H)- Indanone, 4-Damascol, Dulcinyl or Cassione, Gelsone, Hexylon, Isocyclemone E, Methyl Cyclocitrone, Methyl Lavender-Ketone, Orivon, Para-tertiary-Butyl-Cyclohexanone, Verdone, Delphone, Muscone, Neobutenone, Plica tone, Veloutone, 2,4,4,7-Tetramethyl-oct-6-en-3-one, and Tetrameran.

More preferably, the perfume ketones are selected for their odor character from Alpha Damascone, Delta Damascone, Iso Damascone, Carvone, Gamma-methyl-ionone, Iso-E-Super, 2.4.4.7-Tetramethyl-oct-6-en-3-one, Benzyl Acetone, Beta Damascone, Damascenone, methyl dihydrojasmonate, methyl cedrylone, and mixtures thereof.

Preferably, the perfume aldehyde is selected for its odor character from adoxal, anisic aldehyde, cymal, ethylvanillin, florhydral, helional, heliotropin, hydroxycitronellal, koavone, lauric aldehyde, lyral, methyl nonyl acetaldehyde, P. T. bucinal, phenyl acetaldehyde, undecylenic aldehyde, vanillin, 2,6,10-trimethyl-9-undecenal, 3-dodecen-1-al, alpha-n-amyl cinnamic aldehyde, 4-methoxybenzaldehyde, benzaldehyde, 3-(4-tert-butylphenyl)-propanal, 2-methyl-3-(para-methoxyphenyl propanal, 2-methyl-4-(2,6,6-trimethyl-2(1)-cyclohexen-1-yl) butanal, 3-phenyl-2-propenal, cis-/trans-3,7-dimethyl-2,6-octadien-1-al, 3,7-dimethyl-6-octen-1-al. (3,7-dimethyl-6-octenyl)oxyacetaldehyde, 4-isopropylbenzyaldehyde, 1,2,3,4,5,6,7,8-octahydro-8,8-dimethyl-2-naphthaldehyde, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, 2-methyl-3-(isopropylphenyl)propanal, 1-decanal; decyl aldehyde, 2,6-dimethyl-5-heptenal, 4-(tricyclo[5.2.1.0(2,6)-decylidene-8)-butanal, octahydro-4,7-methano-1H-indenecarboxaldehyde, 3-ethoxy-4-hydroxy benzaldehyde, para-ethyl-alpha,alpha-dimethyl hydrocinnamaldehyde, alpha-methyl-3,4-(methylenedioxy)-hydrocinnamaldehyde, 3,4-methylenedioxybenzaldehyde, alpha-n-hexyl cinnamic aldehyde, m-cymene-7-carboxaldehyde, alpha-methyl phenyl acetaldehyde, 7-hydroxy-3,7-dimethyl octanal, Undecenal, 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde, 4-(3)(4-methyl-3-pentenyl)-3-cyclohexen-carboxaldehyde, 1-dodecanal, 2,4-dimethyl cyclohexene-3-carboxaldehyde, 4-(4-hydroxy-4-methylpentyl)-3-cylohexene 1-carboxaldehyde, 7-methoxy-3,7-dimethyloctan-1-al, 2-methyl undecanal, 2-methyl decanal, 1-nonanal, 1-octanal, 2,6,10-trimethyl-5.9-undecadienal, 2-methyl-3-(4-tertbutyl) propanal, dihydrocinnamic aldehyde, 1-methyl-4-(4-methyl 3-pentenyl)-3-cyclohexene-1-carbox aldehyde, 5 or 6 methoxyl-hexahydro-4,7-

methanoindan-1 or 2-carboxaldehyde, 3,7-dimethyloctan-1-al, 1-undecanal, 10-undecen-1-al, 4-hydroxy-3-methoxy benzaldehyde, 1-methyl-3-(4-methylpentyl)-3-cyclhexenecarboxaldehyde, 7-hydroxy-3,7-dimethyl octanal, trans-4-decenal, 2,6-nonadienal, paratolylacetaldehyde, 4-methylphenylacetaldehyde, 2-me thyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butenal, ortho-methoxycinnamic aldehyde, 3,5,6-trimethyl-3-cyclohexene carboxaldehyde, 3,7-dimethyl-2-methylene-6-octenal, phenoxyacetaldehyde, 5,9-dimethyl-4,8-decadienal, peony aldehyde (6,10-dimethyl-3-oxa-5,9-undecadien-1-al), hexahydro-4,7-methanoindan-1-carboxaldehyde, 2-methyloctanal, alpha-methyl-4-(1-methylethyl)benzene acetaldehyde, 6,6-dimethyl-2-norpinene-2-propionaldehyde, para-methyl phenoxyacetaldehyde, 2-methyl-3-phenyl-2-propen-1-al, 3,5,5-trimethylhexanal, Hexahydro-8,8-dimethyl-2-naphthaldehyde, 3-propyl-bicyclo[2.2.1-hept-5-ene-2-carbaldehyde, 9-decenal, 3-methyl-5-phenyl-1-pentanal, methylnonyl acetaldehyde, hexanal, trans-2-hexenal, 1-pmenthene- q-carboxaldehyde and mixtures thereof. More preferred aldehydes are selected for their odor character from 1-decanal, benzaldehyde, florhydral, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, cis/trans-3,7-dim ethyl-2,6-octadien-1-al, heliotropin, 2,4,6-trimethyl-3- cyclohexene-1-carboxaldehyde, 2,6-nonadienal, alphanamyl cinnamic aldehyde, alpha-n-hexyl cinnamic aldehyde, P.T. Bucinal, lyral, cymal, methylnonyl acetaldehyde, hexanal, trans-2-hexenal, and mixture thereof. In the above list of perfume ingredients, some are commercial names conventionally known to one skilled in the art, and also includes isomers. Such isomers are also suitable for use in the present invention.

Component (E) may also be one or more plant extract. Examples of these components are as follows: Ashitaba extract, avocado extract, hydrangea extract, Althea extract, Arnica extract, aloe extract, apricot extract, apricot kernel extract, Ginkgo Biloba extract, fennel extract, turmeric Curcuma extract, oolong tea extract, rose fruit extract, Echinacea extract, Scutellaria root extract, Phellodendro bark extract, Japanese Coptis extract, Barley extract, Hyperium extract, White Nettle extract, Watercress extract, Orange extract, Dehydrated saltwater, seaweed extract, hydrolyzed elastin, hydrolyzed wheat powder, hydrolyzed silk, Chamomile extract, Carrot extract, Artemisia extract, Glycyrrhiza extract, hibiscustea extract, Pyracantha Fortuneana Fruit extract, Kiwi extract, Cinchona extract, cucumber extract, guanocine, Gardenia extract, Sasa albomarginata extract, Sophora root extract, Walnut extract, Grapefruit extract, Clematis extract, Chlorella extract, mulberry extract, Gentiana extract, black tea extract, yeast extract, burdock extract, rice bran ferment extract, rice germ oil, comfrey extract, collagen, cowberry extract, Gardenia extract, Asiasarum root extract, Family of Bupleurum extract, umbilical cord extract, Salvia extract, Saponaria extract, Bamboo extract, Crataegus fruit extract, Zanthoxylum fruit extract, Shiitake extract, Rehmannia root extract,

gromwell extract, Perilla extract, linden extract, Filipendula extract, peony extract, calamus root extract, white birch extract, Horsetail extract, Hedera Helix(Ivy) extract, hawthorn extract, Sambucus migra extract, Achillea millefolium extract, Mentha piperita extract, sage extract, mallow extract, Cnidium officinale root extract, Japanese green gen tian extract, Soybean extract, jujube extract, thyme extract, tea extract, clove extract, Gramineae imperata cyrillo extract, citrus unshiu peel extract Japanese angelica root extract, calendula extract, peach kernel extract, Bitter orange peel extract, Houttuyna cordata extract, tomato extract, natto extract, ginseng extract, green tea extract (camelliea sine sis), garlic extract, wild rose extract, hibiscus extract, Ophio pogon tuber extract, Nelumbo nucifera extract, parsley extract, honey, hamamelis extract, parietaria extract, isodonis herba extract, bisabolol extract, Loquat extract, coltsfoot extract, butterbur extract, Porid cocos wolf extract, extract of butcher's broom, grape extract, propolis extract, lufa extract, safflower extract, peppermintextract, linden tree extract, Paeonia extract, hop extract, pine tree extract, horse chestnut extract, Mizu-bashou Lysichiton camtschatcese extract, Mukurossi peel extract, Melissa extract, peach extract, corn flower extract, eucalyptus extract, saxifrage extract, citron extract, coix extract, mugwort extract, lavender extract, apple extract, lettuce extract, lemon extract, Chinese milk vetch extract, rose extract, rosemary extract, Roman Chamomile extract, and royal jelly extract.

The amount of component (E) present in the Michael addition elastomer gel composition may vary, but typically range as follows: 0.05 to 50 wt %, alternatively 1 to 25 wt %, or alternatively 1 to 10 wt %, based on the amount by weight of Michael addition elastomer gel present in the composition, that is total weight of components (A), (B), (C) and (D) in the Michael addition elastomer gel composition.

The active, component (E), may be added to the Michael addition elastomer gel composition either during the making of the Michael addition elastomer (pre-load method), or added after the formation of the Michael addition elastomer gel (post load method).

The pre-load method involves:

I) mixing:

A) a first reactant comprising one or more molecules, wherein each of the one or more molecules comprises two or more Michael acceptor groups;

B) a second reactant comprising one or more molecules, wherein each of the one or more molecules comprises a Michael donor functional group with two or more Michael donor hydrogen atoms, such that the Michael donor functional group is capable of reacting with a Michael acceptor functional group to form a 1,4-addition product;

C) an optional reaction catalyst; and

D) a topically acceptable carrier fluid, at a concentration of 20% (w/w) to 99.9% (w/w) of the gel composition, preferably 60% (w/w) to 99.9% (w/w) of the gel composition; and

E) a personal care or healthcare active with the Michael addition elastomer gel to form the Michael addition elastomer gel containing active.

In some embodiments, the Michael donor function group comprises a primary or secondary amine, a thiol, a hydroxyl group or a carbon bonded to two Michael donor hydrogen atoms.

The post-load method involves;

I) mixing:

A) a first reactant comprising one or more molecules, wherein each of the one or more molecules comprises two or more Michael acceptor groups;

B) a second reactant comprising one or more molecules, wherein each of the one or more molecules comprises a Michael donor functional group with two or more Michael donor hydrogen atoms, such that the Michael donor functional group is capable of reacting with a Michael acceptor functional group to form a 1,4-addition product;

C) an optional reaction catalyst; and

D) a topically acceptable carrier fluid, at a concentration of 20% (w/w) to 99.9% (w/w) of the gel composition, preferably 60% (w/w) to 99.9% (w/w) of the gel composition,

thereby forming a Michael addition elastomer gel;

II) shearing the Michael addition elastomer gel into a smooth paste; and

III) admixing:

E) a personal care or healthcare active with the Michael addition elastomer gel to form a Michael addition elastomer gel containing active. The personal care active may also be admixed as a component of another mixture with one or more excipients.

In some embodiments, the Michael donor function group comprises a primary or secondary amine, a thiol, a hydroxyl group or a carbon bonded to two Michael donor hydrogen atoms.

The Michael Addition Elastomers.

The Michael addition elastomers of the present invention are obtainable as Michael addition reaction products of components (A), (B), and (C) in (D). The term “Michael addition reaction” means the addition of a first reactant containing one or more Michael donor functional groups (such as component (B) to a second reactant containing one or more Michael acceptor functional groups (such as component (A)), optionally in the presence of a catalyst (such as component (C)). The Michael

addition reaction may be conducted at room temperature or at elevated temperatures up to 120 °C. In some embodiments, the reaction mixture is heated from about 50 °C to about 120 °C, preferably to about 100 °C. In some embodiments, the molar ratio of the first reactant to the second reactant is 1:1. Alternatively, this ratio can range from 8:1 to 0.5:1. In embodiments, the first reactant comprises an acrylate group (e.g., acrylated epoxidized soybean oil or glycerol propoxylate triacrylate), the second reactant comprises a primary amine (e.g., PRIPLAST™ 1075, PRIMAMINE™ 1074, JEFFAMINE® T-403, JEFFAMINE® T-3000, or poly(dimethylsiloxane), or bis(3-aminopropyl) terminated), and the ratio of primary amines to acrylate groups is about 0.25 to 2. In embodiments, the first reactant comprises an acrylate group (e.g., acrylated epoxidized soybean oil or glycerol propoxylate triacrylate), the second reactant comprises a thiol (e.g., Thiocure-332™, Polymercaptan-358™, or Thiocure-1200V™), and the ratio of thiols to acrylate groups is about 0.25 to 2.

In certain embodiments, the Michael addition reaction is conducted in the presence of a solvent, where the solvent is a topically acceptable carrier fluid (such as component (D)) and can optionally be used without further purification.

Methods for Measuring Hardness of Michael Addition Elastomer Gel Compositions.

The Michael addition elastomers are prepared in a carrier fluid (as described above as component (D)) to form gelled compositions. The gelled compositions of the present invention may be characterized by their hardness or firmness. Useful tests to characterize the gels are those recommended by the Gelatin Manufacturers Institute of America such as the use of a "Texture Analyzer" (model TAXT2, Stable Micro Systems, Inc., Godalming, England). The gel sample is subjected to a compression test with the Texture Analyzer having a probe with a 5.0 kg load cell. The probe approaches the surface of the gel at a speed of 1 mm/sec and continues compression into the gel to a distance of 5.0 mm. The Texture Analyzer detects the resistance force the probe experiences during the compression test. The force exhibited by the load cell is plotted as a function of time. The hardness of the Michael addition elastomer, gels, and elastomer blends (SEBs) for the purposes of this invention is defined as the resistance force detected by the probe of the "Texture Analyzer" during the compression test. Hardness is characterized as the force at the maximum compression point (i.e. the 5.0 mm compression point into the gel Surface). The average of a total of 3 tests are typically performed for each gel and gels were made in triplicate.

The value obtained for force (in grams) is converted into Newtons (N), by dividing the gram force value by 101.97. (i.e. 1 Newton equals 101.97g force based on the size of the probe used). The second property reported by Texture Analyzer measurement is Area F-T 1:2, in g force·sec. This is

the area integration of the force vs. test time cure. This property is indicative of a gel network since it indicates ability to sustain resistance to the compression force, which is relevant to elastomers and gels. The value is reported in g force·sec and is converted to Newton·sec in SI unit by dividing the value in force·sec by 101.97.

The Michael addition elastomer gels of the present invention have a compression hardness of at least 0.5 Newton/cm^2, alternatively 1 Newton/cm^2, or alternatively 2 Newton/cm^2 when measured with a 1.27 cm diameter spherical probe and a 50 g gel sample in a 4-ounce round glass jar.

Gel Paste Compositions Containing the Michael Addition Elastomer.

The gelled compositions of the present invention can be used to prepare gel paste or gel blend compositions containing actives by: shearing the Michael addition elastomer gel, as described herein, and combining the sheared Michael addition elastomer gel with additional quantities of the topically acceptable carrier fluid (e.g., Component (D) described herein), and optionally a personal care or health care active (e.g., Component (E) described herein) to form a gel paste or blend composition. The personal care or health care active may also be admixed as a component of another mixture with one or more excipients.

The Michael addition elastomer gel compositions of the present invention may be considered as discrete crosslinked Michael addition elastomer gel particles dispersed in carrier fluids. Thus, the Michael addition elastomer gel compositions are effective rheological thickeners for compatible lower molecular weight solvents. As such they can be used to prepare useful gel blend compositions, such as "gel paste' compositions.

To make such Michael addition elastomer gel pastes, the aforementioned Michael addition elastomer gels of known initial elastomer content (IEC) are sheared to obtain small particle size and further diluted to a final elastomer content (FEC). Shearing, as used herein refers to any shear mixing process, such as obtained from homogenizing, sonolating, or any other mixing processes known in the art as shear mixing. The shear mixing of the Michael addition elastomer gel composition results in a composition having reduced particle size. The subsequent composition having reduced particle size is then further combined with D) the carrier fluid. The carrier fluid may be any carrier fluid as described above, but typically is a linear ester (e.g. heptyl undecylenate), triglyceride (e.g. triheptanoin), or alkane (e.g. isododecane). The technique for combining the topically acceptable carrier fluid with the Michael addition composition having reduced particle size is not critical, and

typically involves simple stirring or mixing. The resulting compositions may be considered as a paste, having a viscosity greater than 2,000 cP (mPas), or greater than 100,000 cP (mPas).

Methods for Measuring Viscosity of Michael Addition Elastomer Gel Pastes.

In embodiments, the viscosity of the elastomer gel pastes described herein is measured by a Brookfield Helipath™ Stand. The Brookfield Helipath™ Stand, when used with a suitable Brookfield Viscometer fitted with a special T-bar type spindle, will permit viscosity/consistency measurements in centipoise values for materials having characteristics similar to paste, putty, cream, gelatin, or wax. In embodiments, the viscosity of Michael addition elastomer blends is determined using a Brookfield Model DV-II+Pro Viscometer with Helipath stand (Brookfield Model D) and T-Bar spindles (Brookfield Helipath Spindle Set). The Brookfield Model DV-II+Pro Viscometer with Helipath stand (Brookfield Model D) and T-Bar spindles (Brookfield Helipath Spindle Set) can be purchased from Brookfield Engineering Laboratories, Inc. (11 Commerce Boulevard Middleboro, Mass., USA). In some embodiments, the measuring is conducted with a sample size of 50 g in a 4-ounce round jar. In further embodiments, the sample is prepared by removing air bubbles from the sample, e.g., centrifuged then placed under vacuum for about two hours. In some embodiments, the sample is condition for at least about 4 hours at 25 °C following the air bubble removal. In embodiments, the measurement is taken according to the typical procedure for a Helipath spindle. In general, spindle 93 (T-bar spindle E) is used and the standard setting for rpm can be 6.0 or 6.5. The spindle speed can be maintained at constant 6.0 rpm or 6.5 rpm.

Topical formulations comprising the gel compositions or gel pastes are also provided herein. In such formulations, the gel compositions or gel pastes are suitably used as thickeners or stabilizers for the topical formulations. Other components of the topical formulations are known in the art, and can include for example, various components such as emulsion stabilizers, emulsifiers skin conditioners, suspending agents, surfactants, etc. The amounts of these additional components can be on the order of about 0.01% to about 50% by weight.

As used herein an "emulsion stabilizer" refers to a composition that aids in keeping an emulsion from separating into its oil and aqueous components. In embodiments, the emulsion stabilizer utilized in the formulations described herein is a naturally derived gum or a modified gum or natural mineral. Exemplary emulsion stabilizers include, but are not limited to, acacia, cellulose, crystalline cellulose, gellan, guar, locust (carob) bean, xanthan, magnesium aluminum silicate, bentonite or hectorite clays and the like, including combinations thereof.

As used herein a "skin conditioner" refers to a composition that acts as a lubricant on the surface of the skin or a composition that increases the water content of the surface of the skin. Exemplary skin conditioners for use in the formulations include, but are not limited to, adipate esters, alkyl benzoates, fatty acid esters of C8 or greater, esterified erucates, laurates, neopentanoates, salicylates, stearates, triglycerides, carbonates, glycols, glycerin, mineral oils and the like, including combinations thereof.

As used herein an "emulsifier" refers to a composition that aids in the formation of an oil in water, or a water in oil, emulsion. Exemplary emulsifiers for use in the formulations include, but are not limited to, polysorbates, ethoxylated fatty acids, fatty acids neutralized with sodium hydroxide, potassium hydroxide or amines, substituted glucosides, sodium lauryl and lauryl ether sulfates, ethoxylated esters, lecithin and lecithin derivatives and the like, including combinations thereof.

As used herein a "suspending agent" refers to a composition that modifies the interface between solid particles and a liquid medium to improve the particles' resistance to coming together and falling out of solution. Exemplary suspending agents for use in the formulations include, but are not limited to, hydroxy stearic acid, polyhydroxystearic acid, sodium polyacrylate polymers, methyl methacrylate crosspolymers and the like, including combinations thereof.

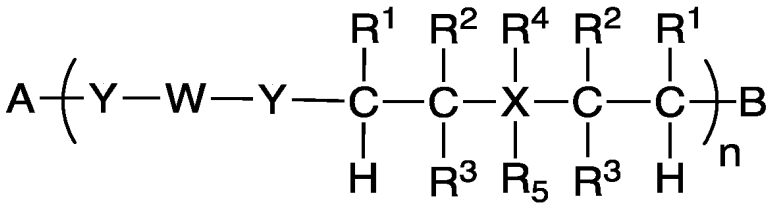
As used herein a "surfactant" refers to a composition that prevents phase separation of the gel paste. Exemplary surfactants for use in the formulations include, but are not limited to, polyglyceryl-6 polyricinoleate, polysorbate 80, ethylhexyl hydroxystearate, glyceryl ricinoleate, glyceryl triacetyl ricinoleate, glyceryl triacetyl hydroxystearate, polyglyceryl-10 hexaoleate (and) polyglyceryl-6 polyricinoleate, capryloyl glycerin/sebacic acid copolymer, including combinations thereof.

In additional embodiments, the Michael addition elastomer or Michael addition elastomer gel composition can be utilized in solid-based formats, including for example, as a foot conforming shoe insert or shoe sole.

The Michael addition elastomer or Michael addition elastomer gel composition can also be used as medically acceptable gels, including for example, medical implants or portions of implants, including as cartilage replacements, bone replacements, etc.

Exemplary embodiments:

1. A Michael addition elastomer of Formula I:



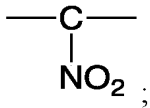
Formula I

wherein:

n is 2 to m;

A is an end group selected from hydrogen, acrylate, acrylamide, methacrylate, vinyl sulfone, maleimide, sulfhydryl, hydroxyl, amine, malonate, and nitroalkane;

B is an end group selected from hydrogen, acrylate, acrylamide, methacrylate, vinyl sulfone, maleimide, sulfhydryl, hydroxyl, amine, malonate, and nitroalkane;

Y is carbonyl, sulfone, or  ;

W is a C_1-C_{30} substituted or unsubstituted linear or branched alkyl group, aliphatic group, cycloaliphatic group, or aryl group, optionally comprising a heteroatom;

X is nitrogen or carbon;

R^1 is independently hydrogen or a C_1-C_{30} substituted or unsubstituted linear or branched alkyl group, aliphatic group, cycloaliphatic group, or aryl group, optionally comprising a heteroatom;

R^2 and R^3 are independently hydrogen or a C_1-C_{30} substituted or unsubstituted linear or branched alkyl group, aliphatic group, cycloaliphatic group, or aryl group, optionally comprising a heteroatom, and also optionally bonded to Y in the case of a maleimide adduct;

R^4 is independently hydrogen or a C_1-C_{30} substituted or unsubstituted linear or branched alkyl group, aliphatic group, cycloaliphatic group, or aryl group, optionally comprising a heteroatom;

R^5 is independently hydrogen or a C_1-C_{30} substituted or unsubstituted linear or branched alkyl group, aliphatic group, cycloaliphatic group, or aryl group, optionally comprising a heteroatom, and in the case where X is nitrogen R^5 is a lone pair of electrons;

wherein m is a whole integer between 3 and 1,000,000,000,000.

2. A gel composition comprising a Michael addition elastomer prepared from the reaction of:

a) a first reactant comprising one or more molecules, wherein each of the one or more molecules comprises two or more Michael acceptor functional groups, optionally wherein the two or more Michael acceptor functional groups are coordinated by zinc, and wherein the first reactant optionally comprises an OH, SH or NH functional group at a vicinal position to each of the Michael acceptor functional groups;

b) a second reactant comprising one or more molecules, wherein each of the one or more molecules comprises a Michael donor functional group capable of reacting with the two or more Michael acceptor functional groups to form 1,4-addition products, wherein the Michael donor functional group comprises a primary or secondary amine, a thiol, a hydroxyl group, or a carbon bonded to two Michael donor hydrogen atoms;

c) an optional reaction catalyst; and

d) a topically acceptable carrier fluid, at a concentration of 0% (w/w) to 99.9% (w/w) of the gel composition, preferably 20% (w/w) to 99.99% (w/w) of the gel composition.

3. The gel composition of embodiment **2**, wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof.

4. The gel composition of embodiment **2**, wherein the topically acceptable carrier fluid is selected from triheptanoin, diisooctyl succinate, caprylic/capric triglyceride, heptyl undecylenate, neopentyl glycol diheptanoate, coco-caprylate/caprate, diisopropyl adipate, isoamyl laurate, isopropyl myristate, jojoba esters, methylheptyl Isostearate, neopentyl glycol diheptanoate, dicaprylin caprylic/capric/myristic/stearic triglyceride, caprylic/capric/succinic triglyceride, ethyl hexyl olivate, C15-C16 branched alkanes, C17-C18 branched alkanes, dodecane, hexadecane, squalene, hemisqualane, tetradecane, undecane, tridecane, coconut alkanes, C9-12 alkane, and combinations thereof.

5. The gel composition of embodiment **2**, further comprising a pharmaceutically active ingredient dissolved in the topically acceptable carrier fluid.

6. The gel composition of embodiment **2**, further comprising a pharmaceutically active ingredient incorporated in the gel.

7. The gel composition of embodiment **2**, wherein the first reactant comprises acrylated epoxidized soybean oil, the second reactant is PRIPLAST® 1075, wherein the ratio of primary amines

to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

8. The gel composition of embodiment **2**, wherein the first reactant comprises acrylated epoxidized soybean oil, the second reactant is PRIPLAST® 1074, wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

9. The gel composition of embodiment **2**, wherein the first reactant comprises acrylated epoxidized soybean oil, the second reactant is JEFFAMINE® T-403, wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

10. The gel composition of embodiment **2**, wherein the first reactant comprises acrylated epoxidized soybean oil, the second reactant is JEFFAMINE® T-3000, wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

11. The gel composition of embodiment **2**, wherein the first reactant comprises acrylated epoxidized soybean oil, the second reactant is poly(dimethylsiloxane), bis(3-aminopropyl) terminated, wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

12. The gel composition of embodiment **2**, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is PRIPLAST® 1075 , wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

13. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is PRIPLAST®1074, wherein the ratio of primary amines to acrylate groups is about 0.25 to 2 equivalents of primary amines to acrylate groups is used, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

14. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is JEFFAMINE® T-403 , wherein the ratio of primary amines to

acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

15. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is JEFFAMINE® T-3000, wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

16. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is poly(dimethylsiloxane), bis(3-aminopropyl) terminated, wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

17. The gel composition of claim 2, wherein the first reactant comprises acrylated epoxidized soybean oil, the second reactant is Thiocure-332™, wherein the ratio of thiols to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

18. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is Polymercaptan-358™, wherein the ratio of thiols to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

19. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is Thiocure-333™, wherein the ratio of thiols to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

20. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is Thiocure-1200V™, wherein the ratio of thiols to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

21. The gel composition of embodiment **2**, wherein the first reactant is zinc acrylate.

22. A method of making a Michael addition elastomer of embodiment **1** comprising:

i) mixing a first reactant comprising one or more molecules, wherein each of the one or more molecules comprises two or more Michael acceptor functional groups and a second reactant comprising one or more molecules, wherein each of the one or more molecules comprises a Michael donor functional group, wherein the Michael donor function group comprises a primary or secondary amine, a thiol, a hydroxyl group, or a carbon bonded to two Michael donor hydrogen atoms;

ii) optionally diluting the first and second reactants in a solvent;

iii) optionally adding a reaction catalyst; and

iv) optionally heating the reaction mixture from about 50 °C to about 120 °C, preferably to about 100 °C, to form the Michael addition elastomer.

23. A method of making the Michael addition elastomer gel of embodiment **2** comprising:

i) mixing the first reactant and the second reactant in a topically acceptable carrier fluid to form a reaction mixture, wherein the first and second reactants are present in a concentration of about 50% (w/w);

ii) optionally adding a reaction catalyst; and

iii) optionally heating the reaction mixture from about 50 °C to about 120 °C, preferably to about 100 °C, to form the Michael addition elastomer.

24. The method of embodiment **22**, wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof.

25. The method of embodiment **22**, wherein the topically acceptable carrier fluid is selected from triheptanoin, diisooctyl succinate, caprylic/capric triglyceride, heptyl undecylenate, neopentyl glycol diheptanoate, coco-caprylate/caprate, diisopropyl adipate, isoamyl laurate, isopropyl myristate, jojoba esters, methylheptyl Isostearate, neopentyl glycol diheptanoate, dicaprylin caprylic/capric/myristic/stearic triglyceride, caprylic/capric/succinic triglyceride, ethyl hexyl olivate, C15-C16 branched alkanes, C17-C18 branched alkanes, dodecane, hexadecane, squalene, hemisqualane, tetradecane, undecane, tridecane, coconut alkanes, C9-12 alkane, and combinations thereof.

26. The method of embodiment **22**, further comprising dissolving a pharmaceutically active ingredient in the topically acceptable carrier fluid.

27. The method of embodiment **22**, wherein the second reactant containing the Michael donors comprises one or more amine, thiol, hydroxyl, or a carbon atom that is located between two electron-withdrawing groups such as C=O and/or C=N; an oxygen atom and has two hydrogen atoms attached.

28. The method of embodiment **22**, further comprising preparing the first reactant from a vegetable oil or mixture thereof, wherein the vegetable oil comprises two or more hydroxyl groups or epoxides.

29. The method of embodiment **22**, further comprising preparing the first reactant molecule with two or more Michael acceptor functional groups from linseed oil, soybean oil, or other vegetable oils.

30. A Michael addition elastomer gel paste made by:

i) shearing the Michael addition elastomer of embodiment **2**;

ii) optionally adding additional quantities of the topically acceptable carrier fluid during shearing to produce a gel paste composition; and

iii) optionally adding a pharmaceutically active ingredient.

31. A topical formulation comprising:

the gel composition of embodiment **5** or embodiment **6**, wherein the pharmaceutically active ingredient is a personal care active ingredient or a healthcare active ingredient.

32. A topical formulation comprising:

the Michael addition elastomer gel paste of embodiment **30**, comprising a personal care active ingredient or a healthcare active ingredient.

33. A gel composition comprising:

a) a first reactant comprising one or more molecules, wherein each of the one or more molecules comprises two or more Michael acceptor functional groups;

b) a second reactant comprising one or more molecules, wherein each of the one or more molecules comprises a Michael donor functional group capable of reacting with a Michael acceptor group to form 1,4-addition products, wherein the Michael donor functional group comprises a primary amine or a carbon bonded to two Michael donor hydrogen atoms;

c) an optional reaction catalyst; and

d) a topically acceptable carrier fluid, at a concentration of 0% (w/w) to 99.9% (w/w) of the gel composition, preferably 20% (w/w) to 99.9% (w/w) of the gel composition.

34. A foot conforming shoe insert or shoe sole comprising:
the Michael addition elastomer of embodiment **1** or the gel composition of embodiment **33**.

35. A medical medically acceptable gel comprising:
the Michael addition elastomer of embodiment **1** or the gel composition of embodiment **33**.

36. A topical formulation comprising:
the Michael addition elastomer of embodiment **1**.

37. A gel composition comprising the Michael addition elastomer of embodiment **1** and a topically acceptable carrier fluid, at a concentration of 0% (w/w) and 99.9% (w/w) of the gel composition, preferably 60% (w/w) and 99.9% (w/w) of the gel composition.

38. A method of making a Michael addition elastomer gel paste comprising the steps of:
i) shearing the gel composition of embodiment **37**;
ii) optionally adding quantities of the topically acceptable carrier fluid during shearing to produce a gel paste composition; and
iii) optionally adding a pharmaceutically active ingredient.

39. A Michael addition elastomer gel paste prepared by the method of embodiment **38**.

40. A topical formulation comprising the gel composition of embodiment **38** or the Michael addition elastomer gel paste of embodiment **39**.

Examples

Example 1 – Preparation of glycerol propoxylate triacrylate/Priamine™ 1075 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1

To a stainless steel or glass reaction vessel was added caprylic/capric triglyceride (279.7 grams) and Priamine™ 1075 (Croda International Plc, 36 grams, 1 equivalent of primary amines to acrylate groups). The mixture was stirred vigorously for 3 minutes before the addition of glycerol propoxylate triacrylate (19.26 grams). The resultant mixture was stirred vigorously for an additional 5 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The reaction mixture and the 50-gram sample were covered and left to stand at room temperature in the dark. After 403 hours a colorless transparent rubber had formed. The hardness of the 50-gram sample was 423 grams force,

as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe, which was inserted 5 mm into the rubber surface.

The aza-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and caprylic/capric triglyceride was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 2 – Preparation of glycerol propoxylate triacrylate/Priamine™ 1075 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5

To a stainless steel or glass reaction vessel was added triheptanoin (261.6 grams) and glycerol propoxylate triacrylate (30.68 g). The mixture was stirred vigorously for 5 minutes before the addition of Priamine™ 1075 (Croda International Plc, 28.69 grams, 0.5 equivalent of primary amines to acrylate groups). The resultant mixture was stirred vigorously an additional 5 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 55 °C. After 69 hours a colorless transparent rubber had formed. The hardness of the 50-gram sample was 301 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe, which was inserted 5 mm into the rubber surface.

The aza-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and triheptanoin was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 3 – Preparation of glycerol propoxylate triacrylate/JEFFAMINE® T-403 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1

To a stainless steel or glass reaction vessel was added diisooctyl succinate (215.0 grams) and glycerol propoxylate triacrylate (44.00 grams). The mixture was stirred vigorously for 3 minutes before the addition of JEFFAMINE® T-403 (Huntsman Corporation, 48.13 grams, 1 equivalent of primary amines to acrylate groups). The resultant mixture was stirred vigorously for an additional 7 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 50 °C. After 90 hours a colorless transparent rubber had formed. The hardness of the 50-gram sample was 601 grams force, as

determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the rubber surface.

The aza-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and diisooctyl succinate was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 4 – Preparation of glycerol propoxylate triacrylate/JEFFAMINE® T-403 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5

To a stainless steel or glass reaction vessel was added diisooctyl succinate (214.4 grams) and glycerol propoxylate triacrylate (59.40 grams). The mixture was stirred vigorously for 3 minutes before the addition of JEFFAMINE® T-403 (Huntsman Corporation, 32.49 grams, 0.5 equivalent of primary amines to acrylate groups). The resultant mixture was stirred vigorously for an additional 7 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 75 °C. After 93 hours a colorless transparent rubber had formed. The hardness of the 50-gram sample of rubber was 241 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe and inserted 5 mm into the rubber surface.

The aza-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and diisooctyl succinate was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 5 – Preparation of glycerol propoxylate triacrylate/poly(dimethylsiloxane), bis(3-aminopropyl) terminated aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1

To a stainless steel or glass reaction vessel was added diisooctyl succinate (214.7 grams) and glycerol propoxylate triacrylate (21.27 grams). The mixture was stirred vigorously for 3 minutes. DMS A12 (Gelest Inc., 70.74 grams, 1 equivalent of primary amines to acrylate groups) was added and the mixture was stirred vigorously for an additional 7 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 50 °C. After 96 hours a colorless transparent rubber had formed. The hardness of the 50-gram sample of rubber was 305.0 grams force, as determined using a Stable Micro Systems

Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe and inserted 5 mm into the rubber surface.

The aza-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and diisooctyl succinate was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 6 – Preparation of glycerol propoxylate triacrylate/poly(dimethylsiloxane), bis(3-aminopropyl) terminated aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5

To a stainless steel or glass reaction vessel was added diisooctyl succinate (212.49 grams) and glycerol propoxylate triacrylate (34.20 grams). The mixture was stirred vigorously for 3 minutes. DMS A12 (Gelest Inc., 56.87 grams, 0.5 equivalent of primary amines to acrylate groups) was added and the mixture was stirred vigorously for an additional 7 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 75 °C. After 163 hours a colorless transparent rubber had formed. The hardness of the 50-gram sample of rubber was 33.7 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe and inserted 5 mm into the rubber surface.

The aza-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and diisooctyl succinate was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 7 – Preparation of acrylated epoxidized soybean oil/Priamine™ 1074 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1

To a stainless steel or glass reaction vessel was added triheptanoin (256.7 grams) and acrylated epoxidized soybean oil (30.87 grams). The mixture was stirred vigorously for 10 minutes before the addition of Priamine™ 1074 (Croda International Plc, 16.21 grams, 1 equivalent of primary amines to acrylate groups). The resultant mixture was stirred vigorously for an additional 5 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 80 °C. After 22 hours a transparent rubber had formed. The

hardness of the 50-gram sample of rubber was 298.2 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe and inserted 5 mm into the gel surface.

The aza-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and triheptanoin was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 8 – Preparation of acrylated epoxidized soybean oil/Priamine™ 1075 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5

To a stainless steel or glass reaction vessel was added triheptanoin (251.4 grams) and acrylated epoxidized soybean oil (50.47 grams). The mixture was stirred vigorously for 7 minutes, before the addition of Priamine™ 1075 (Croda International Plc, 12.38 grams, 0.5 equivalent of primary amines to acrylate groups). The resultant mixture was stirred vigorously for an additional 3 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 75 °C. After 19 hours a transparent rubber had formed. The hardness of the 50-gram sample of rubber was 262 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

The aza-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and triheptanoin was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 9 – Preparation of acrylated epoxidized soybean oil/JEFFAMINE® T-403 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1

To a stainless steel or glass reaction vessel was added triheptanoin (258.4 grams) and acrylated epoxidized soybean oil (49.29 grams). The mixture was stirred vigorously for 10 minutes before the addition of JEFFAMINE® T-403 (Huntsman Corporation, 15.31 grams, 1 equivalent of primary amines to acrylate groups). The resultant mixture was stirred vigorously for an additional 5 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 80 °C. After 19 hours a transparent rubber had

formed. The hardness of the 50-gram sample of rubber was 193 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe and inserted 5 mm into the gel surface.

The aza-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and triheptanoin was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 10 – Preparation of acrylated epoxidized soybean oil/JEFFAMINE® T-403 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5

To a stainless steel or glass reaction vessel was added triheptanoin (214.0 grams) and acrylated epoxidized soybean oil (80.04 grams). The mixture was stirred vigorously for 10 minutes before the addition of JEFFAMINE® T-403 (Huntsman Corporation, 11.66 grams, 0.5 equivalent of primary amines to acrylate groups). The resultant mixture was stirred vigorously for an additional 5 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 80 °C. After 22 hours a transparent rubber was formed. The hardness of the 50-gram sample of rubber was 83 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe and inserted 5 mm into the gel surface.

The aza-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and triheptanoin was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 11 – Preparation of acrylated epoxidized soybean oil/poly(dimethylsiloxane), bis(3-aminopropyl) terminated aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1

To a stainless steel or glass reaction vessel was added diisooctyl succinate (209.35 grams) and acrylated epoxidized soybean oil (47.93 grams). The mixture was stirred vigorously for 7 minutes before the addition of DMS A12 (Gelest Inc., 41.79 grams, 1 equivalent of primary amines to acrylate groups). The resultant mixture was stirred vigorously for an additional 3 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 50 °C. After 20 hours a transparent rubber had formed. The

hardness of the 50-gram sample of rubber was 376 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe and inserted 5 mm into the gel surface.

The aza-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and diisooctyl succinate was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 12 – Preparation of acrylated epoxidized soybean oil/poly(dimethylsiloxane), bis(3-aminopropyl) terminated aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5

To a stainless steel or glass reaction vessel was added diisooctyl succinate (210.0 grams) and acrylated epoxidized soybean oil (62.67 grams). The mixture was stirred vigorously for 7 minutes before the addition of DMS A12 (Gelest Inc., 27.32 grams, 0.5 equivalent of primary amines to acrylate groups). The resultant mixture was stirred vigorously for an additional 3 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 75 °C. After 68 hours a transparent rubber had formed. The hardness of the 50-gram sample of gel was 224 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe and inserted 5 mm into the gel surface.

The aza-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and diisooctyl succinate was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 13 – Preparation of acrylated epoxidized soybean oil/Thiocure-332™ thia-Michael elastomer with an acrylate/thiol functional group ratio of 1:1

To a stainless steel or glass reaction vessel was added caprylic/capric triglyceride 324.7 grams) and acrylated epoxidized soybean oil (120.0 grams). The mixture was stirred and Thiocure-332™ (Bruno Bock Thiochemicals, 54.84 grams) was added. After vigorous stirring to produce a homogenous solution, a catalytic quantity of Priamine 1074™ (Croda International Plc, 380 milligrams) was added. The resultant mixture was stirred vigorously for an additional 5 minutes. 50

grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 80 °C. After 22 hours a transparent rubber had formed. The hardness of the 50-gram sample of rubber was 658.5 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe and inserted 5 mm into the gel surface.

The thia-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and caprylic/capric triglyceride was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 14 – Preparation of a glyceryl propoxy triacrylate/Polymercaptan-358™ thia-Michael elastomer with an acrylate/thiol functional group ratio of 1:1

To a stainless steel or glass reaction vessel was added diisooctyl succinate (217.1 grams) and Polymercaptan-358 (40.0 grams). The mixture was stirred and glyceryl propoxy triacrylate (14.28 grams) was added. After vigorous stirring to produce a homogenous solution, a catalytic quantity of diazabicycloundecene (1080 microliters) was added. The resultant mixture was stirred vigorously for an additional 5 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 80 °C. After 22 hours a transparent rubber had formed. The hardness of the 50-gram sample of rubber was 383.6 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe and inserted 5 mm into the gel surface.

The thia-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and diisooctyl succinate was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 15 – Preparation of glyceryl propoxy triacrylate/ Thiocure-333™ thia-Michael elastomer with an acrylate/thiol functional group ratio of 1:1

To a stainless steel or glass reaction vessel was added diisooctyl succinate (55.7 grams) and Thiocure-333™ (Bruno Bock Thiochemicals, 17.9 grams). The mixture was stirred and glyceryl propoxy triacrylate (6.0 grams) was added. After vigorous stirring to produce a homogenous solution, a catalytic quantity of 1-methylimidazole (490 microliters) was added. The resultant mixture was

stirred vigorously for an additional 5 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 80 °C. After 22 hours a transparent rubber had formed. The hardness of the 50-gram sample of rubber was 435.4 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe and inserted 5 mm into the gel surface.

The thia-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and diisooctyl succinate or triheptanoin was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 16 – Preparation of glyceryl propoxy triacrylate/Thiocure-1200V thia-Michael elastomer with an acrylate/thiol functional group ratio of 1:1

To a stainless steel or glass reaction vessel was added diisooctyl succinate (229.3grams) and Thiocure-1200V (Bruno Bock Thiochemicals, 500 grams). The mixture was stirred and glyceryl propoxy triacrylate (26.4 grams) was added. After vigorous stirring to produce a homogenous solution, a catalytic quantity of 1-methylimidazole (490 microliters) was added. The resultant mixture was stirred vigorously for an additional 5 minutes. 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 80 °C. After 22 hours a transparent rubber had formed. The hardness of the 50-gram sample of rubber was 323.5 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell fitted with a TA-18B Stable Micro Systems probe and inserted 5 mm into the gel surface.

The thia-Michael elastomeric rubber was broken into smaller pieces, placed in a metal container, and diisooctyl succinate or triheptanoin was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 to 10000 revolutions per minute.

Example 17 – Preparation of acrylated epoxidized soybean oil / Priamine 1075® (Croda International, Plc) elastomer

To a stainless steel or glass reaction vessel was added triheptanoin (195.82 grams) and acrylated epoxidized soybean oil (62.36 grams). The mixture was stirred vigorously for 15 minutes, then Priamine® 1075 (Croda International Plc, 43.08 grams, 1 equivalent of amines to acrylate

groups) was added and the mixture was stirred for an additional 5 minutes. Once a homogenous mixture was obtained, 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 80 °C for 24 hours, at which point a translucent rubber was formed. The hardness of the 50-gram sample of gel was 450 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

The Michael addition elastomer rubber was broken into smaller pieces, placed in a metal container, and triheptanoin was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 18 – Preparation of acrylated epoxidized soybean oil / JEFFAMINE® T-3000 (Huntsman Corporation) elastomer

To a stainless steel or glass reaction vessel was added triheptanoin (240.45 grams) and acrylated epoxidized soybean oil (26.79 grams). The mixture was stirred vigorously for 15 minutes, then JEFFAMINE® T-3000 (Huntsman Corporation, 76.26 grams, 1 equivalent of amines to acrylate groups) was added and the mixture was stirred for an additional 5 minutes. Once a homogenous mixture was obtained, 50 grams of the mixture was poured into a 4-ounce glass jar. The remainder of the reaction mixture and the 50-gram sample were covered and heated to 80 °C for 24 hours, at which point a translucent rubber was formed. The hardness of the 50-gram sample of gel was 324 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

The Michael addition elastomer rubber was broken into smaller pieces, placed in a metal container, and triheptanoin was added before homogenizing into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 19 – Preparation of zinc acrylate / castor oil elastomer

To a test tube add a topically acceptable solvent capable of solubilizing the reactants (37.2 grams) and zinc acrylate (2.97 grams). The mixture can be mixed using an overhead for about 5 minutes at 25 °C to ensure proper mixing. Castor oil (9.61 grams, 1 equivalent of alcohol to acrylate groups) can then be added to the mixture and it can be mixed for an additional 5 minutes at

25 °C to produce a homogenous reaction mixture. No additional catalyst or additives are expected to be required as the zinc is expected to catalyze the reaction mixture. The homogenous mixture can be heated to 80 °C overnight, to form a gel. The hardness of the sample of gel is expected to be about 300 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

The elastomer gel can be broken into smaller pieces, placed in a container, and subjected to high shear mixing with the simultaneous addition of triheptanoin or another topically acceptable carrier fluid which may or may not be triheptanoin before being sheared into a smooth gel paste with a desired viscosity. Once scaled up to larger quantities the high shear mixing can be accomplished using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 20 – Preparation of acrylated epoxidized soybean oil / pentaerythritol tetrakis(3-mercaptopropionate) elastomer

To a stainless steel or glass reaction vessel was added heptyl undecylenate (33.02 grams) and acrylated epoxidized soybean oil (12.61 grams). The mixture was stirred for 5 min at 25 °C and pentaerythritol tetrakis(3-mercaptopropionate (4.031 grams, 1 equivalent of thiol to acrylate groups) was added and the mixture was stirred for an additional 5 min. Once homogenous, 1-methylimidazole (0.33 grams) was added and the mixture was stirred for an additional 10 min to ensure proper mixing. The reaction mixture was covered heated to 80 °C for 16 hours, at which point a translucent gel was formed. The hardness of the 50-gram sample of gel is expected to be about 300 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

To produce a gel paste, the gel can be broken into smaller pieces, placed in a metal container, and a topically acceptable carrier fluid, which may or may not be triheptanoin, can be added before the mixture is homogenized into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 21 – Preparation of acrylated epoxidized soybean oil / 2,2'-(ethylenedioxane) diethanethiol elastomer

To a stainless steel or glass reaction vessel was added heptyl undecylenate (37.45 grams) and acrylated epoxidized soybean oil (9.94 grams). The mixture was stirred for 5 min at 25 °C and 2,2'-(Ethylenedioxane) diethanethiol (2.35 grams, 1 equivalent of thiol to acrylate groups) was added and the mixture was stirred for an additional 5 min. Once homogenous, Priamine 1075 (Croda; 0.35 grams) was added and the mixture was stirred for an additional 10 min to ensure proper mixing. The reaction mixture was covered and heated to 80 °C overnight, at which point a translucent gel was formed. The hardness of the 50-gram sample of gel is expected to be about 300 grams force, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

To produce a gel paste, the gel can be broken into smaller pieces, placed in a metal container, and a topically acceptable carrier fluid, which may or may not be triheptanoin, can be added before the mixture is homogenized into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 22 - Fourier-Transform Infrared Spectroscopy of polyurethane elastomers

Fourier-Transform Infrared Spectroscopy (FTIR) was performed to analyze the molecular structures of the polyurethane elastomers.

The FTIR spectrograph of propoxylate triacrylate/Priamine™ 1075 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1 is shown in FIG. 1.

The FTIR spectrograph of glycerol propoxylate triacrylate/Priamine™ 1075 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5 is shown in FIG. 2.

The FTIR spectrograph of glycerol propoxylate triacrylate/Priamine™ 1075 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5 is shown in FIG. 2.

The FTIR spectrograph of glycerol propoxylate triacrylate/JEFFAMINE® T-403 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1 is shown in FIG. 3.

The FTIR spectrograph of glycerol propoxylate triacrylate/JEFFAMINE® T-403 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5 is shown in FIG. 4.

The FTIR spectrograph glycerol propoxylate triacrylate/poly(dimethylsiloxane), bis(3-aminopropyl) terminated aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1 is shown in FIG. 5.

The FTIR spectrograph glycerol propoxylate triacrylate/poly(dimethylsiloxane), bis(3-aminopropyl) terminated aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5 is shown in FIG. 6.

The FTIR spectrograph acrylated epoxidized soybean oil/Priamine™ 1074 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1 is shown in FIG. 7.

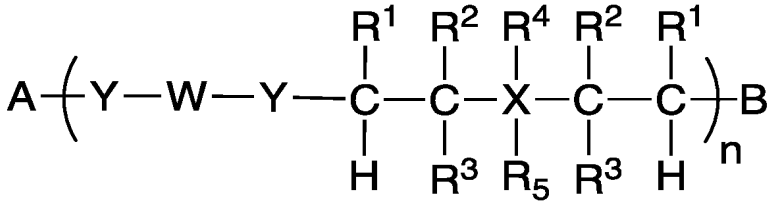
The FTIR spectrograph acrylated epoxidized soybean oil/Priamine™ 1074 aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5 is shown in FIG. 8.

The FTIR spectrograph of acrylated epoxidized soybean oil/poly(dimethylsiloxane), bis(3-aminopropyl) terminated aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:1 is shown in FIG. 9.

The FTIR spectrograph of acrylated epoxidized soybean oil/poly(dimethylsiloxane), bis(3-aminopropyl) terminated aza-Michael elastomer with an acrylate/primary amine functional group ratio of 1:0.5 is shown in FIG. 10.

Claims

1. A Michael addition elastomer of Formula I:



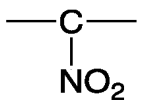
Formula I

wherein:

n is 2 to m;

A is an end group selected from hydrogen, acrylate, acrylamide, methacrylate, vinyl sulfone, maleimide, sulfhydryl, hydroxyl, amine, malonate, and nitroalkane;

B is an end group selected from hydrogen, acrylate, acrylamide, methacrylate, vinyl sulfone, maleimide, sulfhydryl, hydroxyl, amine, malonate, and nitroalkane;

Y is carbonyl, sulfone, or  ;

W is a C_1-C_{30} substituted or unsubstituted linear or branched alkyl group, aliphatic group, cycloaliphatic group, or aryl group, optionally comprising a heteroatom;

X is nitrogen or carbon;

R^1 is independently hydrogen or a C_1-C_{30} substituted or unsubstituted linear or branched alkyl group, aliphatic group, cycloaliphatic group, or aryl group, optionally comprising a heteroatom;

R^2 and R^3 are independently hydrogen or a C_1-C_{30} substituted or unsubstituted linear or branched alkyl group, aliphatic group, cycloaliphatic group, or aryl group, optionally comprising a heteroatom, and also optionally bonded to Y in the case of a maleimide adduct;

R^4 is independently hydrogen or a C_1-C_{30} substituted or unsubstituted linear or branched alkyl group, aliphatic group, cycloaliphatic group, or aryl group, optionally comprising a heteroatom;

R^5 is independently hydrogen or a C_1-C_{30} substituted or unsubstituted linear or branched alkyl group, aliphatic group, cycloaliphatic group, or aryl group, optionally comprising a heteroatom, and in the case where X is nitrogen R^5 is a lone pair of electrons;

wherein m is a whole integer between 3 and 1,000,000,000,000.

2. A gel composition comprising a Michael addition elastomer prepared from the reaction of:

a) a first reactant comprising one or more molecules, wherein each of the one or more molecules comprises two or more Michael acceptor functional groups, optionally wherein the two or more Michael acceptor functional groups are coordinated by zinc, and optionally wherein the first reactant comprises an OH, SH or NH functional group at a vicinal position to each of the Michael acceptor functional groups;

b) a second reactant comprising one or more molecules, wherein each of the one or more molecules comprises a Michael donor functional group capable of reacting with the two or more Michael acceptor functional groups to form 1,4-addition products, wherein the Michael donor functional group comprises a primary or secondary amine, a thiol, a hydroxyl group, or a carbon bonded to two Michael donor hydrogen atoms;

c) an optional reaction catalyst; and

d) a topically acceptable carrier fluid, at a concentration of 0% (w/w) to 99.9% (w/w) of the gel composition, preferably 20% (w/w) to 99.99% (w/w) of the gel composition.

3. The gel composition of claim 2, wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof.

4. The gel composition of claim 2, wherein the topically acceptable carrier fluid comprises triheptanoin, diisooctyl succinate, caprylic/capric triglyceride, heptyl undecylenate, neopentyl glycol diheptanoate, coco-caprylate/caprate, diisopropyl adipate, isoamyl laurate, isopropyl myristate, jojoba esters, methylheptyl Isostearate, neopentyl glycol diheptanoate, dicaprylin caprylic/capric/myristic/stearic triglyceride, caprylic/capric/succinic triglyceride, ethyl hexyl olivate, C15-C16 branched alkanes, C17-C18 branched alkanes, dodecane, hexadecane, squalene, hemisqualane, tetradecane, undecane, tridecane, coconut alkanes, C9-12 alkane, or combinations thereof.

5. The gel composition of claim 2, further comprising a pharmaceutically active ingredient dissolved in the topically acceptable carrier fluid.

6. The gel composition of claim 2, further comprising a pharmaceutically active ingredient incorporated in the gel.

7. The gel composition of claim 2, wherein the first reactant comprises acrylated epoxidized soybean oil, the second reactant is PRIPLAST™ 1075 , wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

8. The gel composition of claim 2, wherein the first reactant comprises acrylated epoxidized soybean oil, the second reactant is PRIAMINE™ 1074, wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

9. The gel composition of claim 2, wherein the first reactant comprises acrylated epoxidized soybean oil, the second reactant is JEFFAMINE® T-403, wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

10. The gel composition of claim 2, wherein the first reactant comprises acrylated epoxidized soybean oil, the second reactant is JEFFAMINE® T-3000, wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

11. The gel composition of claim 2, wherein the first reactant comprises acrylated epoxidized soybean oil, the second reactant is poly(dimethylsiloxane), bis(3-aminopropyl) terminated, wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

12. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is PRIPLAST® 1075 , wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

13. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is PRIAMINE® 1074, wherein the ratio of primary amines to acrylate groups is about 0.25 to 2 equivalents of primary amines to acrylate groups is used, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

14. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is JEFFAMINE® T-403 , wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

15. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is JEFFAMINE® T-3000, wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

16. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is poly(dimethylsiloxane), bis(3-aminopropyl) terminated, wherein the ratio of primary amines to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

17. The gel composition of claim 2, wherein the first reactant comprises acrylated epoxidized soybean oil, the second reactant is Thiocure-332™, wherein the ratio of thiols to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

18. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is Polymercaptan-358™, wherein the ratio of thiols to acrylate groups is about 0.25 to 2 equivalents, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

19. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is Thiocure-333™, wherein the ratio of thiols to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

20. The gel composition of claim 2, wherein the first reactant comprises glycerol propoxylate triacrylate, the second reactant is Thiocure-1200V™, wherein the ratio of thiols to acrylate groups is about 0.25 to 2, and the carrier fluid is triheptanoin, diisooctyl succinate, or caprylic/capric triglyceride.

21. The gel composition of claim 2, wherein the first reactant is zinc acrylate.

22. A method of making a Michael addition elastomer of claim 1 comprising:

i) mixing a first reactant comprising one or more molecules, wherein each of the one or more molecules comprises two or more Michael acceptor functional groups and a second reactant comprising one or more molecules, wherein each of the one or more molecules comprises a Michael donor functional group, wherein the Michael donor functional group comprises a primary or secondary amine, a thiol, a hydroxyl group or a carbon bonded to two Michael donor hydrogen atoms;

ii) optionally diluting the first and second reactants in a solvent;

iii) optionally adding a reaction catalyst; and

iv) optionally heating the reaction mixture from about 50 °C to 120 °C, preferably to about 100 °C, to form the Michael addition elastomer.

23. A method of making the Michael addition elastomer gel of claim 2 comprising:

i) mixing the first reactant and the second reactant in a topically acceptable carrier fluid to form a reaction mixture, wherein the first and second reactants are present in a concentration of about 50% (w/w);

ii) optionally adding a reaction catalyst; and

iii) optionally heating the reaction mixture from about 50 °C to 120 °C, preferably to about 100 °C, to form the Michael addition elastomer.

24. The method of claim 22, wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof.

25. The method of claim 22, wherein the topically acceptable carrier fluid is selected from triheptanoin, diisooctyl succinate, caprylic/capric triglyceride, heptyl undecylenate, neopentyl glycol diheptanoate, coco-caprylate/caprate, diisopropyl adipate, isoamyl laurate, isopropyl myristate, jojoba esters, methylheptyl Isostearate, neopentyl glycol diheptanoate, dicaprylin caprylic/capric/myristic/stearic triglyceride, caprylic/capric/succinic triglyceride, ethyl hexyl olivate, C15-C16 branched alkanes, C17-C18 branched alkanes, dodecane, hexadecane, squalene, hemisqualane, tetradecane, undecane, tridecane, coconut alkanes, C9-12 alkane, and combinations thereof.

26. The method of claim 22, further comprising dissolving a pharmaceutically active ingredient in the topically acceptable carrier fluid.

27. The method of claim 22, wherein the second reactant containing the Michael donors comprises one or more amine, thiol, hydroxyl, or a carbon atom that is located between two electron-withdrawing groups such as C=O and/or C=N; an oxygen atom and has two hydrogen atoms attached.

28. The method of claim 22, further comprising preparing the first reactant from a vegetable oil or mixture thereof, wherein the vegetable oil comprises two or more hydroxyl groups or epoxides.

29. The method of claim 22, further comprising preparing the first reactant molecule with two or more Michael acceptor functional groups from linseed oil, soybean oil, or other vegetable oils.

30. A Michael addition elastomer gel paste made by:

i) shearing the Michael addition elastomer of claim 2;

ii) optionally adding additional quantities of the topically acceptable carrier fluid during shearing to produce a gel paste composition; and

iii) optionally adding a pharmaceutically active ingredient.

31. A topical formulation comprising:

the gel composition of claim 5 or claim 6, wherein the pharmaceutically active ingredient is a personal care active ingredient or a healthcare active ingredient.

32. A topical formulation comprising:

the Michael addition elastomer gel paste of claim 30, comprising a personal care active ingredient or a healthcare active ingredient.

33. A gel composition comprising:

a) a first reactant comprising one or more molecules, wherein each of the one or more molecules comprises two or more Michael acceptor functional groups;

b) a second reactant comprising one or more molecules, wherein each of the one or more molecules comprises a Michael donor functional group capable of reacting with a Michael

acceptor group to form 1,4-addition products, wherein the Michael donor functional group comprises a primary amine or a carbon bonded to two Michael donor hydrogen atoms;

c) an optional reaction catalyst; and

d) a topically acceptable carrier fluid, at a concentration of between 0% (w/w) and 99.9% (w/w) of the gel composition, preferably 20% (w/w) to 99.9% (w/w) of the gel composition.

34. A foot conforming shoe insert or shoe sole comprising:

the Michael addition elastomer of claim 1 or the gel composition of claim 33.

35. A medical medically acceptable gel comprising:

the Michael addition elastomer of claim 1 or the gel composition of claim 33.

36. A topical formulation comprising:

the Michael addition elastomer of claim 1.

37. A gel composition comprising the Michael addition elastomer of claim 1 and a topically acceptable carrier fluid, at a concentration of between 0% (w/w) and 99.9% (w/w) of the gel composition, preferably 60% (w/w) and 99.9% (w/w) of the gel composition.

38. A method of making a Michael addition elastomer gel paste comprising the steps of:

i) shearing the gel composition of claim 37;

ii) optionally adding quantities of the topically acceptable carrier fluid during shearing to produce a gel paste composition; and

iii) optionally adding a pharmaceutically active ingredient.

39. A Michael addition elastomer gel paste prepared by the method of claim 38.

40. A topical formulation comprising the gel composition of claim 38 or the Michael addition elastomer gel paste of claim 39.

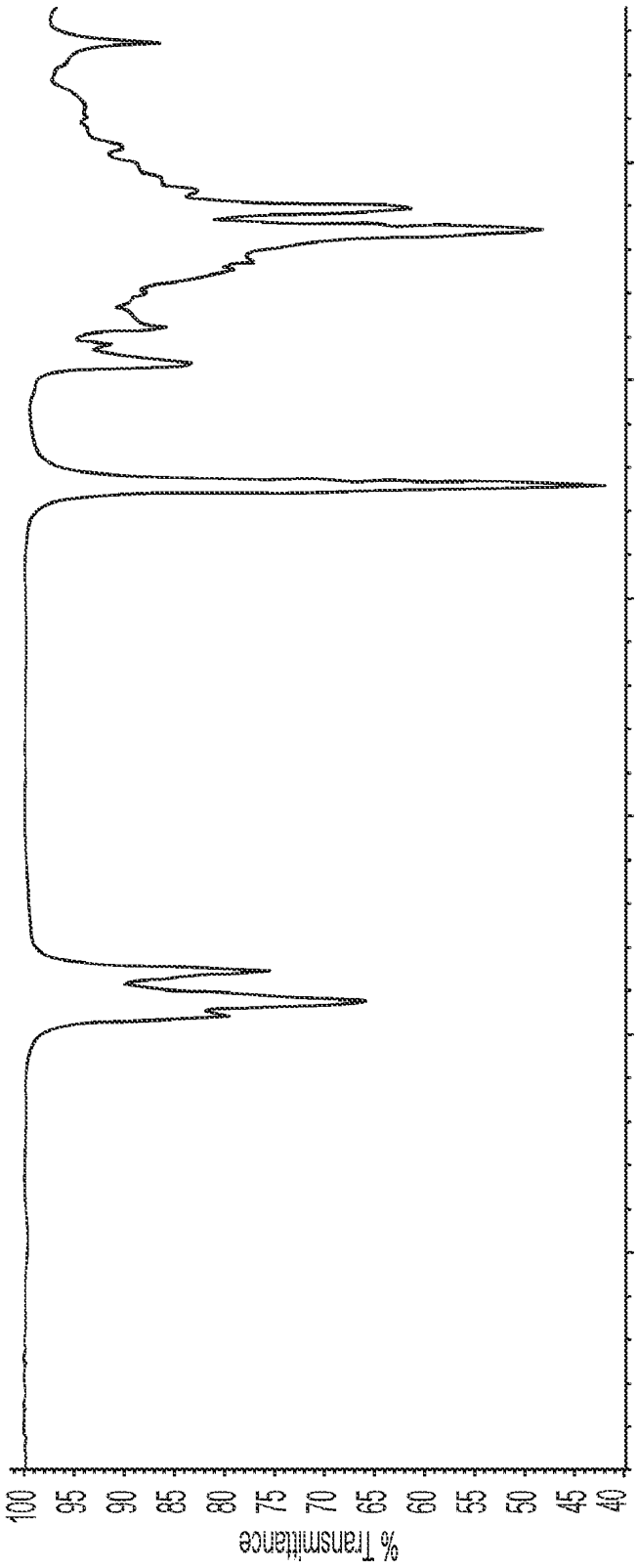

% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

FIG. 1

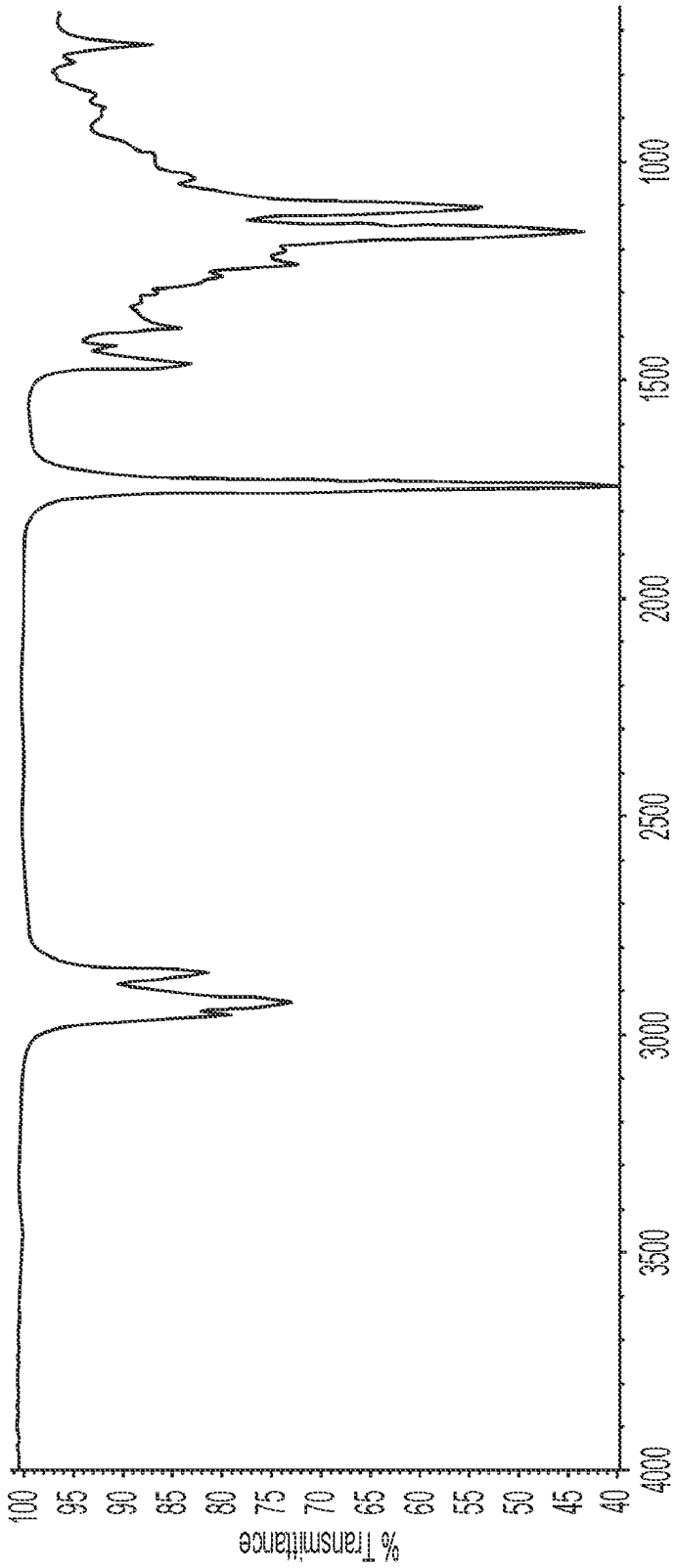

% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

FIG. 2

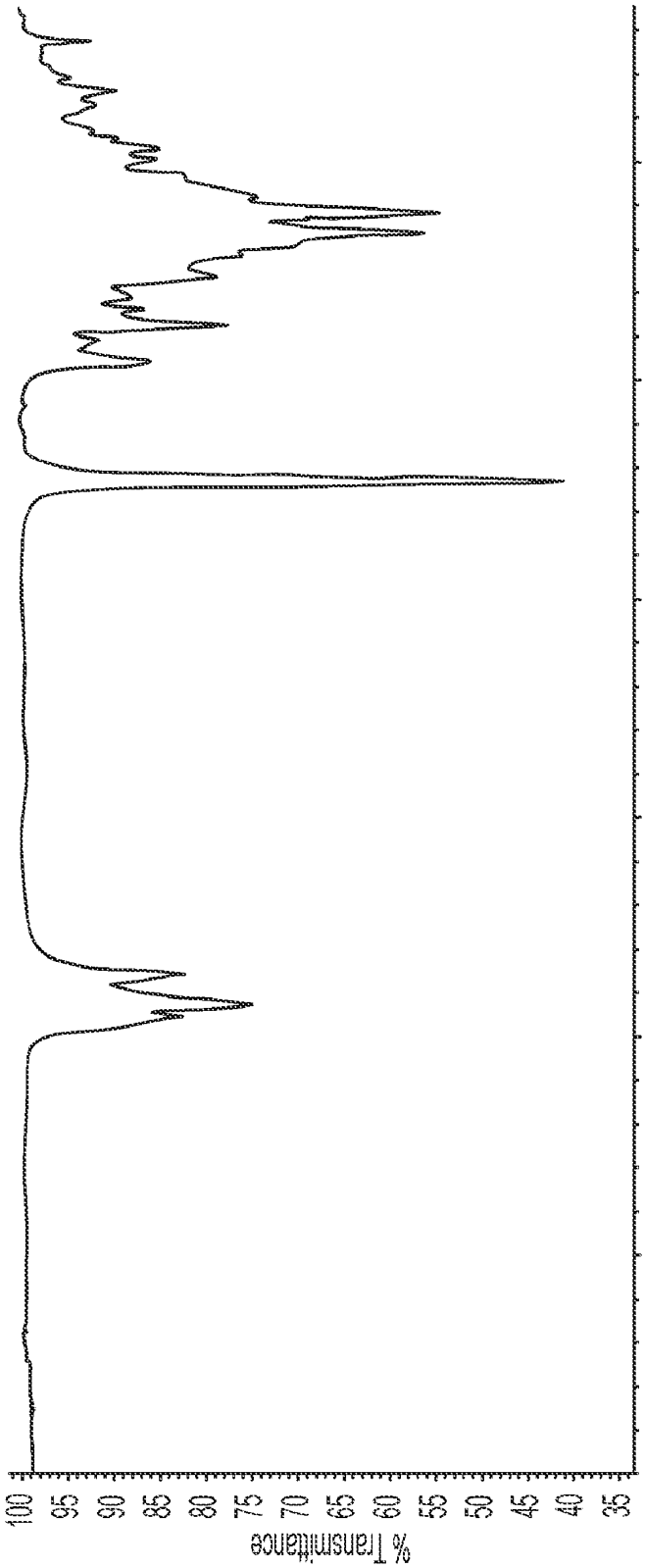

% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

FIG. 3

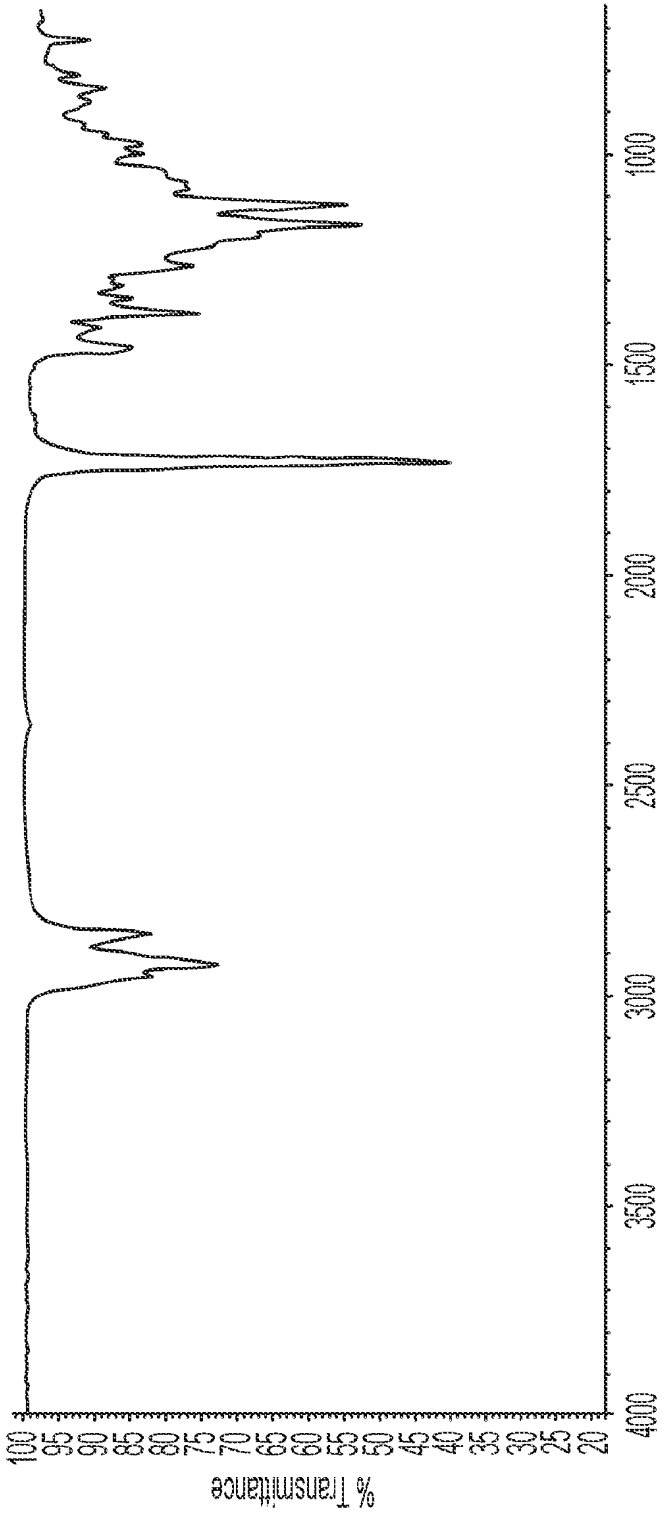

% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

FIG. 4

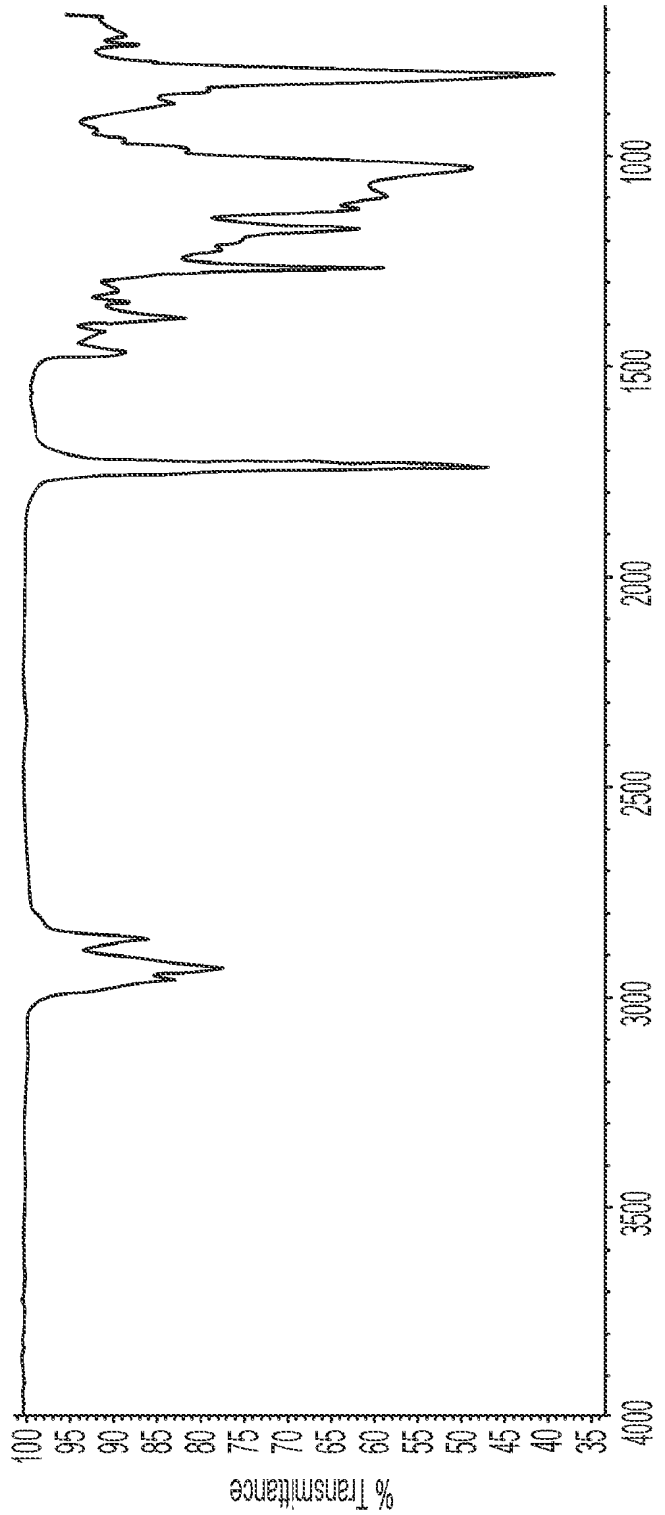

% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

FIG. 5

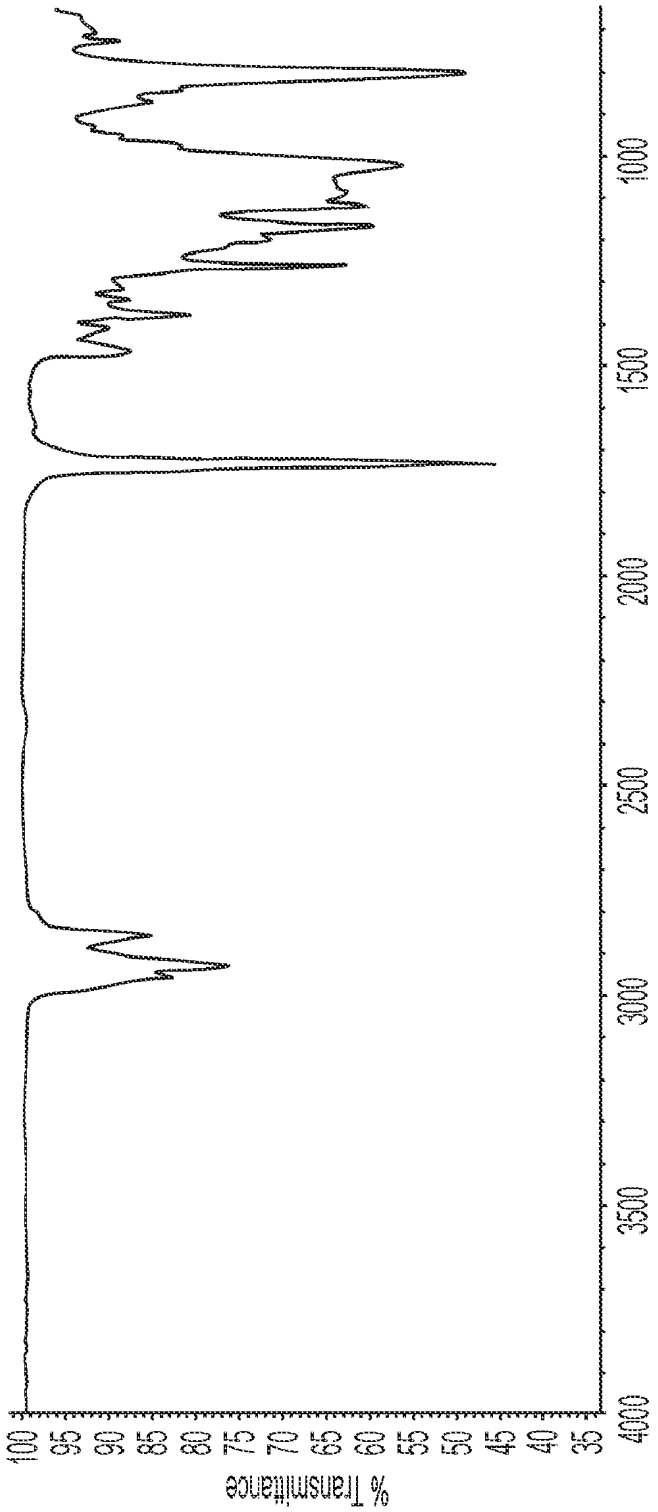

% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

FIG. 6

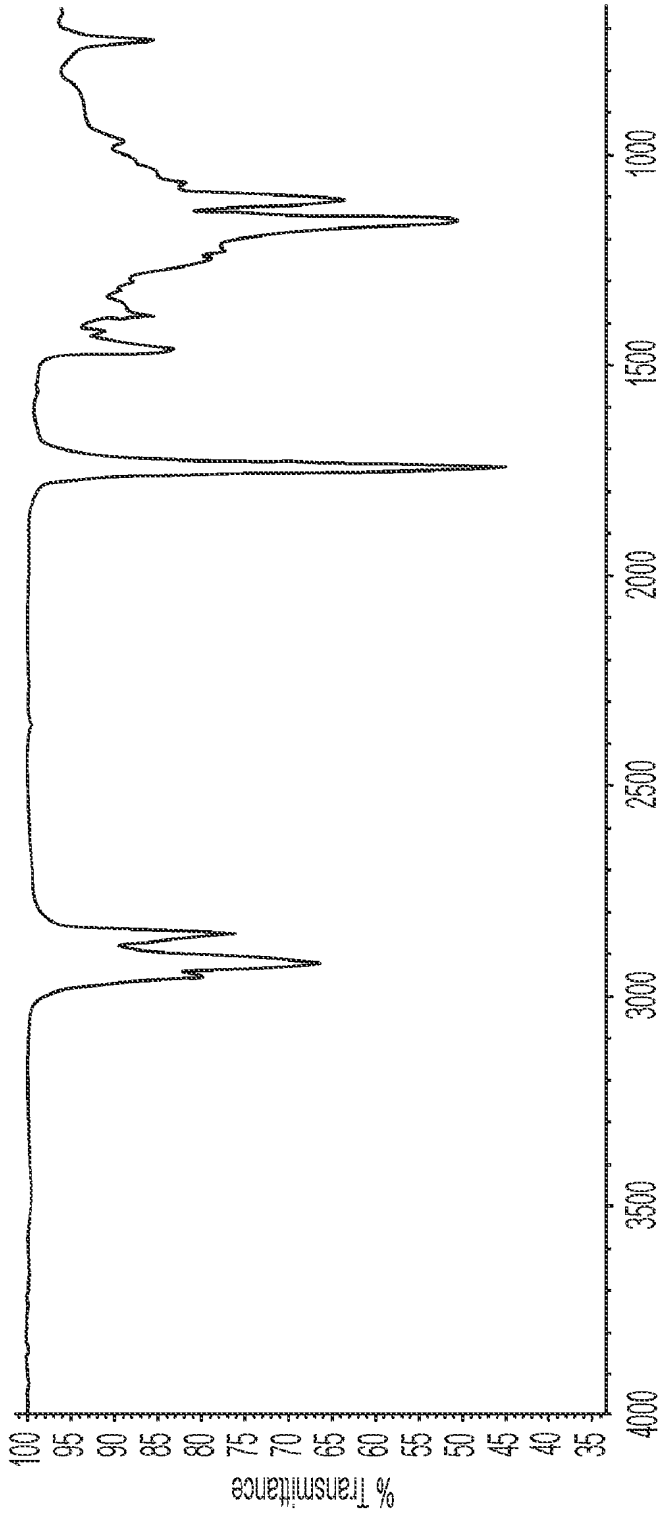

% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

FIG. 7

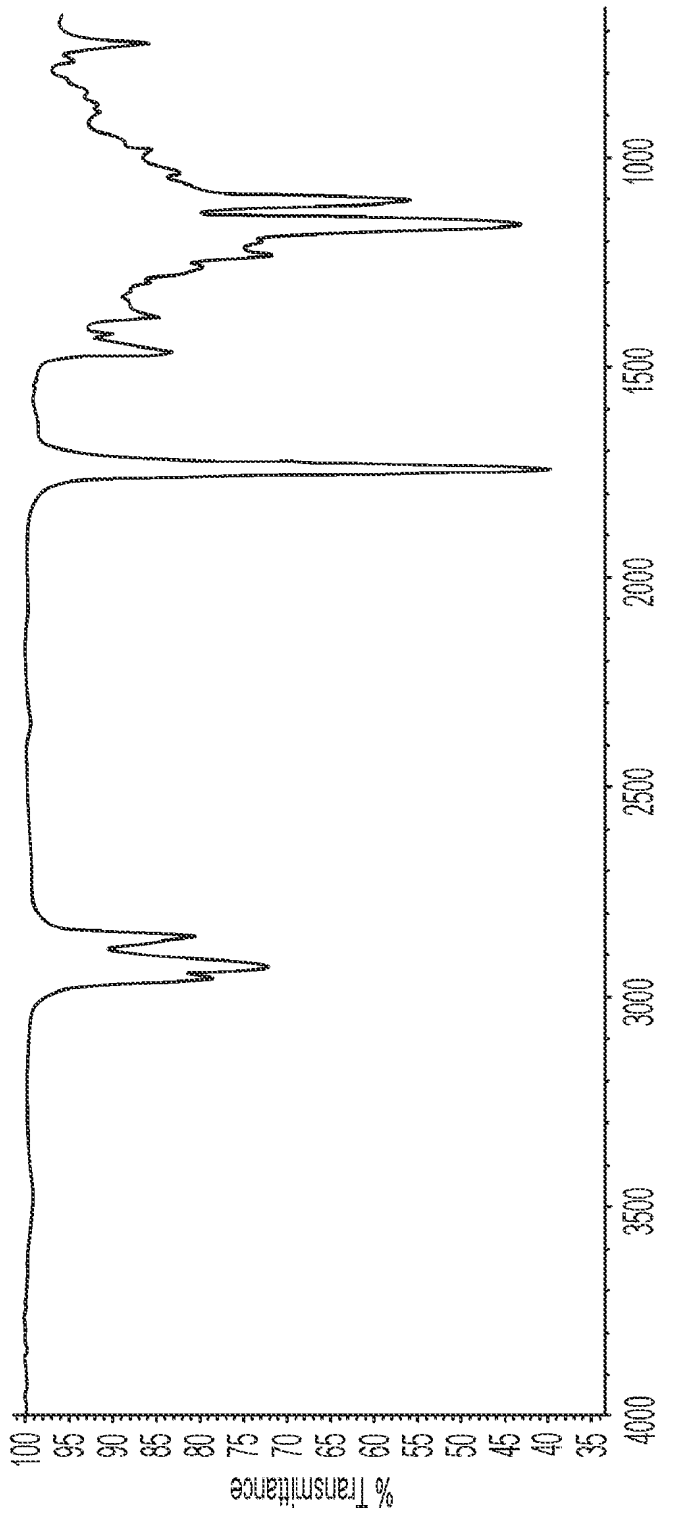

% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

FIG. 8

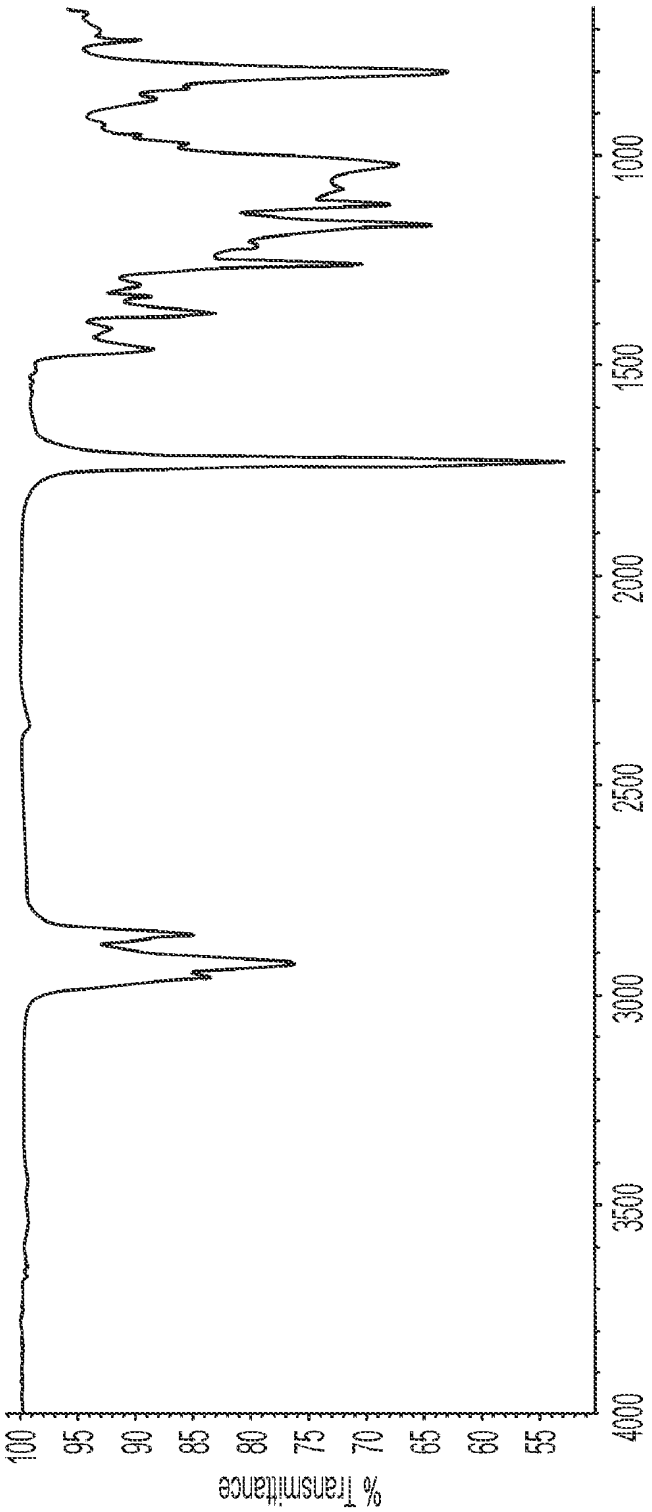

% Transmittance
100
95
90
85
80
75
70
65
60
55
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

FIG. 9

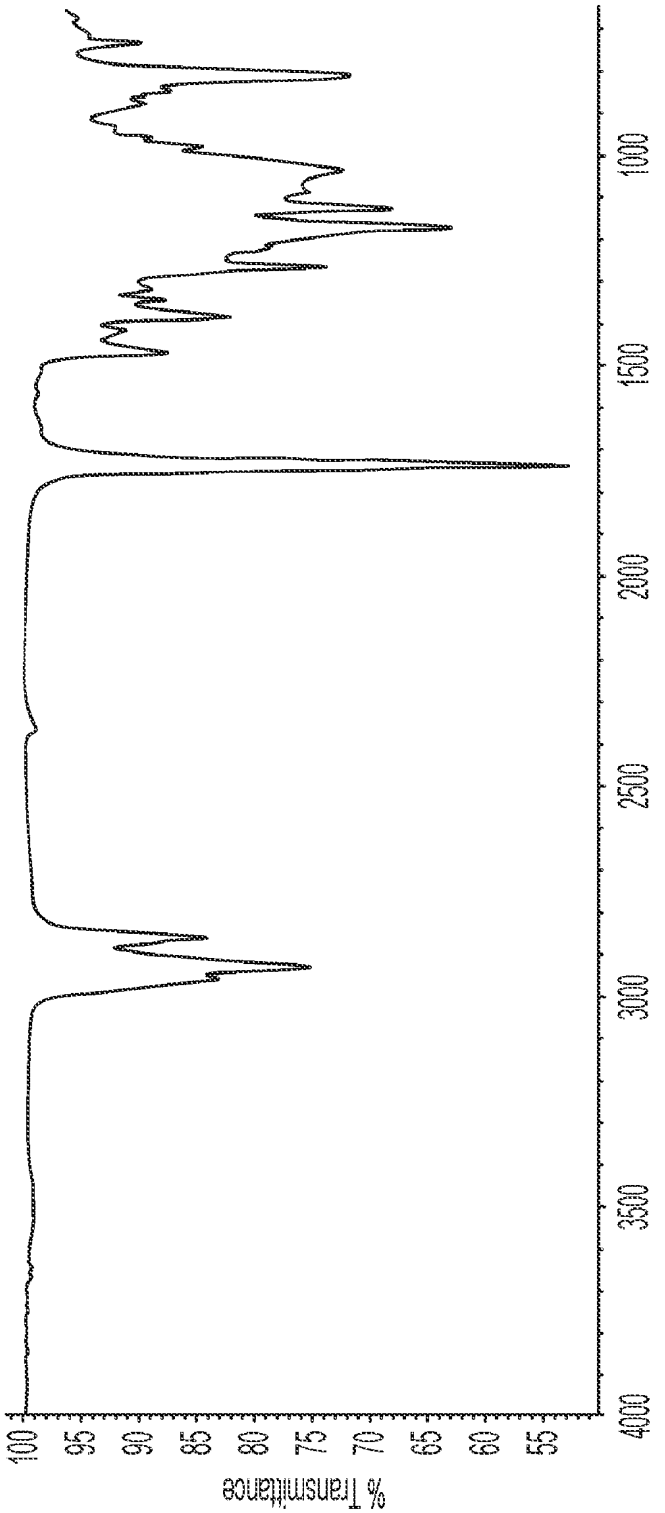

% Transmittance
100
95
90
85
80
75
70
65
60
55
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 21/37992

A. CLASSIFICATION OF SUBJECT MATTER
IPC - A61K 8/87; A61Q 19/00; C08G 18/72 (2021.01)
CPC - A43B 13/04; A61K 8/87; A61Q 19/00; C08G 18/72; A61K 9/0014

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	GENEST et al. 'The aza-Michael Reaction as an Alternative Strategy to Generate Advanced silicon-based (macro)Molecules and Materials', Progress in Polymer Science, 2017, Vol. 72, pp. 61-110. abstract; pg. 67. Scheme 4, structure 91;pg. 73, Scheme 12;pg. 94, Chart 17;pg. 98, Col 2, para 2	1;22;27 ---------- 28;29;34/1;35/1;36-40
Y	KASETAITE et al. 'Effect of Selected Thiols on Cross-linking of Acrylated Epoxidized Soybean Oil and Properties of Resulting Polymers', Polymers, 2018, Vol. 10(439), pp. 1-13. abstract;pg. 2, para 4, Scheme1	28;29
Y	WO 03/076537 A1 (LORD CORPORATION) 18 September 2003 (18.09.2003) para [0062];[0074];[0181];[0192];[0194]	34/1
Y	US 9,752,067 B2 (BYK-CHEMIE GMBH) 05 September 2017 (05.09.2017) Col 1, ln 50-55; Col 1, ln 61-67; Col 9, ln 7-10;Col 9, ln 17-21; Col 10, ln 11-16;Col 10, ln 23-27;Col 13, ln 56-64;Col 23, ln 29-38	35/1; 36-40
Y	US 7,431,789 B2 (MACK et al.) 07 October 2008 (07.10.2008) Col 3, ln 36-42; Col 7, ln 3-5	38-40
A	WU et al. '2A2 + BB'B" Approach to Hyperbranched Poly(amino ester)s', Macromolecules 2005, Vol. 38, pp. 5519-5525. ENTIRE DOCUMENT	1;22;27-29;34/1;35/1; 36-40

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 OCTOBER 2021 (12.10.2021)	NOV 15 2021
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Kari Rodriquez Telephone No. PCT Helpdesk: 571-272-4300

Form PCT/ISA/210 (second sheet) (July 2019)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 21/37992

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
--Please see attached sheet---

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1, 22, 27-29, 34/1, 35/1 and 36-40

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (July 2019)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 21/37992

Attachment to Box.No.III:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I+: Claims 1-40 directed to a Michael addition elastomer selected from a compound represented by Formula I, an elastomer prepared from the reaction of a first reactant selected from acrylated epoxidized soybean oil, glycerol propoxylate triacrylate, and zinc acrylate; and a second reactant selected from PRIPLAST 1075, PRIAMINE 1074, JEFFAMINE T-403, JEFFAMINE T-3000, bis(3-aminopropyl) terminated polysiloxane, Polymercaptan-358, Thiocure-332, Polymercaptan-358, Thiocure 333 and Thiocure-1200V; a gel, gel-paste or topical composition comprising a Michael addition elastomer and to a method of making said Michael addition elastomer. The Michael addition elastomer, topical composition and method of preparation will be searched to the extent that the elastomer encompasses the compound represented by Formula I. It is believed that claims 1, 22, 24-29, 34/1, 35/1 and 36-40 read on this first named invention, and thus these claims will be searched without fee to the extent that they encompass the elastomer of Formula I. Applicant is invited to elect additional elastomer(s) and method of preparation(s), wherein each additional elastomer and method elected will require one additional invention fee. Applicants must specify the claims that encompass any additionally elected elastomer and method. Applicants must further indicate, if applicable, the claims which encompass the first named invention, if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the '+' group(s) will result in only the first claimed invention to be searched. Additionally, an exemplary election wherein different actual variables are selected is suggested. An exemplary election would be a Michael addition elastomer prepared from the reaction of acrylated epoxidized soybean oil and PRIPLAST 1075, a gel composition comprising said elastomer, and a method of preparing said gel composition (i.e., claims 2-7, 12, 23, 30-33, 34/33 and 35/33).

The group of inventions listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I+ includes the technical feature of a unique Michael addition elastomer, which is not required by any other invention of Group I+.

Common technical features:

The inventions of Group I+ share the technical features of a Michael addition elastomer prepared from the reaction of:
a) a first reactant comprising one molecule, wherein each one molecule comprises two or more Michael acceptor functional groups; and b) a second reactant comprising one molecule, wherein the one molecule comprises a Michael donor functional group capable of reacting with the two or more Michael acceptor functional groups to form 1,4-addition products, wherein the Michael donor functional group comprises a primary amine, bonded to two Michael donor hydrogen atoms; and a method of preparing said Michael addition elastomer.

These shared technical features, however, do not provide a contribution over the prior art, as being anticipated by the article entitled "The aza-Michael Reaction as an Alternative Strategy to Generate Advanced Silicon-based (Macro)molecules and Materials', published in Progress in Polymer Science 72 (2017) 61-110 by GENEST et al. (hereinafter Genest), which discloses a Michael addition elastomer (abstract) prepared from the reaction of: a) a first reactant comprising one molecule, wherein each one molecule comprises two or more Michael acceptor functional groups (pg. 73, Scheme 12, second reactant, 81); b) a second reactant comprising one molecule, wherein the one molecule comprises a Michael donor functional group capable of reacting with the two or more Michael acceptor functional groups to form 1,4-addition products, wherein the Michael donor functional group comprises a primary amine, bonded to two Michael donor hydrogen atoms (pg. 73, Scheme 12, first reactant, 3) and further teaches a a method of preparing said Michael addition elastomer (pg. 73, Scheme 12).

The inventions of Group I+ further share the technical feature a gel composition comprising a Michael addition elastomer and a topically acceptable carrier.

This shared technical feature, however, does not provide a contribution over the prior art, as being obvious over Genest in view of US 9,752,067 B2 to BYK-CHEMIE GMBH (hereinafter Byk). Genest discloses a Michael addition elastomer as described above, but does not disclose a gel composition comprising the Michael addition elastomer and d) a topically acceptable carrier fluid. Byk discloses a gel composition comprising a Michael addition adduct that is the product of an amine donor and a Michael acceptor (Col 1, ln 50-55; Col 1, ln 61-67; Col 10, ln 11-16, 'gelcoats') and a topically acceptable carrier fluid (Col 9, ln 7-10;Col 9, ln 17-21; Col 13, ln 56-64) , at a concentration of about 7% (w/w) of the gel composition (Col 23, ln 29-38, "7.8% xylene"). It would have been obvious to one ordinary skill in the art to combine the teachings of Genest and Byk to design a gel composition comprising a Michael addition elastomer for topical use, because both Genest and Byk teach Michael addition reaction products of an amine and an acrylate or ester, wherein the product is a polymer that can be used in gel compositions.

As said elastomer, gel composition and method were known in the art at the time of the invention, these cannot be considered special technical features, that would otherwise unify the inventions of Groups I+.

The inventions of Group I+, thus lack unity under PCT Rule 13.

**** Note *** Claims 24-26, written as dependent on claim 22, discusses a topically acctable carrier fluid. However the topically acceptable carrier fluid is first discussed in claim 23. Therefore for the purposes of this serarch and opinion, claims 24-26 have each been treated as dependent from claim 23. Since claim 23 is directed to a non-elected invention, Claims 24-26 have not been searched in the first invention.

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 142 959 A1

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:
10.10.2001 Bulletin 2001/41

(21) Application number: **00954907.2**

(22) Date of filing: **23.08.2000**

(51) Int Cl.[7]: **C08L 101/00**, C08L 75/04, C08K 5/36, A01N 25/04

(86) International application number:
PCT/JP00/05620

(87) International publication number:
WO 01/14478 (01.03.2001 Gazette 2001/09)

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

(30) Priority: **25.08.1999 JP 23814299**
06.10.1999 JP 28554399
14.10.1999 JP 29258399
30.11.1999 JP 34006999

(71) Applicant: **Dai-Ichi Kogyo Seiyaku Co., Ltd.**
Kyoto-shi, Kyoto 600-8873 (JP)

(72) Inventors:
- **KATAOKA, Hironori**
  Ikoma-gun, Nara 636-0801 (JP)
- **HIRATSUNA, Satoshi**
  Kyoto-shi, Kyoto 604-8411 (JP)

(74) Representative: **West, Alan Harry et al**
R.G.C. Jenkins & Co.
26 Caxton Street
London SW1H 0RJ (GB)

(54) GEL-FORM MOLDED RESIN COMPOSITION, PACKAGED VOLATILE GEL-FORM CHEMICAL, AND PROCESS FOR PRODUCING THE SAME

(57) A gel-like resin molded object composition prepared by forming a resin molded object comprising allyl isothiocyanate and a resin base into a gel is provided. This gel-like resin molded object composition is used as a gel-like repellent composition or a gel-like antimicrobial and antifungal composition. The content of allyl isothiocyanate is within a range of more than 20% by weight and not more than 85% by weight based on the total weight of the gel-like resin molded object. The rubber hardness of the gel-like resin molded object is within a range from 0.1 to 100. The gel-like resin molded object of the present invention can be formed into a bulk, sheet, film, particle, powder or coating. The gel-like resin molded object can be used as a volatile gel-like packaged drug obtained by filling a container partly comprising at least a packaging material, through which a volatile gas of said volatile drug can permeate, with a drug mixture containing a volatile drug and a gelling drug, and gelling the drug mixture.

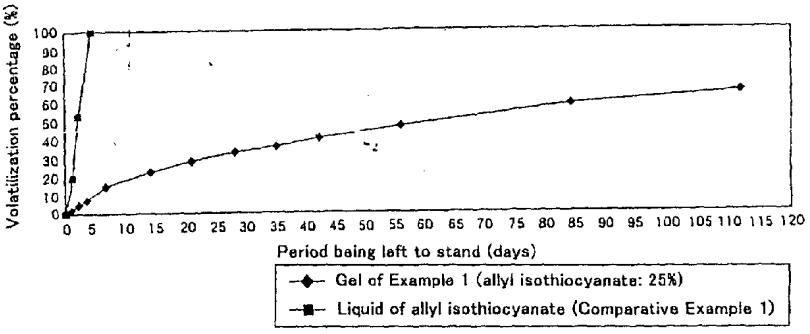


Fig. 1

EP 1 142 959 A1

Description

Field of The Invention

[0001] The present invention relates to a gel-like resin molded object and, more particularly, to a gel-like resin molded object containing allyl isothiocyanate as an active ingredient, which exerts an effect in repellent purposes of noxious organisms and antimicrobial and antifungal purposes for a long period of time, a volatile gel-like packaged drug containing the gel-like resin molded object in a container, and a method of preparing the same.

Prior Art

[0002] Allyl isothiocyanate has been known as a principal ingredient of green mustard and various applications have been suggested utilizing its stimulant action. For example, it has been suggested to utilize it as an active ingredient of antimicrobial drugs, antifungal drugs, preservatives, and repellents to noxious organisms. However, allyl isothiocyanate can not be used as it is because of its comparatively high volatility. Accordingly, it is necessary to control the volatilization rate of allyl isothiocyanate on use by setting the volatilization duration period of time of allyl isothiocyanate according to the purposes.

[0003] In light of these points, various products have been suggested. For example, there is suggested a synthetic resin film having a bactericidal action, in which allyl isothiocyanate is adsorbed on a synthetic resin film and a trace amount of vapor of allyl isothiocyanate is released from the surface thereof (Japanese patent Publication No. Hei 3-151972(A)). It is also suggested that an adsorbent is contained in a polymer molded object such as film and allyl isothiocyanate is adsorbed in the adsorbent and, furthermore, vapor of allyl isothiocyanate is released from the surface of the polymer molded object, thereby exerting an antibacterial action (Japanese Patent Publication No. Hei 3-2235(A)).

[0004] However, when using allyl isothiocyanate as a repellent, an antimicrobial and antifungal drug, etc. for noxious organisms, there is a problem that the effect does not remain in case where allyl isothiocyanate is adsorbed on the film. As a result of solution of this problem, a resin molded object is disclosed in Japanese Patent Publication No. Hei 9-151317(A). This molded object can contain a large amount of allyl isothiocyanate as an active ingredient so that the durability can be expected to some degree.

[0005] However, since this molded object is a rigidly hardened article, when allyl isothiocyanate in the vicinity of the surface is volatilized with a lapse of time, hardening of the surface proceeds and allyl isothiocyanate contained in the interior of the molded object can not transfer to the surface. Therefore, the volatilization amount of allyl isothiocyanate is lowered within about one month at most and the durability is not enough to use as a repellent, an antimicrobial and antifungal drug, etc. Moreover, The shape of the resulting molded object is not easy to deform and work, thus causing a problem about handling on manufacturing of the product.

[0006] The present invention has been made to solve the above problems of the prior art and an object of the present invention is to provide a gel-like resin molded object composition, which exerts a repellent action to noxious organisms and an antimicrobial and antifungal action for a long period of time.

[0007] In case where the volatile drug is gelled by using a gelling drug, it is made possible to transfer the active ingredient to the surface of the molded object with a lapse of time and to improve the handling. However, since the gelled resin molded object composition described above contains a comparatively large amount of a volatile drug, the volatilization rate of the drug is too large sometimes. Accordingly, it becomes necessary to control the volatilization rate of allyl isothiocyanate by containing the gel-like resin molded object composition in a packaging material through which a volatile gas of the volatile drug can permeate.

[0008] Accordingly, another object of the present invention is to provide a volatile gel-like packaged drug comprising a gel-like resin molded object composition and a container, the gel-like resin molded object composition being contained in container to control the volatilization rate of the drug.

[0009] In case of preparing the volatile gel-like packaged drug comprising a gel-like resin molded object composition and a container, the gel-like resin molded object composition being contained in container to control the volatilization rate of the drug, gelling of the volatile drug requires a certain degree of time. Therefore, it requires a comparatively long period of time and much labor to package after forming into a gel having a predetermined shape.

[0010] Also the present invention has been made to solve such a problem and another object of the present invention is to provide a volatile gel-like packaged drug which can be packaged without waiting for gelling, and a method of preparing the same.

[0011] In case where the volatilization rate of the volatile drug other than allyl isothiocyanate must be controlled, a molded object must be formed by using a resin. Also in this case, the durability of the volatilization of the volatile drug for a long period was poor.

[0012] Also the present invention has been made to solve such a problem and a still another object of the present invention is to provide a gel-like resin molded object composition capable of continuously volatilizing the volatile drug

for a long period of time.

Disclosure of the Invention

[0013] The gel-like resin molded object of the present invention is characterized by forming a resin molded object containing allyl isothiocyanate and a resin base into a gel. By forming the resin molded object containing allyl isothiocyanate into a gel, not a conventional cured article, it is made possible to transfer allyl isothiocyanate as the active ingredient to the surface of the molded object with a lapse of time, thereby lengthening the duration period of time when using as a repellent for noxious organisms.

[0014] In the above, the gel-like resin molded object preferably contains allyl isothiocyanate in the amount within a range of more than 20% by weight and not more than 85% by weight based on the total weight. When the content of allyl isothiocyanate is-within the range described above, gelling easily occurs, thereby making it possible to lengthen the duration period of time when using as a repellent for noxious organisms.

[0015] The gel-like resin molded object of the present invention can be used as a repellent composition because it has long volatilization duration period of time of allyl isothiocyanate.

[0016] The gel-like resin molded object of the present invention can also be used as an antimicrobial and antifungal drug because it has long volatilization duration period of time of allyl isothiocyanate.

[0017] Drugs such as allyl isothiocyanate are preferably used as a volatile gel-like packaged drug contained in a container to control the volatilization rate because almost all of them have comparatively high volatility. Whereby it is made possible to control the volatilization rate and to secure the volatility for a long period of time, thus making it easy to control the volatilization duration period of time of the repellent and antimicrobial and antifungal drug.

[0018] In the present specification, the volatile gel-like packaged drug include both of a drug contained in a container after gelling the gel-like resin molded object composition and a drug gelled after filling a container with a gel-like resin molded object composition before gelling. The volatile gel-like packaged drug in the present specification is referred to as a "gel-like repellent in a container" when using for repellent purposes, while it is referred to as a "gel-like antimicrobial and antifungal drug" when using for antimicrobial and antifungal purposes.

[0019] The method of the present invention is a method of preparing a volatile gel-like packaged drug in which a gel-like resin molded object composition containing a volatile drug and a gel base is contained in a container partly comprising at least a packaging material through which a volatile gas of said volatile drug can permeate, said gel-like resin molded object composition being contained in said container, said method comprises: preparing a drug mixture containing a volatile drug and a gelling drug; filling said container with said drug mixture; and gelating said drug mixture thereby to form a gel-like resin molded object composition.

[0020] Filling of the container with the gelling drug before gelating makes it unnecessary to leave or cool until the gelating of the gelling drug is completed. For example, immediately after filling a container with the gelling drug and putting the container in a corrugated cardboard box, for example, the gelling drug can be galated in the box. Accordingly, it can be stored in a warehouse before gelating the gelling drug and the manufacturing process can be drastically reduced. In the resulting gel-like resin molded object composition, it becomes possible to transfer the volatile drug as the active ingredient to the surface with a lapse of time and to lengthen the volatilization duration period of time of the drug.

[0021] Allyl isothiocyanate contained in the gel-like resin molded object and volatile gel-like packaged drug has been known as a stimulant ingredient of green mustard, as described above. In the present invention, any of natural substances and chemically synthesized substances can be used. The content of allyl isothiocyanate is within a range of more than 20% by weight and not more than 85% by weight based on the total weight of the gel-like resin molded object. When the content is not more than 20% by weight, the resulting molded object composition becomes hard without being gelled and allyl isothiocyanate does not transfer from the interior of the molded object composition to the surface, thereby shortening the volatilization duration period of time of allyl isothiocyanate, which is not preferable. On the other hand, when the content of allyl isothiocyanate is more than 85% by weight, it becomes difficult for the resulting molded object composition to maintain the gel-like form, resulting in poor handling, which is not preferable.

[0022] In the present invention, any gelling drug can be used as far as it can swell or dissolve in a volatile drug at normal temperature. Specific examples thereof include polyurethane resin, polyacrylamide, polystyrene, polyamide, polyacrylate, and copolymers of two or more monomers thereof. When using allyl isothiocyanate, mentha oil and jasmine oil as the volatile drug, a polyurethane resin is preferable in view of the solubility and sustained release of these volatile drugs as well as ease of manufacturing.

[0023] In the present invention, the polyurethane resin can be preferably used as the resin base. The polyurethane resin suited for use as the gelling drug is obtained by using the following polyisocyanates as a raw material. Examples of the polyisocyanate are bifunctional isocyanates such as phenylene diisocyanate, tolylene diisocyanate, hexamethylene diisocyanate, diphenylmethane diisocyanate, naphthalene diisocyanate, xylylene diisocyanate, polymeric diphenylmethane diisocyanate, isophorone diisocyanate, tolidine diisocyanate, hydrogenated xylylene diisocyanate, hydro-

genated diphenylmethane diisocyanate, lysine diisocyanate, tetramethylxylene diisocyanate, and trimethylhexamethylene diisocyanate; and trifunctional isocyanates such as 1,6,11-undecane triisocyanate, 1,8-diisocyanate-4-isocyanatemethyloctane, 1,3,6- hexamethylene triisocyanate, triphenylmethane triisocyanate, tris(isocyanatephenyl) thiophosphate, and lysine ester triisocyanate. It further includes adducts of the above bifunctional and trifunctional isocyanates and glycol, hexanetriol, trimethylolpropane, pentaerythritol, polyether polyol, and polyester polyol, and isocyanurate-modified compounds, buret-modified compounds and derivatives of bifunctional and trifunctional polyisocyanates. These polyisocyanates can be used alone or in combination. Among these polyisocyanates, hexamethylene diisocyanate, isophorone diisocyanate, tetramethylxylene diisocyanate, isocyanurate-modified compounds, buret-modified compounds and derivatives thereof, 1,3,6-hexamethylene triisocyanate, hydrogenated xylylene diisocyanate and hydrogenated diphenylmethane diisocyanate are preferably used because they do not cause yellowing as a result of the reaction with light and do not lower the commercial value.

[0024] Similarly, examples of the polyol as a raw material of the polyurethane resin include aliphatic polyols such as trimethylolpropane, hexanetriol, ethylene glycol, propylene glycol, and hexanediol; aromatic polyols such as xylylene glycol; polyhydric phenols such as hydroquinone and catechol; condensates of these polyhydric alcohols and alkylene oxide; and polyol prepolymers such as polyester polyol and polyether polyol. These polyols are used alone or in combination. There can also be used, as the polyol, castor oil; polyether polyols such as polyoxyalkylene polyol and polytetramethylene ether glycol; and polyester polyols such as condensed polyester polyol, lactone polyester diol and polycarbonate diol. These polyols can-be used alone or in combination. Among these polyols, castor oil is preferably used in view of the reactivity.

[0025] When using polyurethane as the resin base and using allyl isothiocyanate as the volatile drug, it depends on the kinds of polyisocyanates and polyols as well as an incorporation ratio of three ingredients, i.e. allyl isothiocyanate, polyisocyanate and polyol whether or not the resulting drug is in the form of a gel. Table 1 shows the results obtained by testing whether or not a good gel-like form is obtained by changing the incorporation ratio of the polyisocyanate (isocyanurate type hexamethylene diisocyanate) to the polyol (glyceryl triricinoleate) in case where the content of allyl isothiocyanate is controlled to 40% by weight based on the total weight of the gel-like resin molded object. Similarly, the test results in case where the content of allyl isothiocyanate is controlled to 60% by weight and 80% by weight based on the total weigh of the gel-like resin molded object are shown in Table 2 and Table 3, respectively.

Table 1

Allyl isothiocyanate	40% by weight								
Polyisocyanate* % by weight	53.91	47.92	41.93	35.94	29.95	23.96	17.97	11.98	5.99
(Weight ratio to polyl)	(90)	(80)	(70)	(60)	(50)	(40)	(30)	(20)	(10)
Polyol** % by weight	5.99	11.98	17.97	23.96	29.95	35.94	41.93	47.92	53.91
(Weight ratio to isocyanate)	(10)	(20)	(30)	(40)	(50)	(60)	(70)	(80)	(90)
Dibutyltin dilaurate	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Solidified state	○	○	○	○	○	○	○	○	×
State after one day	good	good	good	good	good	good	good	good	-
Rubber hardness	5-8	19-21	55-58	65-67	73-75	72-74	50-54	26-27	-

*: Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)
**: Castor oil (glyceryl triricinoleate)
Solidified state:

○: solidified into gel-like form within 24 hours

×: not solidified

State after one day:

Good: no change

Bleed: allyl isothiocyanate solution oozed out

Rubber hardness: measured value using Asker rubber hardness tester, Type C

Table 2

Allyl isothiocyanate	60% by weight								
Polyisocyanate* % by weight	35.91	31.92	27.93	23.94	19.95	15.96	11.97	7.98	3.99
(Weight ratio to polyl)	(90)	(80)	(70)	(60)	(50)	(40)	(30)	(20)	(10)
Polyol** % by weight	3.99	7.98	11.97	15.96	19.95	23.94	27.93	31.92	35.91
(Weight ratio to isocyanate)	(10)	(20)	(30)	(40)	(50)	(60)	(70)	(80)	(90)
Dibutyltin dilaurate	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Solidified state	○	○	○	○	○	○	○	○	×
State after one day	bleed	bleed	good	good	good	good	good	good	-
Rubber hardness	-	-	48-49	53-55	58-61	64-67	45-48	22-25	-

*: Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)
**: Castor oil (glyceryl triricinoleate)
Solidified state:
○: solidified into gel-like form within 24 hours
×: not solidified
State after one day:
Good: no change
Bleed: allyl isothiocyanate solution oozed out
Rubber hardness: measured value using Asker rubber hardness tester, Type C

Table 3

Allyl isothiocyanate	80% by weight								
Polyisocyanate* % by weight	17.91	15.92	13.93	11.94	9.95	7.96	5.97	3.98	1.99
(Weight ratio to polyl)	(90)	(80)	(70)	(60)	(50)	(40)	(30)	(20)	(10)
Polyol** % by weight	1.99	3.98	5.97	7.96	9.95	11.94	13.93	15.92	17.91
(Weight ratio to isocyanate)	(10)	(20)	(30)	(40)	(50)	(60)	(70)	(80)	(90)
Dibutyltin dilaurate	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Solidified state	○	○	○	○	○	○	○	×	×
State after one day	bleed	bleed	bleed	good	good	good	good	-	-
Rubber hardness	-	-	-	15-17	16-18	7-8	0.1-1	-	-

*: Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)
**: Castor oil (glyceryl triricinoleate)
Solidified state:
○: solidified into gel-like form within 24 hours
×: not solidified
State after one day:
Good: no change
Bleed: allyl isothiocyanate solution oozed out
Rubber hardness: measured value using an Asker rubber hardness tester, Type C

[0026] As is apparent from the results of Tables 1 to 3, gelling occurs regardless of the ratio of the polyisocyanate to the polyol in case where the content of allyl isothiocyanate is low, whereas, gelling occurs only in case where the ratio of the polyisocyanate to the polyol is close to 1:1 with the increase of the content of allyl isothiocyanate.

[0027] In the present invention, the resulting composition is in the form of a gel, as described above. Concretely, the composition preferably has a rubber strength within a range from 0.1 to 100, and more preferably within a range from 5 to 85. As used herein, the term "rubber strength" refers to a value measured by using an Asker rubber hardness tester, Type C. When the rubber strength is smaller than 0.1, the molded object composition is not formed into a gel, resulting in poor handling, which is not preferable. On the other hand, when the rubber strength is larger than 100, the molded object composition become hard so that allyl isothiocyanate does not transfer from the interior of the molded object to the surface and the volatility of allyl isothiocyanate is lowered, which is not preferable.

[0028] The gel-like resin molded object composition of the present invention can be used in various forms of bulk, sheet, film, particle, powder, or a coating formed on the surface of articles in various forms. Such a gel-like resin molded object composition can be used as a gel-like repellent composition or a gel-like antimicrobial and antifungal drug composition because it volatilizes allyl isothiocyanate for a long period of time. Such a gel-like resin molded object composition is preferably used as a volatile gel-like packaged drug contained in a container for controlling the volatilization rate.

[0029] The gel-like repellent composition and the gel-like repellent contained in a container can be used for noxious organisms. The noxious organisms includes cockroaches, weevils, termites, rats, moles, dogs, cats, deer, crows, bears, and pigeons.

[0030] The gel-like repellent composition and the gel-like repellent contained in a container of the present invention can be used in various places, for example, transport facilities such as freight car, ship, and aircraft, warehouse (especially cereal warehouse), greenhouse (including glass and vinyl houses), chest, closet, rice chest, dumping ground, plantation, garden, sandbox, electric wiring position, switchboard, and steel tower, including spaces adjacent to space of residence including underfloor and ceiling of architectural structures such as building and house. In these places, the gel-like repellent composition and the gel-like repellent contained in a container of the present invention can be disposed by various methods such as placing, mounting to the wall or ceiling, and hanging on the wall or ceiling.

[0031] The gel-like resin molded object composition of the present invention can be used as a gel-like antimicrobial and antifungal composition because it volatilizes allyl isothiocyanate for long period of time. The gel-like resin molded object composition of the present invention is preferably used as a gel-like antimicrobial and antifungal drug after being contained in a container for controlling the volatilization rate of allyl isothiocyanate. The volatilization rate of allyl isothiocyanate can be made nearly uniform by containing the gel-like resin molded object composition of the present invention in a container.

[0032] The gel-like antimicrobial and antifungal composition and the gel-like antimicrobial and antifungal drug contained in a container of the present invention can be used in various places, for example, refrigerators for domestic and business uses, electrical appliances such as cleaner, air conditioner, and ventilator, transport facilities such as freight car, ship, and aircraft, warehouse (especially cereal warehouse), greenhouse (including glass and vinyl houses), underfloor and ceiling of architectural structures such as building and house, shoe box, bath room, washstand, kitchen, and closet. In these places, the gel-like antimicrobial and antifungal composition and the gel-like antimicrobial and antifungal drug contained in a container of the present invention can be disposed by various methods such as put down as it stands, mounting to the wall or ceiling, and hanging on the wall or ceiling.

[0033] The container in which the gel-like resin molded object composition of the present invention is contained includes, for example, a container as shown in Fig. 6. This container comprises a container body 1 in which the gel-like resin molded object composition of the present invention is contained, a cap 2 which is removably attached to an opening portion of the container body, and a vent hole 3 with which the cap 2 is provided. According to this container, the volatilization rate of allyl isothiocyanate can be controlled by changing the size and number of the vent hole 3.

[0034] The container used in the present invention includes, for example, a bag comprising a thermoplastic resin film through which allyl isothiocyanate can permeate. Examples of such a film are polyethylene, polypropylene, ethylene-vinyl acetate, polyethylene terephthalate, polyvinyl chloride, nylon and polyacetal films, and laminated films thereof. In the present invention, there can be those prepared by laminating the above film with the other packaging material such as nonwoven fabric. A combination with the other packaging material makes it possible to reinforce the film and to print, resulting in improvement of the appearance of the product.

[0035] The packaging bag in the present invention includes, for example, those shown in Fig. 7. This packaging bag 4 is made of a laminated film prepared by laminating a film, through which allyl isothiocyanate can permeate, with a nonwoven fabric, and the gel-like resin molded object composition of the present invention is contained therein by sealing at three sealing positions 5, 6 and 7. According to this packaging film 4, the volatilization rate of allyl isothiocyanate can be controlled by changing the thickness and kinds of the allyl isothiocyanate-permeable film.

[0036] Furthermore, the container can further comprises an aluminum foil laminated with a gas-permeable packaging material on the outer surface. Such an aluminum foil makes it possible inhibit the volatilization of the volatile drug until

the beginning of the use of volatile gel-like packaged drug.

[0037] The gel-like resin molded object composition of the present invention can be used alone, but can also be used in combination with known aromatics containing various perfumes and known deodorants for preventing bad smell.

[0038] The method of preparing the volatile gel-like packaged drug of the present invention can be applied to the case where the volatile gel-like packaged drug is in the form of a sheet. The sheet-like and gel-like packaged drug is widely used because of its non-bulky form. Such a sheet-like and gel-like packaged drug is obtained by filling the same bag-shaped container as that in Fig. 7 with a mixture containing a volatile drug and a gelling drug before gelating of the gelling drug. After filling the container with the drug and gelling drug, these bag-shaped containers can be stored in the state of being laid one upon another and the manufacturing process can be drastically shortened.

[0039] The polyurethane resin used as the gelling drug in the present invention can also be used to gelate the volatile drug other than allyl isothiocyanate. Specific examples thereof include repellents, insect repellents, germicides, insecticides, antimicrobials, and pesticides.

[0040] The repellent and insect repellent include, for example, various synthetic chemical substances, in addition to vegetable oil, natural perfume, and synthetic perfume. Specific examples of the vegetable oil are Japanese cypress oil, hiba oil(*Thujopsis dolabrata* oil), alpina speciosae semn oil, citrus oil, ginger oil, cedar oil, red paper oil, and mustard oil, in addition to allyl isothiocyanate. Specific examples of the natural perfume and synthetic perfume are bouquet oil, rose oil, green floral oil, eucalyptus oil, lavender oil, jasmine oil, lemon oil, and mentha oil. Specific examples of the synthetic chemical substance are methyl salicylate, diethyltoluamide, dimethyl phthalate, denatonium benzoate, phenethyl alclohol, bis(2-chloro-1-methylethyl)ether, naphthalene, C_{1-8} dialkyl phthalate, and 2-(4-ethoxyphenyl)-2-methylpropyl 3-phenoxy ether.

[0041] Specific examples of the germicide and insecticide are dimethyl-2,2-dichlorovinyl phosphate (DDVP), pyrethrin, parathion, chlorodimethylphenol, and bromomethylbenzaldehyde, in addition to allyl isothiocyanate.

[0042] Specific examples of the antimicrobial are eucalyptus oil, hiba oil, hinokitiol, linanool, limonene, diethyltoluamide, mentha oil, and mugwort oil, in addition to allyl isothiocyanate.

[0043] Specific example of the pesticide are those used for insecticide and fungicide, such as diemthyl-2,2-dichlorovinyl phosphate (DDVP), o,o-dimethyl-o-(3-methyl-4-nitrophenyl) thiophosphate, dimethyldicarbethoxyethyl dithiphosphate, 2-(4-ethoxydiphenyl)-2-methylpropyl 3-phenoxybenzyl ether, and bis(dimethylthiocarbamoyl) disulfide. Examples of these used as the herbicide are S-(2-chlorobenzyl) N,N-diethyl thiocarbamate and S-benzyl 1,2-dimethyl propyl(ethyl)thiocarbamate. Examples of the fumigant are methyl isothiocyanate, methyl bromide, and chloropicrin. Examples of the attractant are turpentine oil and pinene oil.

[0044] When using mentha oil or jasmine oil as the volatile drug, mentha oil or jasmine oil is preferably contained in the amount within a range of more than 20% by weight and not more than 40% by weight. When the amount is not more than 20% by weight, the volatilization amount of mentha oil or jasmine oil is small and the volatilization duration period of time is shortened, which is not preferable. On the other hand, when the amount is more than 40% by weight, the resulting composition is not in the form of a gel, which is not preferable.

[0045] When using polyurethane as the resin base, it depends on the kinds of polyisocyanates and polyols as the raw material as well as an incorporation ratio of three ingredients, i.e. volatile drug, polyisocyanate and polyol whether or not the resulting drug is in the form of a gel. Tables 4 to 8 show the results of the test which examines whether or not a good gel-like form is obtained when mentha oil is used as the volatile drug and the incorporation ratio of polyisocyanate (isocyanurate type hexamethylene diisocyanate) to polyol (glyceryl triricinoleate) is changed. Tables 4 to 8 show the test results in case where the content of mentha oil is controlled to 5, 10, 20, 40 or 60% by weight relative to the total weight of the resulting gel-like resin molded object.

[0046] As is apparent from the results of Tables 4 to 8, gelling occurs regardless of the ratio of the polyisocyanate to the polyol in case where the content of mentha oil is low, whereas, gelling occurs only in case where the weight ratio of the polyisocyanate to the polyol is close to 80:20 with the increase of the content of allyl isothiocyanate.

Table 4

Mentha oil	5%								
Isocyanate* % by weight	85.41	75.92	66.43	56.94	47.45	37.96	28.47	19.98	9.49
Weight ratio to polyl)	(90)	(80)	(70)	(60)	(50)	(40)	(30)	(20)	(10)
Polyol** % by weight	5.49	19.98	28.47	37.96	47.45	56.94	66.43	75.92	85.41
(Weight ratio to isocyanate)	(10)	(20)	(30)	(40)	(50)	(60)	(70)	(80)	(90)
Tin catalyst	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Solidified state	○	○	○	○	○	○	○	○	○
State after one day	good	good	good	good	good	good	good	good	good
Rubber hardness	31-33	60-64	85-87	88-91	86-89	78-83	56-60	37-42	20-24

*: Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)
**: Castor oil (glyceryl triricinoleate)
Solidified state:
○: solidified into gel-like form within 24 hours
×: not solidified
State after one day:
Good: no change
Bleed: allyl isothiocyanate solution oozed out
Rubber hardness: measured value using Asker rubber hardness tester, Type C

0294

Table 5

Mentha oil	10%								
Isocyanate* % by weight	80.91	71.92	62.93	53.94	44.95	35.96	26.97	17.98	8.99
(Weight ratio to polyl)	(90)	(80)	(70)	(60)	(50)	(40)	(30)	(20)	(10)
Polyol** % by weight	8.99	17.98	26.97	35.96	44.95	53.94	62.93	71.92	80.91
(Weight ratio to isocyanate)	(10)	(20)	(30)	(40)	(50)	(60)	(70)	(80)	(90)
Tin catalyst	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Solidified state	○	○	○	○	○	○	○	○	○
State after one day	good	good	good	good	good	good	good	good	good
Rubber hardness	28-30	58-61	82-86	85-88	81-85	75-78	51-54	29-33	10-13

*: Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)
**: Castor oil (glyceryl triricinoleate)
Solidified state:
○: solidified into gel-like form within 24 hours
×: not solidified
State after one day:
Good: no change
Bleed: allyl isothiocyanate solution oozed out
Rubber hardness: measured value using Asker rubber hardness tester, Type C

Table 6

Mentha oil	20%								
Isocyanate* % by weight	71.91	63.92	55.93	47.94	39.95	31.96	23.97	15.98	7.99
(Weight ratio to polyl)	(90)	(80)	(70)	(60)	(50)	(40)	(30)	(20)	(10)
Polyol** % by weight	7.99	15.98	23.97	31.96	39.95	47.94	55.93	63.92	71.91
(Weight ratio to isocyanate)	(10)	(20)	(30)	(40)	(50)	(60)	(70)	(80)	(90)
Tin catalyst	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Solidified state	○	○	○	○	○	○	○	○	×
State after one day	good	good	good	good	good	good	good	good	-
Rubber hardness	17-21	48-51	74-77	78-81	72-64	64-67	40-43	12-14	-

*: Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)
**: Castor oil (glyceryl triricinoleate)
Solidified state:
○: solidified into gel-like form within 24 hours
×: not solidified
State after one day:
Good: no change
Bleed: allyl isothiocyanate solution oozed out
Rubber hardness: measured value using Asker rubber hardness tester, Type C

Table 7

Mentha oil	40%								
Isocyanate* % by weight (Weight ratio to polyl)	53.91 (90)	47.92 (80)	41.93 (70)	35.94 (60)	29.95 (50)	23.96 (40)	17.97 (30)	11.98 (20)	5.99 (10)
Polyol** % by weight (Weight ratio to isocyanate)	5.99 (10)	11.98 (20)	17.97 (30)	23.96 (40)	29.95 (50)	35.94 (60)	41.93 (70)	47.92 (80)	53.91 (90)
Tin catalyst	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Solidified state	○	○	○	○	○	×	×	×	×
State after one day	good	good	good	good	good	-	-	-	-
Rubber hardness	1-3	13-17	28-34	27-32	4-6	-	-	-	-

*: Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)
**: Castor oil (glyceryl triricinoleate)
Solidified state:
○: solidified into gel-like form within 24 hours
×: not solidified
State after one day:
Good: no change
Bleed: allyl isothiocyanate solution oozed out
Rubber hardness: measured value using Asker rubber hardness tester, Type C

Table 8

Mentha oil	60%								
Isocyanate* % by weight	35.91	31.92	27.93	23.94	19.95	15.96	11.97	7.98	3.99
(Weight ratio to polyl)	(90)	(80)	(70)	(60)	(50)	(40)	(30)	(20)	(10)
Polyol** % by weight	3.99	7.98	11.97	15.96	19.95	23.94	52.93	31.92	35.91
(Weight ratio to isocyanate)	(10)	(20)	(30)	(40)	(50)	(60)	(70)	(80)	(90)
Tin catalyst	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Solidified state	○	○	×	×	×	×	×	×	×
State after one day	bleed	good	-	-	-	-	-	-	-
Rubber hardness	-	0.5-1	-	-	-	-	-	-	-

*: Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)
**: Castor oil (glyceryl triricinoleate)
Solidified state:
○: solidified into gel-like form within 24 hours
×: not solidified
State after one day:
Good: no change
Bleed: allyl isothiocyanate solution oozed out
Rubber hardness: measured value using Asker rubber hardness tester, Type C

[0047] Similarly, Tables 9 to 15 show the results of the test which examines whether or not a good gel-like form is obtained when jasmine oil is used as the volatile drug and the incorporation ratio of polyisocyanate (isocyanurate type hexamethylene diisocyanate) to polyol (glycerin triricinoleate) is changed. Tables 9 to 15 show the test results in case where the content of jasmine oil is controlled to 5, 10, 20, 40 or 60% by weight relative to the total weight of the resulting gel-like resin molded object.

[0048] As is apparent from the results of Tables 9 to 15, gelling occurs regardless of the ratio of the polyisocyanate to the polyol in case where the content of jasmine oil is low, whereas, gelling occurs only in case where the weight ratio of the polyisocyanate to the polyol is close to 80:20 with the increase of the content of allyl isothiocyanate.

Table 9

Jasmine oil	5%								
Isocyanate* % by weight	85.41	75.92	66.43	56.94	47.45	37.96	28.47	19.98	9.49
(Weight ratio to polyl)	(90)	(80)	(70)	(60)	(50)	(40)	(30)	(20)	(10)
Polyol** % by weight	9.99	19.98	28.47	37.96	47.45	56.94	66.43	75.92	85.41
(Weight ratio to isocyanate)	(10)	(20)	(30)	(40)	(50)	(60)	(70)	(80)	(90)
Tin catalyst	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Solidified state	○	○	○	○	○	○	○	○	○
State after one day	good	good	good	good	good	good	good	good	good
Rubber hardness	12-15	35-37	60-65	71-74	80-85	78-82	58-62	40-43	22-24

*: Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)
**: Castor oil (glyceryl triricinoleate)
Solidified state:
○: solidified into gel-like form within 24 hours
×: not solidified
State after one day:
Good: no change
Bleed: allyl isothiocyanate solution oozed out
Rubber hardness: measured value using Asker rubber hardness tester, Type C

Table 10

Jasmine oil	10%								
Isocyanate* % by weight	80.91	71.92	62.93	53.94	44.95	35.96	26.97	17.98	8.99
(Weight ratio to polyl)	(90)	(80)	(70)	(60)	(50)	(40)	(30)	(20)	(10)
Polyol** % by weight	8.99	17.98	26.97	35.96	44.95	53.94	62.93	71.92	80.91
(Weight ratio to isocyanate)	(10)	(20)	(30)	(40)	(50)	(60)	(70)	(80)	(90)
Tin catalyst	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Solidified state	○	○	○	○	○	○	○	○	○
State after one day	good	good	good	good	good	good	good	good	good
Rubber hardness	11-13	32-34	58-63	67-69	78-82	76-80	56-59	36-39	20-22

*: Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)
**: Castor oil (glyceryl triricinoleate)
Solidified state:
○: solidified into gel-like form within 24 hours
×: not solidified
State after one day:
Good: no change
Bleed: allyl isothiocyanate solution oozed out
Rubber hardness: measured value using Asker rubber hardness tester, Type C

Table 11

Jasmine oil	20%								
Isocyanate* % by weight	71.91	63.92	55.93	47.94	39.95	31.96	23.97	15.98	7.99
(Weight ratio to polyl)	(90)	(80)	(70)	(60)	(50)	(40)	(30)	(20)	(10)
Polyol** % by weight	7.99	15.98	23.97	31.96	39.95	47.94	55.93	63.92	71.91
(Weight ratio to isocyanate)	(10)	(20)	(30)	(40)	(50)	(60)	(70)	(80)	(90)
Tin catalyst	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Solidified state	○	○	○	○	○	○	○	○	×
State after one day	good	good	good	good	good	good	good	good	-
Rubber hardness	2-4	20-22	47-50	56-59	65-69	66-70	46-50	16-20	-

*: Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)
**: Castor oil (glyceryl triricinoleate)
Solidified state:
○: solidified into gel-like form within 24 hours
×: not solidified
State after one day:
Good: no change
Bleed: allyl isothiocyanate solution oozed out
Rubber hardness: measured value using Asker rubber hardness tester, Type C

Table 12

Jasmine oil	40%								
Isocyanate* % by weight	53.91	47.92	41.93	35.94	29.95	23.96	17.97	11.98	5.99
(Weight ratio to polyl)	(90)	(80)	(70)	(60)	(50)	(40)	(30)	(20)	(10)
Polyol** % by weight	5.99	11.98	17.97	23.96	29.95	35.94	41.93	47.92	53.91
(Weight ratio to isocyanate)	(10)	(20)	(30)	(40)	(50)	(60)	(70)	(80)	(90)
Tin catalyst	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Solidified state	○	○	○	○	○	×	×	×	×
State after one day	good	good	good	good	good	-	-	-	-
Rubber hardness	0.5-1	9-12	38-40	50-52	18-20	-	-	-	-

*: Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)
**: Castor oil (glyceryl triricinoleate)
Solidified state:
○: solidified into gel-like form within 24 hours
×: not solidified
State after one day:
Good: no change
Bleed: allyl isothiocyanate solution oozed out
Rubber hardness: measured value using Asker rubber hardness tester, Type C

Table 13

Jasmine oil	60%								
Isocyanate* % by weight (Weight ratio to polyl)	35.91 (90)	31.92 (80)	27.93 (70)	23.94 (60)	19.95 (50)	15.96 (40)	11.97 (30)	7.98 (20)	3.99 (10)
Polyol** % by weight (Weight ratio to isocyanate)	3.99 (10)	7.98 (20)	11.97 (30)	15.96 (40)	19.95 (50)	23.94 (60)	52.93 (70)	31.92 (80)	35.91 (90)
Tin catalyst	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Solidified state	○	○	×	×	×	×	×	×	×
State after one day	bleed	good	-	-	-	-	-	-	-
Rubber hardness	-	1-2	-	-	-	-	-	-	-

*: Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)
**: Castor oil (glyceryl triricinoleate)
Solidified state:
○: solidified into gel-like form within 24 hours
×: not solidified
State after one day:
Good: no change
Bleed: allyl isothiocyanate solution oozed out
Rubber hardness: measured value using Asker rubber hardness tester, Type C

0304

[0049] Concretely, the composition of the present invention prepared by gelling the volatile drug using polyurethane as a gelling agent preferably has a rubber strength measured by using an Asker rubber hardness tester Type C, within a range from 0.1 to 100, and more preferably from 5 to 85. Similar to the above case, when the rubber strength is smaller than 0.1, the resulting molded object composition is not formed into a gel, resulting in poor handling, which is not preferable. On the other hand, when the rubber strength is larger than 100, the molded object composition becomes hard and allyl isothiocyanate does not transfer from the interior of the molded object to the surface, thereby lowering the volatility of allyl isothiocyanate, which is not preferable.

[0050] The gel-like resin molded object composition prepared by gelling the volatile drug of the present invention using polyurethane as a gelling drug can be used in various forms of bulk, sheet, film, particle, powder, or a coating formed on the surface of articles in various forms. Such a gel-like resin molded object composition can be used for various purposes because it volatilizes the volatile drug for a long period of time.

Brief Description of the Drawings

[0051]

Fig. 1 is a graph showing the results of a volatilization test of a gel-like repellent contained in a container of a styrol container which contains a gel-like repellent composition including an allyl isothiocyanate content of 25%.
Fig. 2 is a graph showing the results of a volatilization test of a gel-like repellent contained in a container of a styrol container which contains a gel-like repellent composition including an allyl isothiocyanate content of 40%.
Fig. 3 is a graph showing the results of a volatilization test of a gel-like repellent contained in a container of a styrol container which contains a gel-like repellent composition having an allyl isothiocyanate content of 60%.
Fig. 4 is a graph showing the results of a volatilization test of a gel-like repellent contained in a container of a styrol container which contains a gel-like repellent composition including an allyl isothiocyanate content of 80%.
Fig. 5 is a graph showing the results of a volatilization test using a gel-like molded object sheet.
Fig. 6 is a schematic view showing an example of a container containing a gel-like molded object composition.
Fig. 7 is a schematic view showing an example of a packaging bag containing a gel-like molded object composition.
Fig. 8 is a schematic view showing the arrangement of chambers A to B and T for carrying out a repellence test.
Fig. 9 is a graph showing the results of a volatilization test of mentha oil using a gel-like molded object contained in a styrol container.
Fig. 10 is a graph showing the results of a volatilization test of mentha oil using a gel-like molded object sheet.
Fig. 11 is a graph showing the results of a volatilization test of jasmine oil using a gel-like molded object contained in a styrol container.
Fig. 12 is a graph showing the results of a volatilization test of jasmine oil using a gel-like molded object sheet.

Best Mode for Carrying out the Invention

(Examples 1 to 4)

[0052] In accordance with each formulation shown in the column of Examples 1 to 4 of Table 14, ingredients were mixed and dissolved in the order from the upper column of the same table. Finally, dibutyltin dilaurate was added and mixed and a styrol container (having an inner diameter of 35 mm and a height of 35 mm) was filled with 15 g of the mixture, and then left to stand at room temperature. After two hours have passed since the filling, gel-like molded objects with no fluidity were obtained, thereby gel-like repellents contained in a container of Examples 1 to 4 were obtained.

Table 14

	Example 1 Example 12	Example 2 Example 13	Example 3 Example 14	Example 4
Castor oil (Glyceryl triricinoleate)	37.45	29.95	19.95	9.95
Polyisocyanate*	37.45	29.95	19.95	9.95
Allyl isothiocyanate	25.0	40.0	60.0	80.0
Dibutyltin dilaurate (10% ethyl acetate solution)	0.1	0.1	0.1	0.1

* Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)

(Examples 5 to 8)

[0053] In accordance with each formulation shown in the column of Examples 1 to 4 of Table 14, ingredients were mixed and dissolved in the order from the upper column of the same table in the same procedure as in Examples 1 to 4. Finally, dibutyltin dilaurate was added and mixed, and then 25 g of the mixture was poured into an aluminum mold of 10 cm × 5 cm in size and left to stand at room temperature in the horizontal position. After two hours have passed since leaving to stand, gel-like molded object sheets having a thickness of 0.5 cm with no fluidity were obtained.

(Examples 9 to 11)

[0054] The sheets obtained in Example 6 (content of allyl isothiocyanate: 40%) were respectively put in an aluminum bag laminated with polyethylene on the inner surface, one surface of which is provided with three openings having a diameter of 1 cm (6 cm × 6 cm in size), a polypropylene bag (6 cm × 6 cm in size) and a polyethylene bag (6 cm × 6 cm in size) to obtain gel-like repellents contained in a container of Examples 9 to 11, respectively.

<Volatility test>

[0055] Using the gel-like molded objects contained in a styrol container of Examples 1 to 4, a volatility test of allyl isothiocyanate was performed. The results are shown in Figs. 1 to 4. The volatilization rate was represented by a weight loss (% by weight). For comparison, allyl isothiocyanate was charged in the same container as that used in Examples 1 to 4 as it is in the state of liquid, and then the volatilization test was performed simultaneously with the volatilization test of the gel-like molded object (Comparative Examples 1 to 4). The weight of liquid allyl isothiocyanate in Comparative Examples 1 to 4 is the same as that of allyl isothiocyanate contained in the corresponding gels of Examples 1 to 4.

[0056] As is apparent from Figs. 1 to 4, the volatilization rate of allyl isothiocyanate can be controlled by gelling allyl isothiocyanate. The total amount of any liquid allyl isothiocyanate is volatilized within 15 days, whereas, the duration period of time of two to three months or more is attained by gelling.

[0057] Using the gel-like molded object sheets of Examples 5 to 8, the volatilization test was performed. The results are shown in Fig. 5. As is apparent from Fig. 5, the volatilization rate of allyl isothiocyanate can be controlled by gelling allyl isothiocyanate.

<Repellence test>

[0058] Using the respective gel-like repellents of Examples 1 to 4, Examples 5 to 8 and Comparative Examples 9 to 11, a repellence test of black rats was performed. As shown in Fig. 8, a center chamber T made of an acrylic plate was prepared and chambers A, B, C and D, which is also made of the same acrylic plate, were prepared around the chamber T. The center chamber T was connected with the respective chambers A, B, C and D through a passage made of a wire netting, while each entrance of the chambers A, B, C and D is provided with a door through which black rats can go in and out. The center chamber T is employed as a space of residence, while the chambers A, B, C and D were employed as a feed place.

[0059] In the chamber A, only water and feed (solid feed, vegetable) were disposed. In the chamber B, water, feed (solid feed, vegetable) and the gel-like repellents contained in a container of Examples 1 to 4 were disposed. In the chamber C, water, feed (solid feed, vegetable) and the gel-like repellents of Examples 5 to 8 were disposed. In the chamber D, water, feed (solid feed, vegetable) and the gel-like repellent sheets contained in a packaging bag of Examples 9 to 11 were disposed. Samples of the respective repellents were used by controlling the weight so that the total amount of allyl isothiocyanate becomes 5 g, though they differ in shape.

[0060] After arranging the respective chambers as described above, five black rats were put into the center chamber T and the state of each black rat was observed for five days. The weight loss of water and feed was also checked. Samples of the gel-like repellents were maintained as they are and, after one month, water and feed were disposed again in the respective chambers A to D and new black rats were put into the chambers. The state of each black rat was observed for five days and the weight loss of water and feed was also checked. The repellent effect was evaluated by repeatedly performing this test every one month.

[0061] In the chamber B, the test was performed by using the repellents contained in a container of Examples 1 to 4, as described above. In case of the repellent (content of allyl isothiocyanate: 80%) of Example 4, the amount of feed began to be reduced after two months. In case of the repellent (content of allyl isothiocyanate: 60%) of Example 3, the amount of feed began to be reduced after four months. In case of the repellent (content of allyl isothiocyanate: 40%) of Example 2, the amount of feed began to be reduced after eight months. In case of the repellent (content of allyl isothiocyanate: 25%) of Example 1, the amount of feed began to be reduced after ten months. In case where the repellents of Examples 1 to 4 are provided with an inner cap with 20 openings of 1 mm in diameter, intake of feed was

not recognized even after one year has passed.

[0062] In the chamber C, the test was performed by using the sheet-like repellents of Examples 5 to 8. In case of the sheet-like repellent (content of allyl isothiocyanate: 80%) of Example 8, the amount of feed began to be reduced after one month. In case of the sheet-like repellent (content of allyl isothiocyanate: 60%) of Example 7, the amount of feed began to be reduced after 1.5 months. In case of the sheet-like repellent (content of allyl isothiocyanate: 40%) of Example 6, the amount of feed began to be reduced after two months. In case of the sheet-like repellent (content of allyl isothiocyanate: 25%) of Example 5, the amount of feed began to be reduced after three months.

[0063] In the chamber D, any of the polyethylene-, polypropylene-and aluminum-packaged repellents (any content of allyl isothiocyanate: 40%) of Examples 9 to 11, the amount of feed began to be reduced after four months.

[0064] As is apparent from the above results, any of the repellents of Examples 1 to 11 exerts the repellent effect to black rat for a long period of time.

[0065] Although the repellent effect was examined to black rats as described above, it was confirmed that the gel-like molded object composition of the present invention also exerts the repellent effect to other noxious organisms such as cockroaches, weevils, termites, moles, dogs, cats, deer, crows, bears, and pigeons.

(Examples 12 to 14)

[0066] In accordance with each formulation shown in Table 14, ingredients were mixed and dissolved in the order from the upper column of the same table. Then, dibutyltin dilaurate was added and mixed to prepare a drug mixture. A bag-shaped polypropylene container made of 4.5 cm × 4.5 cm in inner side was filled with 5 g of the drug mixture and then heat-sealed. After three hours have passed since leaving to stand in the horizontal position, sheet-like and volatile gel-like packaged drugs with no fluidity were obtained.

(Examples 15 to 17)

[0067] A bag-shaped polypropylene container was filled with 5 g of each of the drug mixtures prepared in accordance with each formulation of Examples 12 to 14 (Table 14), and then put in an aluminum foil bag laminated with polyethylene on the inner surface prior to gelling. This bag was left to stand in the horizontal position and sheet-like and volatile gel-like packaged drugs with no fluidity were obtained after three hours from filling.

(Examples 18 to 20)

[0068] In accordance with the same formulation as in Examples 12 to 14 (Table 14), drug mixtures were prepared. A bag-shaped container (4.5 cm × 4.5 cm in inner side) of an aluminum foil laminated with polyethylene on the inner surface was filled with 5 g of each drug mixture and then heat-sealed. This bag was left to stand in the horizontal position and sheet-like and volatile gel-like packaged drugs with no fluidity were obtained after three hours from filling.

(Comparative Examples 5 to 7)

[0069] In accordance with the same formulation as in Examples 12 to 14 (Table 14), drug mixtures were prepared. 5 g of each drug mixture was poured into an aluminum mold of 4.5 cm × 4.5 cm in size and left to stand at room temperature in the horizontal position. After three hours have passed, sheet-like and gel-like resin molded object compositions with no fluidity were obtained.

<Volatility test>

[0070] Using the volatile gel-like packaged drugs of Examples 12 to 14, the volatile gel-like packaged drugs (aluminum foil is peeled off) of Examples 15 to 17, the volatile gel-like packaged drugs (aluminum foil is peeled off) of Examples 18 to 20, and the sheet-like and gel-like packaged drugs of Comparative Examples 5 to 7, a volatilization test of allyl isothiocyanate was performed. As a result, almost all of allyl isothiocyanate was volatilized within 50 days in the gel-like resin molded object compositions, which are not contained in a container, of Comparative Examples 5 to 7, whereas, the duration period of time of allyl isothiocyanate was attained for three to four months or more in the volatile gel-like packaged drugs of Examples 12 to 20.

(Examples 21 and 22)

[0071] In accordance with each formulation shown in Examples 21 and 22 of Table 15, ingredients were mixed and dissolved in the order from the upper column of the same table. Finally, dibutyltin dilaurate was added and mixed and

a styrol container (having an inner diameter of 35 mm and a height of 35 mm) was filled with 15 g of the mixture, and then left to stand at room temperature. After two hours have passed since the filling, gel-like molded objects with no fluidity were obtained. Thus, gel-like repellents contained in a container of Examples 21 and 22 were prepared.

Table 15

	Example 21	Example 22	Example 23	Example 24
Castor oil (Glyceryl triricinoleate)	29.95	29.95	23.96	23.96
Polyisocyanate*	29.95	29.95	35.94	35.94
Mentha oil	40.0	-	40.0	-
Jasmine oil	-	40.0	-	40.0
Dibutyltin dilaurate (10% ethyl acetate solution)	0.1	0.1	0.1	0.1

* Duranate THA-100 (isocyanurate type hexamethylene diisocyanate, manufactured by Asahi Chemical Industries Co., Ltd.)

(Examples 23 and 24)

[0072] In accordance with each formulation shown in the column of Examples 21 and 22 of Table 15, ingredients were mixed and dissolved in the order from the upper column of the same table in the same procedure as in Examples 21 and 22. Finally, dibutyltin dilaurate was added and mixed, and then 25 g of the mixture was poured into an aluminum mold of 10 cm × 5 cm in size and left to stand at room temperature in the horizontal position. After two hours have passed, gel-like molded object sheets having a thickness of 0.5 cm with no fluidity were obtained.

Volatility test>

[0073] Using the gel-like molded objects contained in a styrol container of Examples 21 and 22, a volatilization test of mentha oil and jasmine oil was performed. The results are shown in Fig. 9 and Fig. 11. The volatilization rate was represented by a weight loss (% by weight) relative to an initial weight of a gel. For comparison, each of mentha oil and jasmine oil was charged in the same container as that used in Examples 21 and 22 as it is-in the state of liquid, and then the volatilization test was performed simultaneously with the volatilization test of the gel-like molded object (Comparative Examples 8 and 9). Each weight of mentha oil and jasmine oil in Comparative Examples 8 and 9 is the same as that of mentha oil and jasmine oil contained in the corresponding gels of Examples 21 and 22.

[0074] As is apparent from Fig. 9 and Fig. 11, the volatilization rate of mentha oil and jasmine oil can be controlled by gelling mentha oil and jasmine oil. The total amount of any of mentha oil and jasmine oil is volatilized within 60 days, whereas, the duration period of time of eight or more months is attained by gelling.

[0075] Using the gel-like molded object sheets of Examples 23 to 24, the volatilization test was performed. The results are shown in Fig. 10 and Fig. 12, respectively. As is apparent from Fig. 10 and Fig. 12, the volatilization rate of mentha oil and jasmine oil can be controlled by gelling mentha oil and jasmine oil.

[0076] The above embodiment illustrated the case where the drug mixture is prepared in a batch fashion, but the present invention is not limited thereto and can also be applied to the case where the drug mixture is continuously prepared by using, e.g. a static mixer.

[0077] As described above, regarding the gel-like resin molded object composition of the present invention, because the resin molded object containing allyl isothiocyanate and a base resin is in the form of a gel, it is made possible to transfer allyl isothiocyanate as the active ingredient to the surface of the molded object with a lapse of time, thereby lengthening the duration period of time when using as a repellent and an antimicrobial and antifungal drug for noxious organisms.

[0078] The gel-like resin molded object contains allyl isothiocyanate in the amount within a range of more than 20% by weight and not more than 85% by weight based on the total weight. Therefore, it is made possible to maintain the volatilization of allyl isothiocyanate for a long period of time.

[0079] Accordingly, the gel-like resin molded object composition containing allyl isothiocyanate of the present invention can exert the effect of an antimicrobial and antifungal drug for noxious organisms for a long period of time.

[0080] Furthermore, the gel-like repellent in a container and the gel-like antimicrobial and antifungal drug in a container of the present invention can control the volatilization of allyl isothiocyanate having comparatively high volatility. Therefore, it is made possible to exert the effect of an antimicrobial and antifungal drug for noxious organisms for a long period of time.

[0081] According to the method of preparing the volatile gel-like packaged drug of the present invention, a container is filled with a drug mixture containing a volatile drug and a gelling drug-before curing of the gelling drug. Therefore, it becomes unnecessary to leave until the curing of the gelling drug is completed, thereby making it possible to drastically shorten the manufacturing process.

[0082] In the gel-like resin molded object composition prepared by gelling a volatile drug of the present invention using polyurethane as a gelling drug, a volatile substance as an active ingredient is retained in a gel. Therefore, it is made possible to transfer the volatile substance to the surface of the molded object with a lapse of time, thereby maintaining the volatilization of the volatile drug for a long period of time.

Claims

1. A gel-like resin molded object composition comprising allyl isothiocyanate and a resin base.

2. A gel-like resin molded object composition according to claim 1, wherein said allyl isothiocyanate is contained in the amount within a range of more than 20% by weight and not more than 85% by weight based on the total weight of said gel-like resin molded object.

3. A gel-like resin molded object composition according to any one of claims 1 to 2, wherein the rubber hardness of said gel-like resin molded object is within a range from 0.1 to 100.

4. A gel-like resin molded object composition according to any one of claims 1 to 3, wherein said gel-like resin molded object is in the form of a bulk, sheet, film, particle, powder or coating.

5. A gel-like resin molded object composition according to any one of claims 1 to 4, wherein said resin base is a polyurethane resin.

6. A gel-like repellent composition comprising the gel-like resin molded object composition of any one of claims 1 to 5.

7. A gel-like repellent composition according to claim 6, which is used for noxious organisms.

8. A gel-like repellent composition according to claim 7, wherein said noxious organisms are selected from the group consisting of cockroaches, weevils, termites, rats, moles, dogs, cats, deer, crows, bears, and pigeons.

9. A gel-like repellent composition according to any one of claims 6 to 8, which is disposed under the floor of buildings.

10. A gel-like repellent composition according to any one of claims 6 to 8, which is disposed on the rear side of the ceiling of buildings.

11. A gel-like repellent composition according to any one of claims 6 to 8, which is disposed in transport facilities.

12. A gel-like antimicrobial and antifungal composition comprising the gel-like resin molded object composition of any one of claims 1 to 5.

13. A gel-like antimicrobial and antifungal composition according to claim 12, which is disposed in electrical appliances.

14. A gel-like antimicrobial and antifungal composition according to claim 12, which is disposed in transport facilities.

15. A volatile gel-like packaged drug comprising the gel-like resin molded object composition of any one of claims 1 to 5 and a container, said gel-like resin molded object composition being contained in said container to control the volatilization rate of said allyl isothiocyanate.

16. A volatile gel-like repellent contained in a container, **characterized in that** the gel-like resin molded object composition in the volatile gel-like packaged drug of claim 15 is used as a repellent contained in a container for noxious organisms.

17. A gel-like repellent according to claim 16, wherein said noxious organisms are selected from the group consisting of cockroaches, weevils, termites, rats, moles, dogs, cats, deer, crows, bears and pigeons.

18. A gel-like repellent contained in a container according to claim 16 or 17, wherein said container is a container provided with vent holes.

19. A gel-like repellent contained in a container according to claim 16 or 17, wherein said container is a packaging bag comprising a film through which said allyl isothiocyanate can permeate.

20. A gel-like repellent contained in a container according to any one of claims 16 to 19, which is disposed under the floor of buildings.

21. A gel-like repellent contained in a container according to any one of claims 16 to 19, which is disposed on the rear side of the ceiling of buildings.

22. A gel-like repellent contained in a container according to any one of claims 16 to 19, which is disposed in transport facilities.

23. A gel-like antimicrobial and antifungal drug contained in a container, **characterized in that** the gel-like resin molded object composition in the volatile gel-like packaged drug of claim 15 is used as a gel-like antimicrobial and antifungal

drug.

24. A gel-like antimicrobial and antifungal drug contained in a container according to claim 23, wherein said container is a container provided with vent holes.

25. A gel-like antimicrobial and antifungal drug contained in a container according to claim 23, wherein said container is a packaging bag comprising a film through which said allyl isothiocyanate can permeate.

26. A gel-like antimicrobial and antifungal drug contained in a container according to any one of claims 23 to 25, which is disposed in electrical appliances.

27. A gel-like antimicrobial and antifungal drug contained in a container according to any one of claims 23 to 25, which is disposed in transport facilities.

28. A method of preparing a volatile gel-like packaged drug comprising a gel-like resin molded object composition containing a volatile drug and a gel base, and a container partly comprising at least a packaging material through which a volatile gas of said volatile drug can permeate, said gel-like resin molded object composition being contained in said container, said method comprises:

preparing a drug mixture containing a volatile drug and a gelling drug;
filling said container with said drug mixture; and
gelling said drug mixture thereby to form a gel-like resin molded object composition.

29. A method of preparing a volatile gel-like packaged drug according to claim 28, wherein said volatile drug is allyl isothiocyanate.

30. A method of preparing a volatile gel-like packaged drug according to claim 29, wherein said allyl isothiocyanate is contained in the amount within a range of more than 20% by weight and not more than 85% by weight based on the total weight of said drug mixture.

31. A method of preparing a volatile gel-like packaged drug according to any one of claims 28 to 30, wherein said gelling drug is a polyurethane resin.

32. A method of preparing a volatile gel-like packaged drug according to claim 31, wherein the rubber hardness of said gel-like resin molded object after gelling is within a range from 0.1 to 100.

33. A method of preparing a volatile gel-like packaged drug according to any one of claims 28 to 32, wherein said packaging material through which a volatile gas of said volatile drug can permeate is a film made of a material selected from the group consisting of polyethylene, polypropylene, ethylene-vinyl acetate, polyethylene terephthalate, polyvinyl chloride, nylon, polyacetal, and laminate films thereof.

34. A method of preparing a volatile gel-like packaged drug according to any one of claims 28 to 33, wherein said container is in the form of a bag and said volatile gel-like packaged drug is in the form of a sheet.

35. A method of preparing a volatile gel-like packaged drug according to any one of claims 28 to 34, wherein the exterior of said container is further provided with an aluminum foil laminated on said gas-permeable packagirg material.

36. A gel-like resin molded object composition comprising a volatile drug and polyurethane.

37. A gel-like resin molded object composition according to claim 36, wherein the rubber hardness of said gel-like resin molded object is within a range from 0.1 to 100.

38. A gel-like resin molded object composition according to claim 36 or 37, wherein said polyurethane is prepared from polyisocyanate which has two or more isocyanate functionalities.

39. A gel-like resin molded object composition according to claim 38, wherein said polyurethane is prepared from a polyisocyanate compound selected from the group consisting of hexamethylene diisocyanate, isophorone diiso-

cyanate, tetramethylxylene diisocyanate, isocyanurate-modified compounds, buret-modified compounds and derivatives thereof, 1,3,6-hexamethylene triisocyanate, hydrogenated xylylene diisocyanate, and hydrogenated diphenylmethane diisocyanate.

40. A gel-like resin molded object composition according to any one of claims 36 to 39, wherein said volatile drug is a compound selected from the group consisting of repellents, insect repellents, fungicides, insecticides, antimicrobials, and pesticides.

41. A gel-like resin molded object composition according to claim 40, wherein said volatile drug is mentha oil.

42. A gel-like resin molded object composition according to claim 41, wherein said mentha oil is contained in the amount within a range of more than 20% by weight and not more than 40% by weight based on the total weight of said gel-like resin molded object.

43. A gel-like resin molded object composition according to claim 40, wherein said volatile drug is jasmine oil.

44. A gel-like resin molded object composition according to claim 43, wherein said jasmine oil is contained in the amount within a range of more than 20% by weight and not more than 40% by weight based on the total weight of said gel-like resin molded object.

45. A gel-like resin molded object composition according to any one of claims 36 to 44, wherein said gel-like resin molded object is in the form of a bulk, sheet, film, particle, powder or coating.

46. A volatile gel-like packaged drug comprising the gel-like resin molded object of any one of claims 36 to 45 and a container, said gel-like resin molded object being contained in said container to control the volatilization rate of said volatile drug.

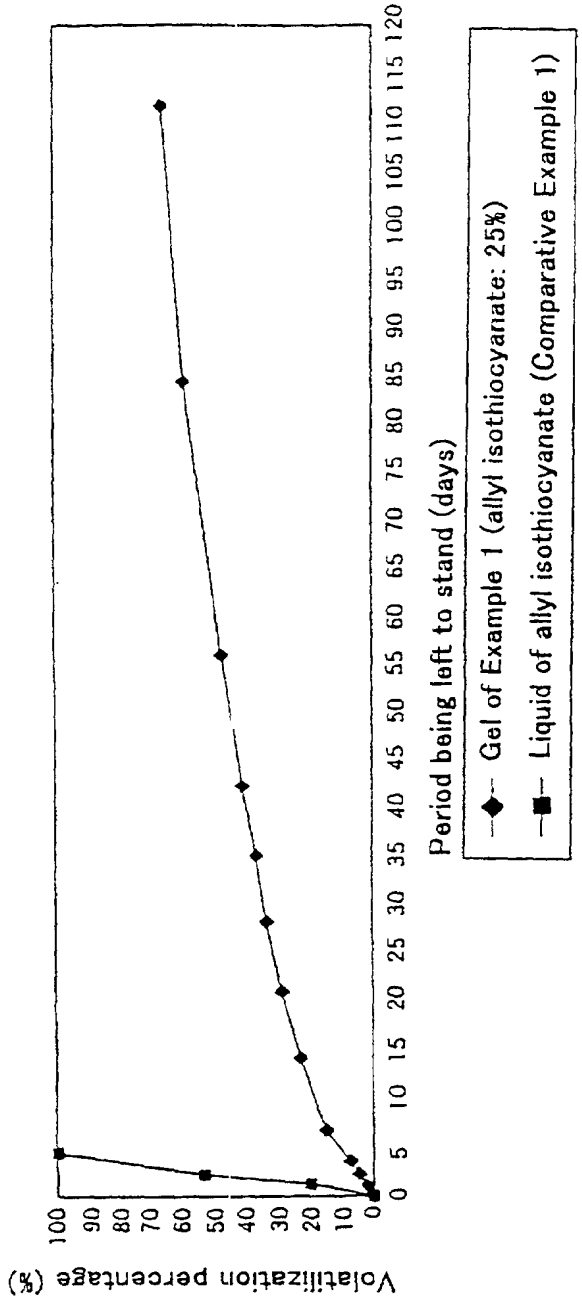

Volatilization percentage (%)
100
90
80
70
60
50
40
30
20
10
0
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120
Period being left to stand (days)
Gel of Example 1 (allyl isothiocyanate: 25%)
Liquid of allyl isothiocyanate (Comparative Example 1)

Fig. 1

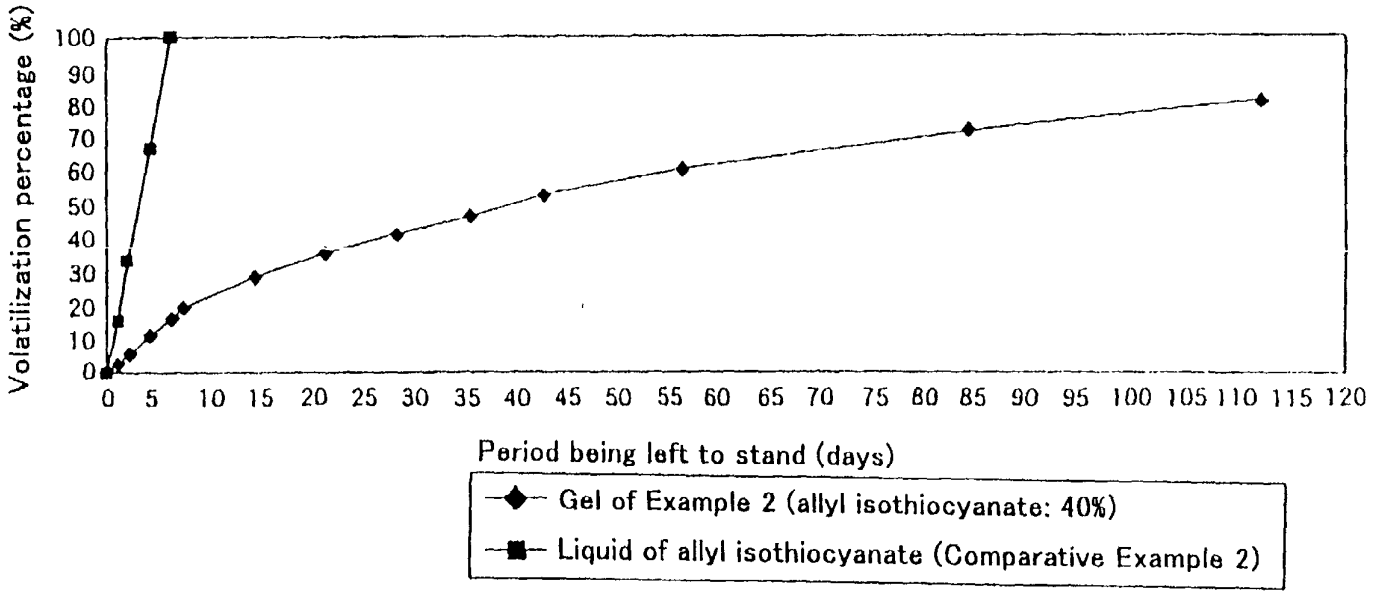

Volatilization percentage (%)
100
90
80
70
60
50
40
30
20
10
0
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120
Period being left to stand (days)
Gel of Example 2 (allyl isothiocyanate: 40%)
Liquid of allyl isothiocyanate (Comparative Example 2)

Fig. 2

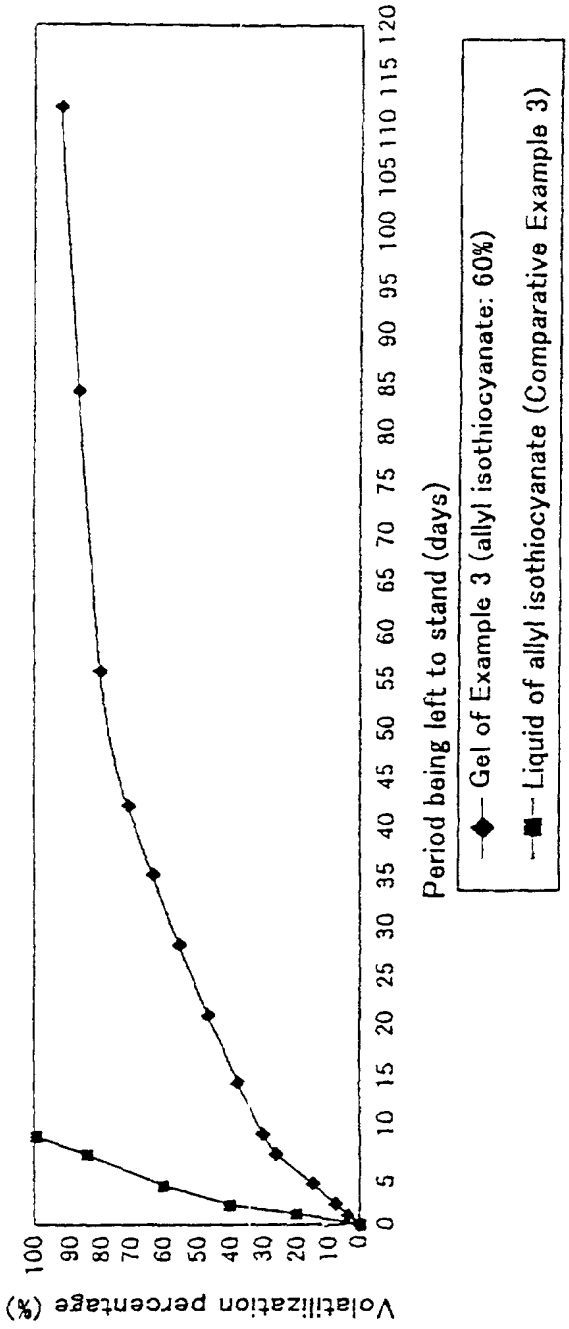

Volatilization percentage (%)
0
10
20
30
40
50
60
70
80
90
100
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120
Period being left to stand (days)
Gel of Example 3 (allyl isothiocyanate: 60%)
Liquid of allyl isothiocyanate (Comparative Example 3)

Fig. 3

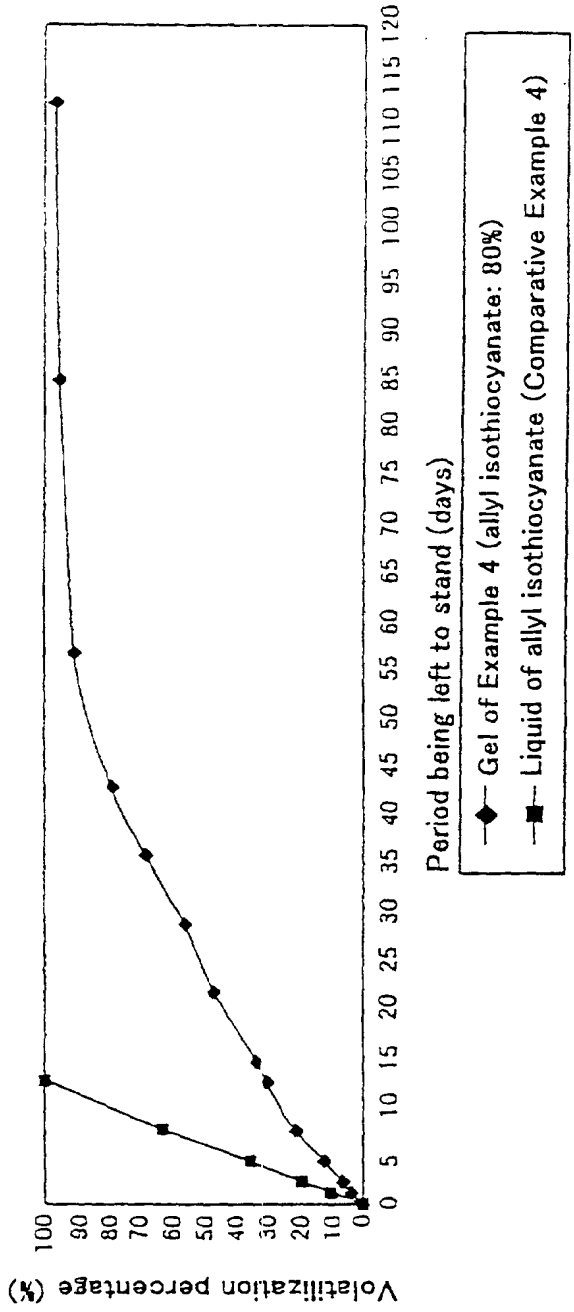

Volatilization percentage (%)
100
90
80
70
60
50
40
30
20
10
0
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120
Period being left to stand (days)
Gel of Example 4 (allyl isothiocyanate: 80%)
Liquid of allyl isothiocyanate (Comparative Example 4)

Fig. 4

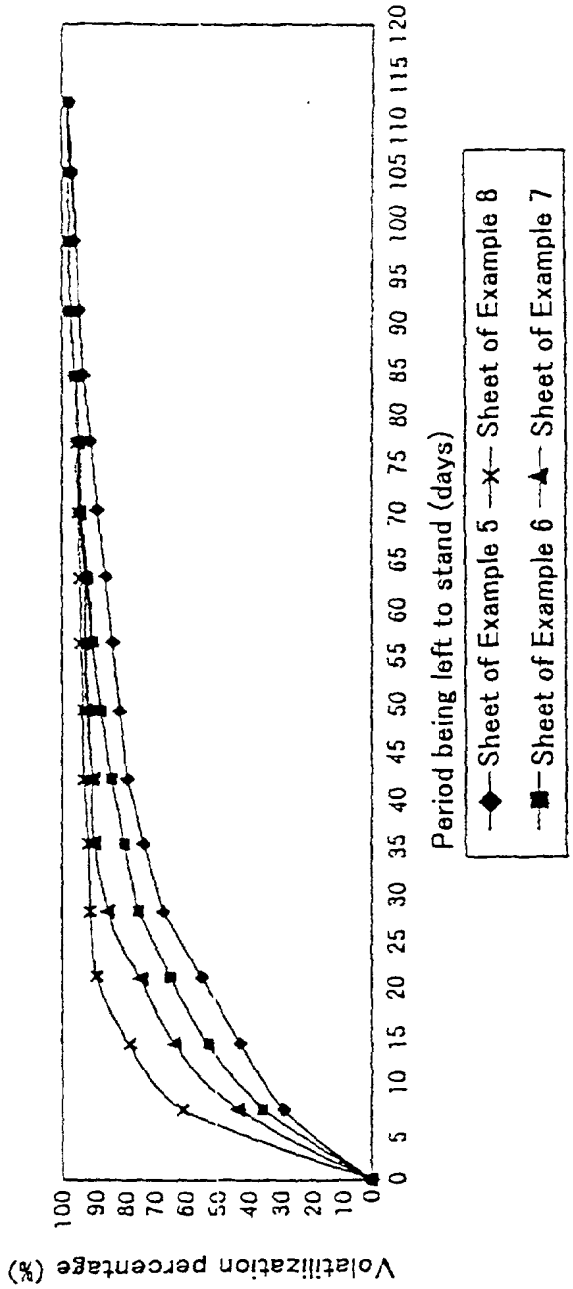

Volatilization percentage (%)
100
90
80
70
60
50
40
30
20
10
0
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120
Period being left to stand (days)
Sheet of Example 5
Sheet of Example 8
Sheet of Example 6
Sheet of Example 7

Fig. 5

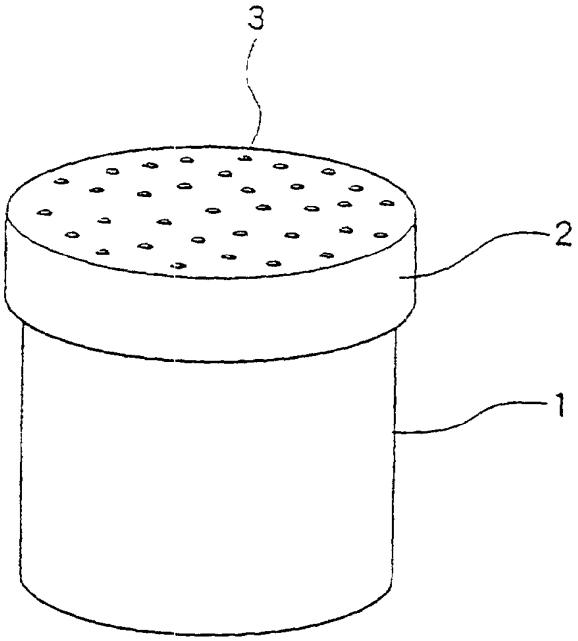


Fig. 6

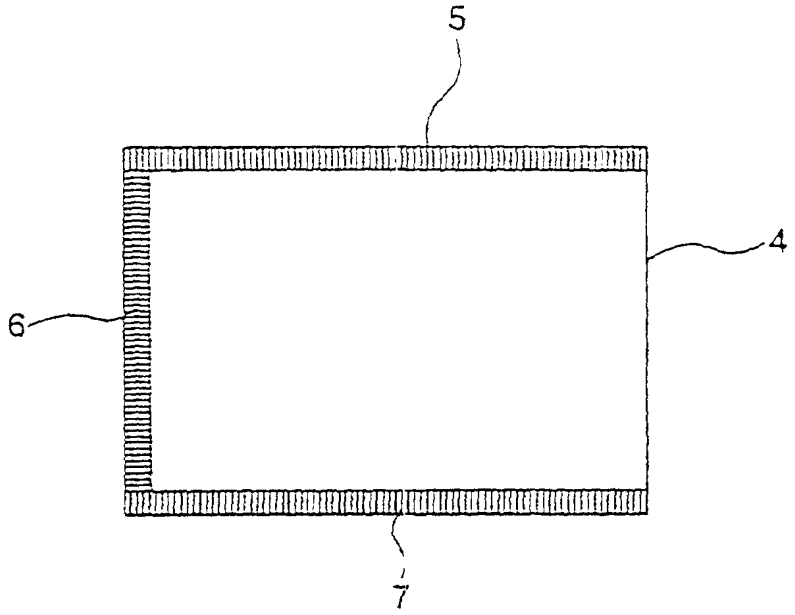


Fig. 7

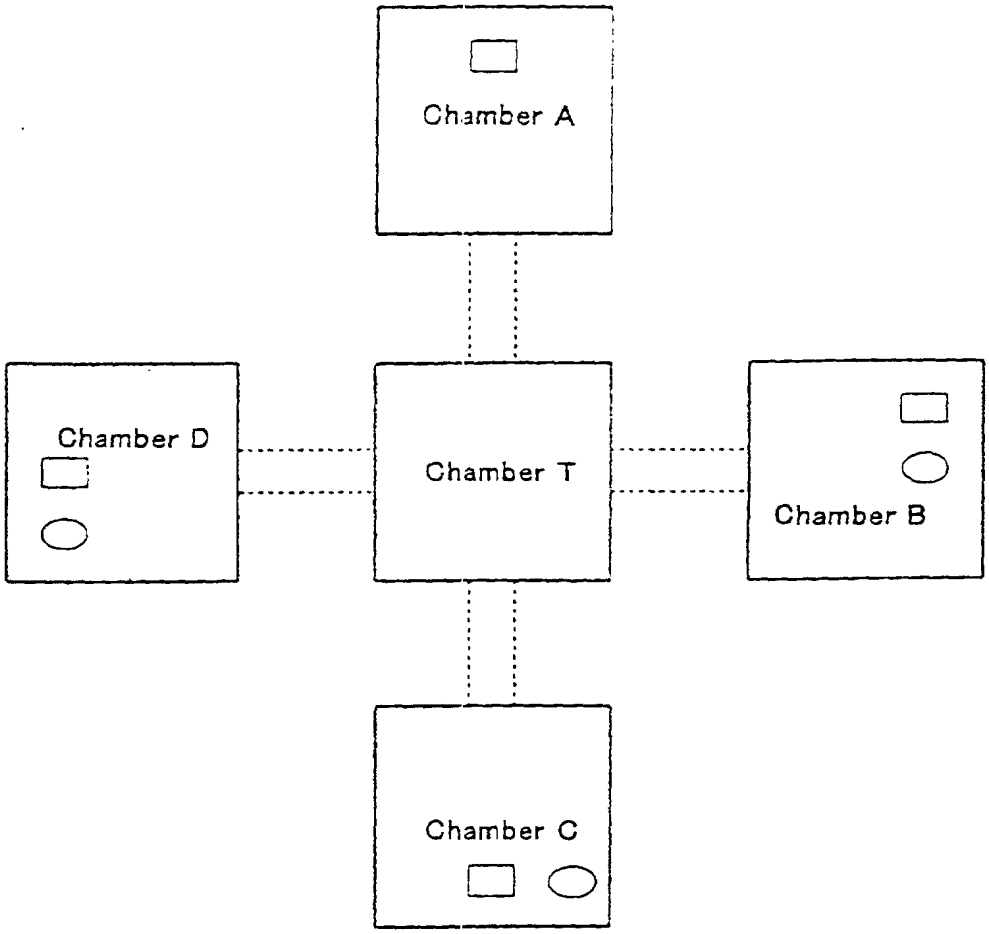


Fig. 8

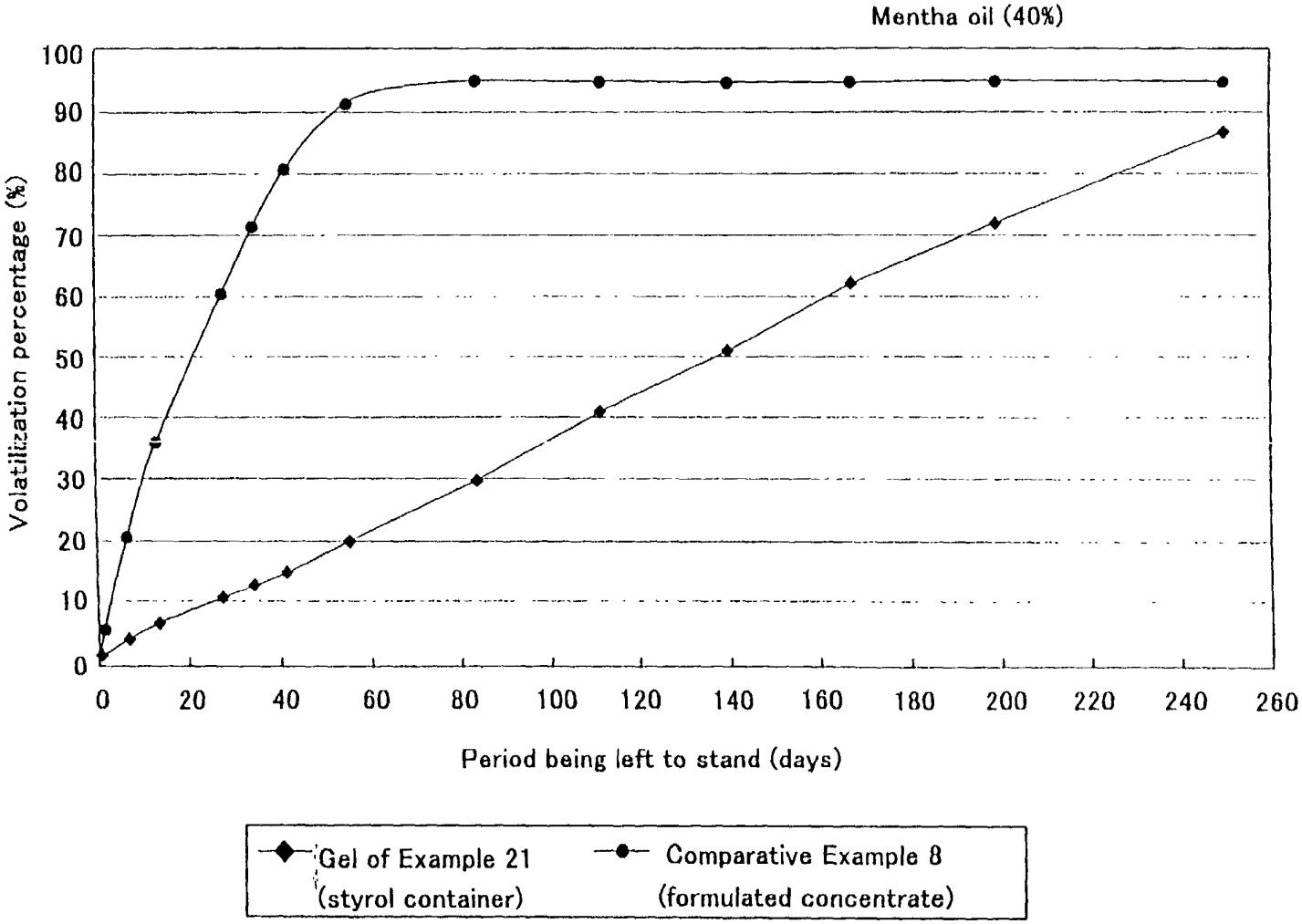

Mentha oil (40%)
Volatilization percentage (%)
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
200
220
240
260
Period being left to stand (days)
Gel of Example 21
(styrol container)
Comparative Example 8
(formulated concentrate)

Fig. 9

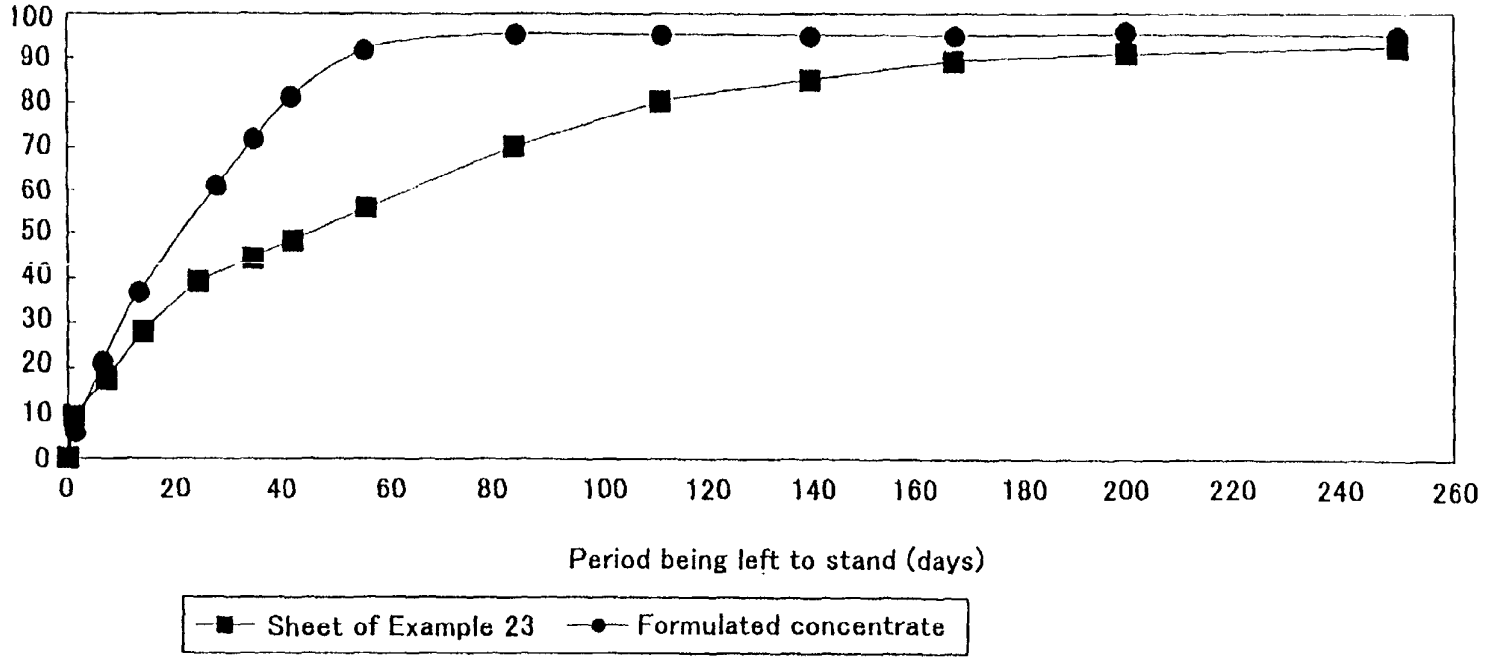

100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
200
220
240
260
Period being left to stand (days)
Sheet of Example 23
Formulated concentrate

Fig. 10

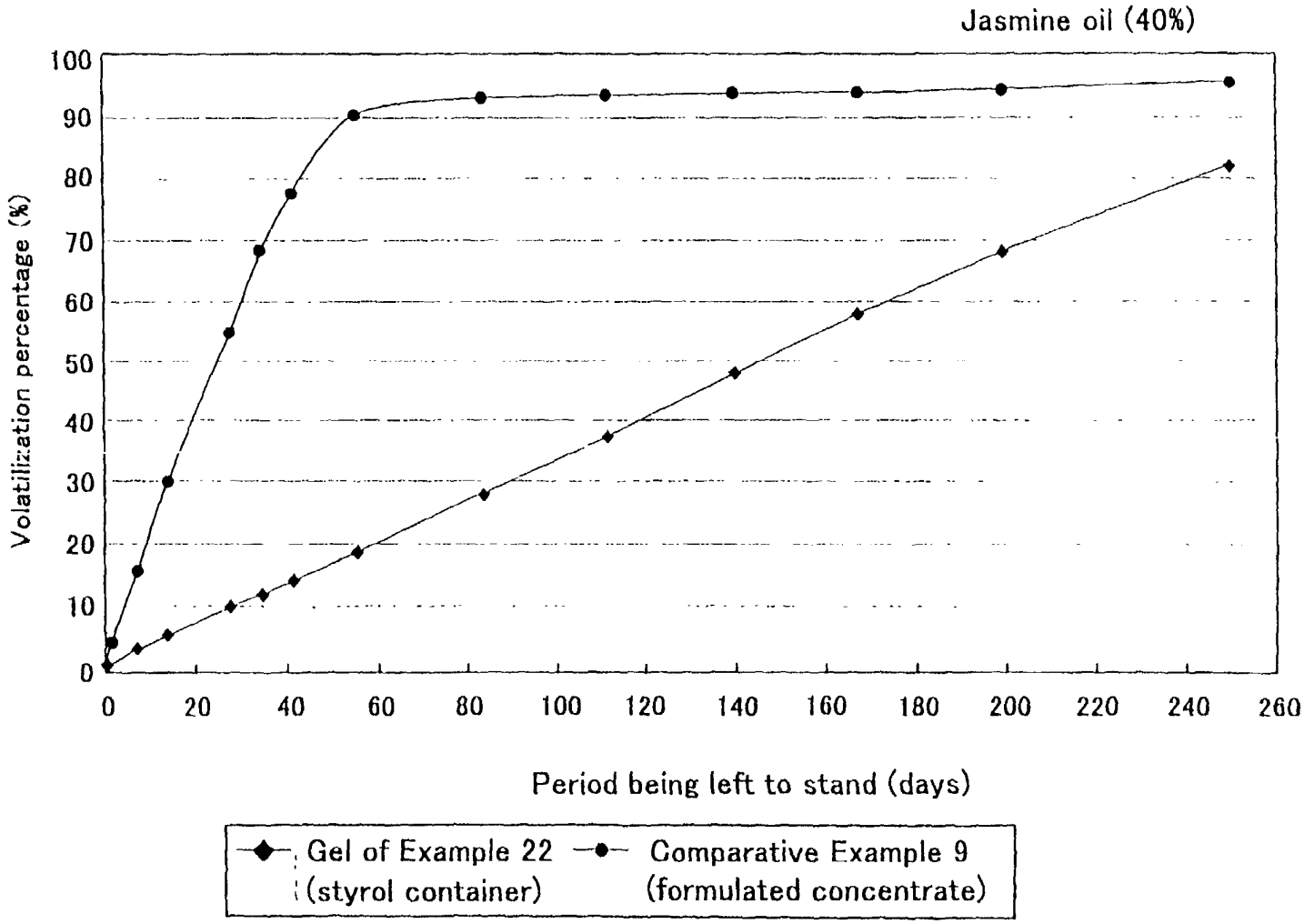

Jasmine oil (40%)
Volatilization percentage (%)
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
200
220
240
260
Period being left to stand (days)
Gel of Example 22 (styrol container)
Comparative Example 9 (formulated concentrate)

Fig. 11

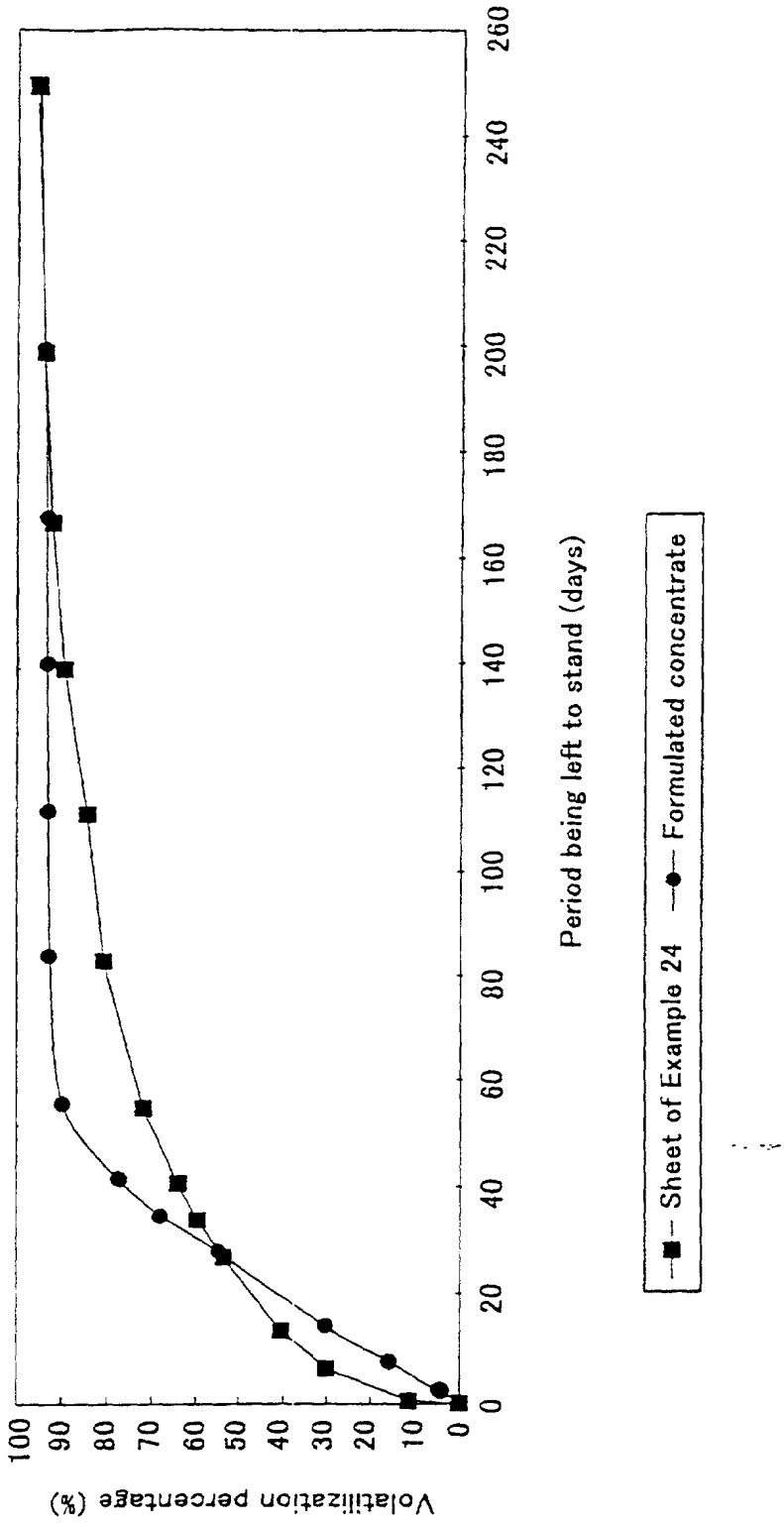

Volatilization percentage (%)
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240
260
Period being left to stand (days)
Sheet of Example 24
Formulated concentrate

Fig. 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP00/05620

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] C08L101/00, C08L75/04, C08K5/36, A01N25/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[7] C08L1/00-101/16, C08K3/00-13/08, A01N25/04, A01N25/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2000
Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI/L

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 3-8162, U (Minato Sangyo K.K.), 25 January, 1991 (25.01.91), Claims of Utility Model; page 7, line 16 to page 8, line 12; page 10, lines 1 to 8; page 11, lines 3 to 17 (Family: none)	1-40,45,46
X	JP, 10-87404, A (DAI-ICHI KOGYO SEIYAKU CO., LTD.), 07 April, 1998 (07.04.98), Claims; Par. Nos. [0006], [0018] (Family: none)	36-40,45,46
PX	JP, 2000-281505, A (Rengou K.K.), 10 October, 2000 (10.10.00), Claims; Par. Nos. [0016] to [0022], [0025] to [0027] (Family: none)	36-46
X	JP, 10-130636, A (Ron Chemical K.K.), 19 May, 1998 (19.05.98), Claims; Par.Nos. [0002], [0012] to [0065] (Family: none)	1-4,12
X	JP, 9-151317, A (DAI-ICHI KOGYO SEIYAKU CO., LTD.), 10 June, 1997 (10.06.97), Claims (Family: none)	36-40,45

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 November, 2000 (08.11.00)	21 November, 2000 (21.11.00)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP00/05620

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 7-316420, A (SUNSTAR INC.), 05 December, 1995 (05.12.95), Claims; Par. No. [0016] (Family: none)	36-45
A	US, 5246663, A (MINATO CO LTD), 21 September, 1993 (21.09.93), Claims & JP, 03-002235, A Claims & WO, 9011686, A & EP, 427862, A	1-46

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76) AND ASSIGNMENT FOR SINGLE ASSIGNEE

TITLE OF INVENTION	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

As the below named inventor, I hereby declare that:

This declaration is directed to:

☒ The attached application, or

☐ United States application or PCT international application number _____ filed on _____.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. § 1001 by fine or imprisonment of not more than five (5) years, or both.

WHEREAS, I, the below-identified Inventor, have invented certain new and useful improvements in the Invention identified above and described in the above-identified patent application(s) and/or patent(s) (hereinafter "Invention");

WHEREAS, Grant Industries, Inc. (hereinafter "Assignee") having place of business at: 103 Main Avenue, Elmwood Park, NJ 07407 , is desirous of acquiring the entire right, title and interest in and to said invention and in and to any Letters Patent that may be granted therefore in the United States or its territorial possessions and in any and all foreign countries;

NOW, this indenture witnesseth, that in consideration of the sum of ONE DOLLAR ($1.00), the receipt of which is hereby acknowledged, and for other good and valuable consideration;

I hereby assign, sell and transfer my above-identified rights, title and interest in said Invention, said application(s) as identified above, including any divisions, continuations, and continuations-in-part thereof, and in and to any and all Letters Patent of the United States, and countries foreign thereto, which may be granted for said Invention, and in and to any and all reissues and reexaminations thereof, which may be granted or have granted for said Invention, and in and to any and all priority rights, Convention rights, and other benefits accruing or to accrue to us with respect to the filing of applications for patents or securing of patents in the United States and countries foreign thereto, unto said Assignee;

And I hereby authorize and request the Commissioner of Patents and Trademarks to issue any United States Letters Patent which may issue for said Invention to said Assignee, as assignee of the whole right, title and interest thereto;

And I further agree to sign and execute all necessary and lawful future documents, including applications for foreign patents, for filing divisions, continuations and continuations-in-part of said application for patent and/or for obtaining any reissue or reissues of any Letters Patent which may be granted for my aforesaid Invention, as the Assignee or its successors and designees may from time to time require and prepare at its own expense.

The undersigned hereby grants the firm of LUCAS & MERCANTI, LLP, located at 30 Broad Street, New York, New York, 10004, the power to insert on this assignment any further identification which may be necessary or desirable in order to comply with the rules of the United States Patent Office for recordation of this document.

LEGAL NAME OF INVENTOR	Inventor: Anna K. CROOM Signature: _____	Date: 08/18/2020

LUCAS & MERCANTI, LLP
30 BROAD STREET, 21ST FLOOR
NEW YORK, NY 10004

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76) AND ASSIGNMENT FOR SINGLE ASSIGNEE

TITLE OF INVENTION	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

As the below named inventor, I hereby declare that:

This declaration is directed to:

☒ The attached application, or

☐ United States application or PCT international application number _____ filed on _____.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. § 1001 by fine or imprisonment of not more than five (5) years, or both.

WHEREAS, I, the below-identified Inventor, have invented certain new and useful improvements in the Invention identified above and described in the above-identified patent application(s) and/or patent(s) (hereinafter "Invention");

WHEREAS, Grant Industries, Inc. (hereinafter "Assignee") having place of business at: 103 Main Avenue, Elmwood Park, NJ 07407 , is desirous of acquiring the entire right, title and interest in and to said invention and in and to any Letters Patent that may be granted therefore in the United States or its territorial possessions and in any and all foreign countries;

NOW, this indenture witnesseth, that in consideration of the sum of ONE DOLLAR ($1.00), the receipt of which is hereby acknowledged, and for other good and valuable consideration;

I hereby assign, sell and transfer my above-identified rights, title and interest in said Invention, said application(s) as identified above, including any divisions, continuations, and continuations-in-part thereof, and in and to any and all Letters Patent of the United States, and countries foreign thereto, which may be granted for said Invention, and in and to any and all reissues and reexaminations thereof, which may be granted or have granted for said Invention, and in and to any and all priority rights, Convention rights, and other benefits accruing or to accrue to us with respect to the filing of applications for patents or securing of patents in the United States and countries foreign thereto, unto said Assignee;

And I hereby authorize and request the Commissioner of Patents and Trademarks to issue any United States Letters Patent which may issue for said Invention to said Assignee, as assignee of the whole right, title and interest thereto;

And I further agree to sign and execute all necessary and lawful future documents, including applications for foreign patents, for filing divisions, continuations and continuations-in-part of said application for patent and/or for obtaining any reissue or reissues of any Letters Patent which may be granted for my aforesaid Invention, as the Assignee or its successors and designees may from time to time require and prepare at its own expense.

The undersigned hereby grants the firm of LUCAS & MERCANTI, LLP, located at 30 Broad Street, New York, New York, 10004, the power to insert on this assignment any further identification which may be necessary or desirable in order to comply with the rules of the United States Patent Office for recordation of this document.

LEGAL NAME OF INVENTOR	Inventor: Ronald V. LERUM Signature: _____	Date: 8/19/2025

LUCAS & MERCANTI, LLP
30 BROAD STREET, 21ST FLOOR
NEW YORK, NY 10004

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76) AND ASSIGNMENT FOR SINGLE ASSIGNEE

TITLE OF INVENTION	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

As the below named inventor, I hereby declare that:

This declaration is directed to:

☒ The attached application, or

☐ United States application or PCT international application number _____ filed on _____.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. § 1001 by fine or imprisonment of not more than five (5) years, or both.

WHEREAS, I, the below-identified Inventor, have invented certain new and useful improvements in the Invention identified above and described in the above-identified patent application(s) and/or patent(s) (hereinafter "Invention");

WHEREAS, Grant Industries, Inc. (hereinafter "Assignee") having place of business at: 103 Main Avenue, Elmwood Park, NJ 07407 , is desirous of acquiring the entire right, title and interest in and to said invention and in and to any Letters Patent that may be granted therefore in the United States or its territorial possessions and in any and all foreign countries;

NOW, this indenture witnesseth, that in consideration of the sum of ONE DOLLAR ($1.00), the receipt of which is hereby acknowledged, and for other good and valuable consideration;

I hereby assign, sell and transfer my above-identified rights, title and interest in said Invention, said application(s) as identified above, including any divisions, continuations, and continuations-in-part thereof, and in and to any and all Letters Patent of the United States, and countries foreign thereto, which may be granted for said Invention, and in and to any and all reissues and reexaminations thereof, which may be granted or have granted for said Invention, and in and to any and all priority rights, Convention rights, and other benefits accruing or to accrue to us with respect to the filing of applications for patents or securing of patents in the United States and countries foreign thereto, unto said Assignee;

And I hereby authorize and request the Commissioner of Patents and Trademarks to issue any United States Letters Patent which may issue for said Invention to said Assignee, as assignee of the whole right, title and interest thereto;

And I further agree to sign and execute all necessary and lawful future documents, including applications for foreign patents, for filing divisions, continuations and continuations-in-part of said application for patent and/or for obtaining any reissue or reissues of any Letters Patent which may be granted for my aforesaid Invention, as the Assignee or its successors and designees may from time to time require and prepare at its own expense.

The undersigned hereby grants the firm of LUCAS & MERCANTI, LLP, located at 30 Broad Street, New York, New York, 10004, the power to insert on this assignment any further identification which may be necessary or desirable in order to comply with the rules of the United States Patent Office for recordation of this document.

LEGAL NAME OF INVENTOR	Inventor: John Gormley Signature: _____	Date: August 10, 2020

LUCAS & MERCANTI, LLP
30 BROAD STREET, 21ST FLOOR
NEW YORK, NY 10004

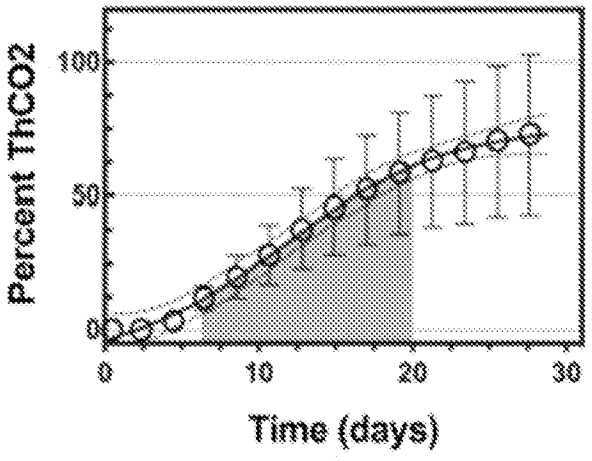


FIG. 1

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
18 November 2021 (18.11.2021)

WIPO | PCT

(10) International Publication Number
WO 2021/231527 A1

(51) International Patent Classification:
C08J 9/12 (2006.01) *C08J 9/232* (2006.01)
C08J 9/18 (2006.01)

(21) International Application Number:
PCT/US2021/031916

(22) International Filing Date:
12 May 2021 (12.05.2021)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/023,372 12 May 2020 (12.05.2020) US

(71) Applicant: **NANOMETICS LLC (D.B.A. PHD BIOSCIENCES)** [US/US]; 180 Varick Street, 6th Floor, New York, New York 10014 (US).

(72) Inventors: **MAHON, Andrew Bernard**; 217 West 106 Street, Apartment 2A, New York, New York 10025 (US). **ISAACMAN, Michael Joseph**; 50 East 8th Street, Apartment 4U, New York, New York 10003 (US). **ISAACMAN, Steven**; 248 Oak Beach Road, Oak Beach, New York 11702 (US).

(74) Agent: **MILLS, Jeffrey K.**; MEDLER FERRO WOODHOUSE & MILLS PLLC, 8201 Greensboro Dr., Ste. 1060, McLean, Virginia 22102 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:
— *with international search report (Art. 21(3))*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) Title: NON-ISOCYANATE POLYURETHANE ELASTOMERS AND COMPOSITIONS COMPRISING SUCH ELASTOMERS

(57) Abstract: The present disclosure relates to gel compositions of, or containing, a non-isocyanate polyurethane (NIPU) elastomer formed from the reaction of a polycarbonate, where carbonate groups may be cyclic or non-cyclic, and a polyamine, where amines are either primary or secondary, in an optional topically acceptable carrier fluid. The gelled compositions may further contain a personal or healthcare active. The actives may be incorporated into the gel via either a pre or post load method.

WO 2021/231527 A1

NON-ISOCYANATE POLYURETHANE ELASTOMERS AND COMPOSITIONS COMPRISING SUCH ELASTOMERS

Technical Field

This invention relates to gel compositions containing a NIPU elastomer from the reaction of a polycyclic or poly-non-cyclic carbonate and a polyamine, and may optionally utilize a catalyst to increase the rate of formation of the elastomer, and is suitably contained in a topically acceptable carrier fluid to form a gel. The gel compositions may contain a personal or healthcare active. The actives may be incorporated into the gel via either a pre or post load method. Gel compositions may be further used as components in personal care compositions.

Background

Silicone elastomers have been used extensively in personal care applications for their thickening and gelling efficiency, and unique silky and powdery sensory profile. Silicone elastomers are compatible with silicone-based fluids, however, silicone based fluids for topical use are being phased out of the personal care industry due to health and environmental concerns. There is a need to develop alternatives to silicone elastomers which demonstrate efficient thickening and gelling capabilities with non-silicone based topically acceptable solvents (e.g., esters, triglycerides, and alkanes) while imparting a silky and powdery skin feel comparable to silicone elastomers. Polyurethane elastomers can potentially satisfy this need and provide desirable alternatives to silicone elastomers. Non-isocyanate polyurethane (NIPU) elastomers offer an environmentally friendly alternative to isocyanate derived polyurethanes, which require starting materials synthesized from toxic precursors.

Summary

This disclosure relates to a gel composition comprising a non-isocyanate polyurethane NIPU (NIPU) elastomer from the reaction of:

A) a polycarbonate, where the carbonate groups are either cyclic or non-cyclic, which may optionally contain siloxanes in its backbone,

B) a polyamine, where the amine groups are either primary or secondary,

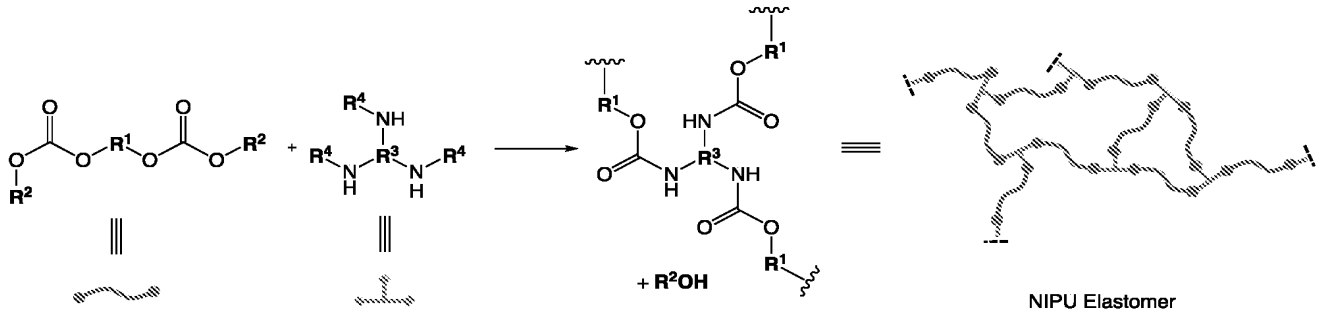
C) an optional reaction catalyst,

D) an optional topically acceptable carrier fluid, wherein the topically acceptable carrier fluid is a reaction solvent or wherein the topically acceptable carrier fluid is added to the reaction after elastomer formation.

A personal care or healthcare active (E) may be incorporated into the NIPU elastomer gel by dissolving it in the topically acceptable solvent during the formation of the NIPU elastomer gel (pre-load method) or admixing it with a formed NIPU elastomer gel (post-load method).

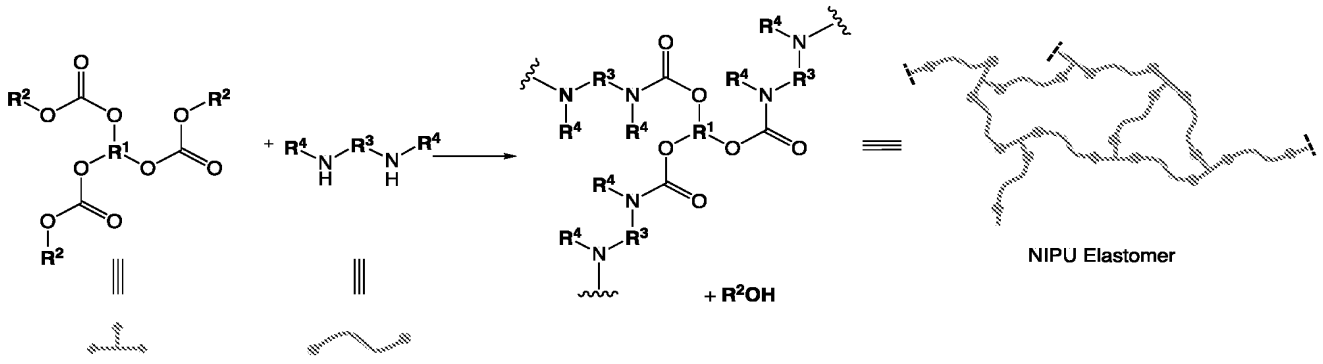
The invention is directed to the following:

A cross-linked NIPU elastomer network with the following general structure:



where R^1 is an aromatic ring, heterocycle, cyclic alkyl group, linear alkyl group, or branched alkyl group with two or more carbonate functional groups and where R^2 is a hydrogen atom, heteroatom, aromatic ring, heterocyclic ring, or alkyl chain. R^3 is an aromatic ring, heterocycle, cyclic alkyl group, linear alkyl group, or branched alkyl group with two or more primary or secondary amines. R^4 is a hydrogen atom, heteroatom, aromatic ring, heterocycle, cyclic alkyl group, or linear alkyl chain.

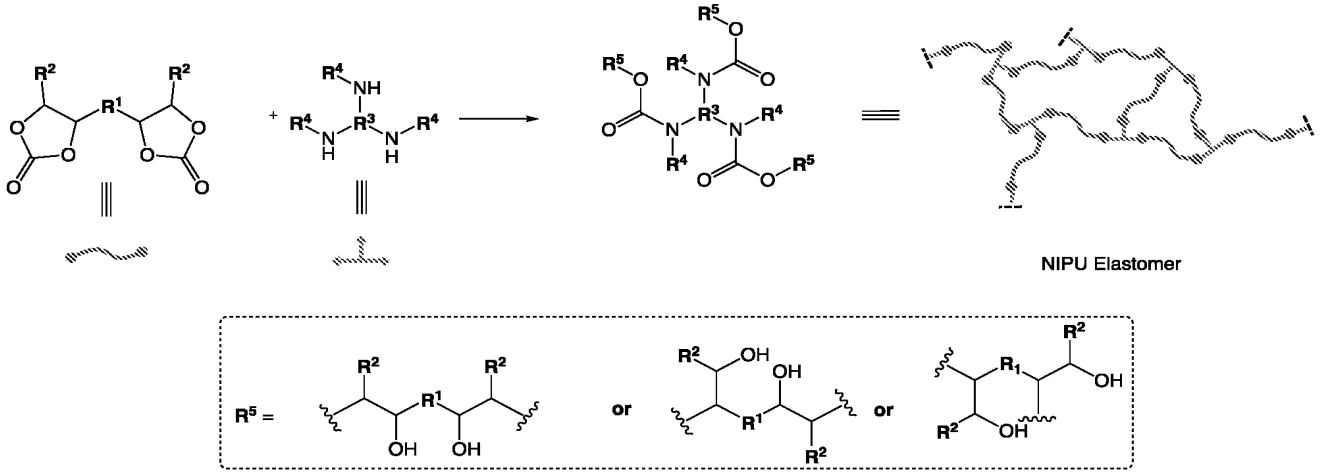
A cross-linked NIPU elastomer network with the following general structure:



where R^1 is an aromatic ring, heterocycle, cyclic alkyl group, linear alkyl group, or branched alkyl group with three or more carbonate functional groups and where R^2 is a hydrogen atom, heteroatom,

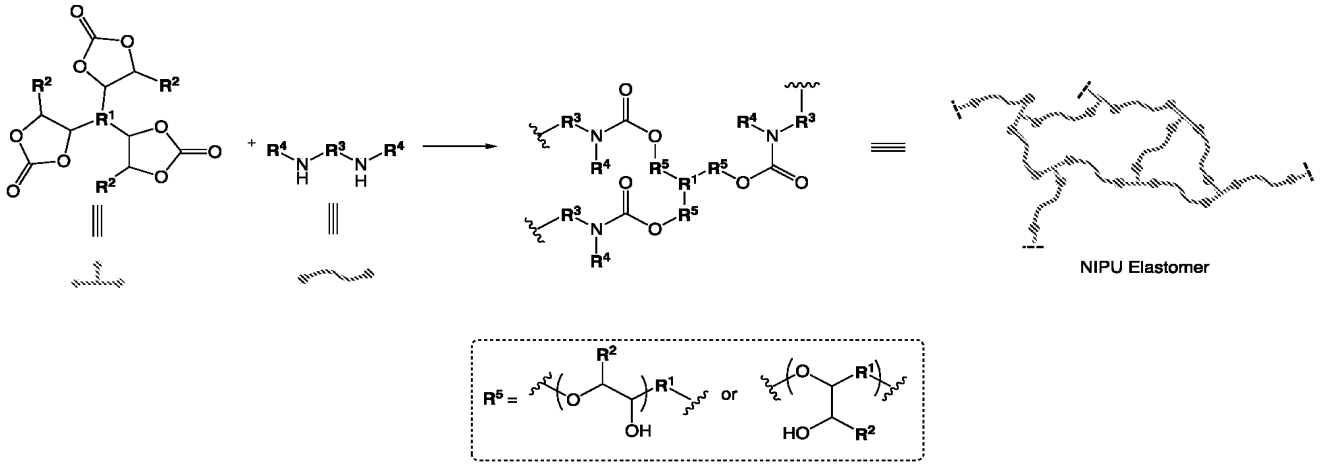
aromatic ring, heterocyclic ring, or alkyl chain. R^3 is an aromatic ring, heterocycle, cyclic alkyl group, linear alkyl group, or branched alkyl group with two or more primary or secondary amines. R^4 is a hydrogen atom, heteroatom, aromatic ring, heterocycle, cyclic alkyl group, or linear alkyl chain.

A cross-linked NIPU elastomer network with the following general structure:



where R^1 is an aromatic ring, heterocycle, cyclic alkyl group, linear alkyl group, or branched alkyl group with three or more cyclic carbonate groups and where R^2 is a hydrogen atom, heteroatom, aromatic ring, heterocyclic ring, or alkyl chain. R^3 is an aromatic ring, heterocycle, cyclic alkyl group, linear alkyl group, or branched alkyl group with two or more primary or secondary amines. R^4 is a hydrogen atom, heteroatom, aromatic ring, heterocycle, cyclic alkyl group, or linear alkyl chain.

A cross-linked NIPU elastomer network with the following general structure:



where R^1 is an aromatic ring, heterocycle, cyclic alkyl group, or linear or branched alkyl group with three or more cyclic carbonate functional groups and where R^2 is a hydrogen atom, heteroatom,

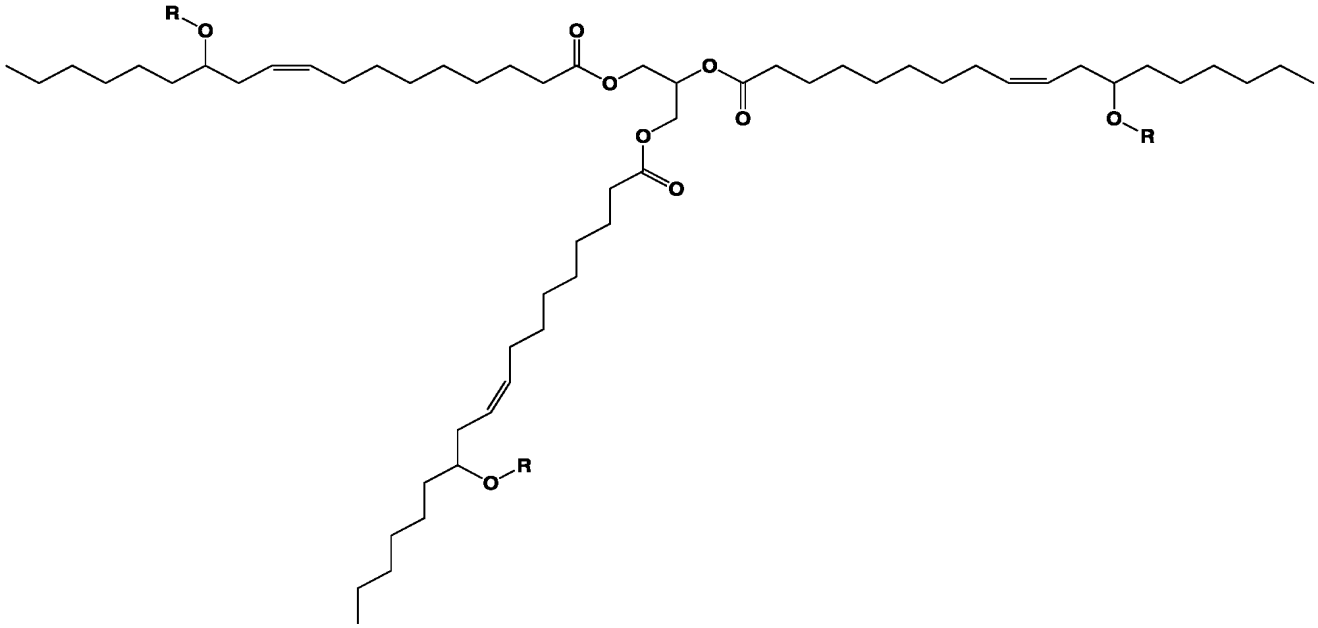
aromatic ring, heterocyclic ring, or alkyl chain. R^3 is an aromatic ring, heterocycle, cyclic alkyl group, linear alkyl group, or branched alkyl group with two or more primary or secondary amines. R^4 is a hydrogen atom, heteroatom, aromatic ring, heterocycle, cyclic alkyl group, or linear alkyl chain.

Detailed Description

This disclosure relates to a gel composition comprising a polyurethane elastomer requiring no purification and formed in a topically acceptable solvent from the reaction of:

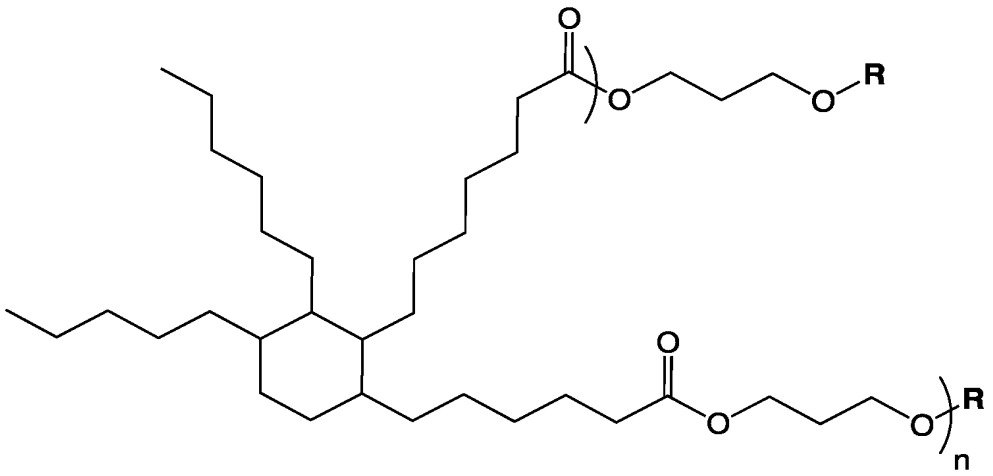
(A) A polycarbonate.

Component (A) has a molecular structure containing more than one cyclic or non-cyclic carbonate and can be produced by a number of methods from alkenes, alkynes, epoxides, vicinal diols, isolated hydroxyl groups, 2-halo alcohols, among others, and should have two or more reactive carbonate functional groups in its molecular structure. One preferred example of a polycarbonate is based on castor oil and has the following structure:



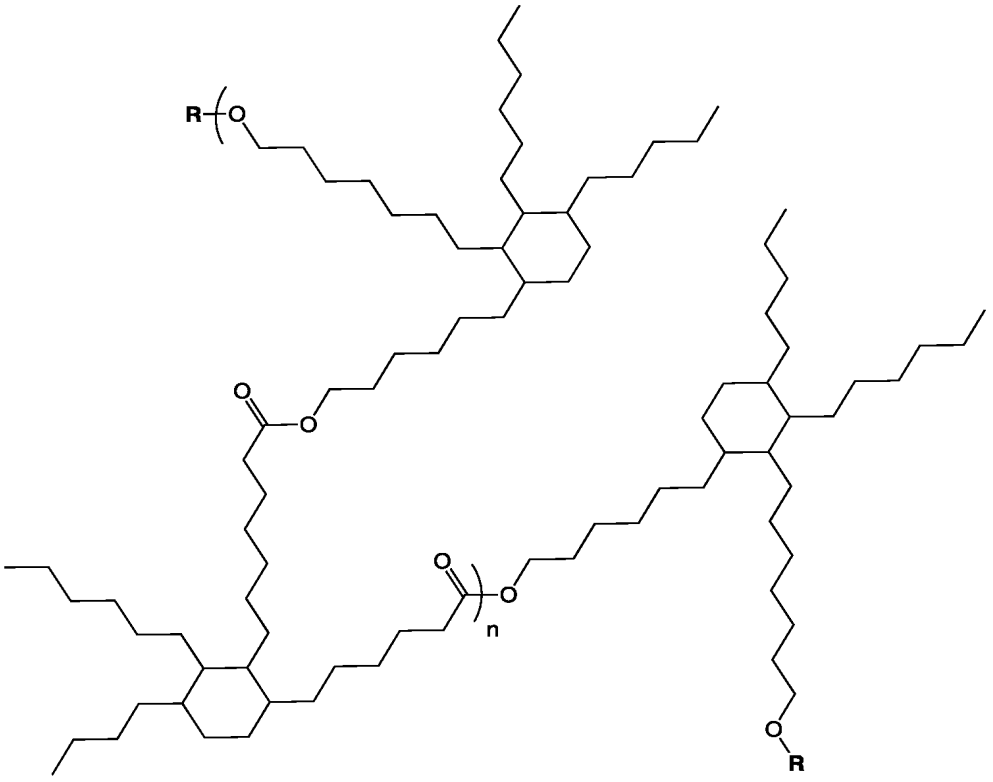
where R contains a cyclic or non-cyclic carbonate.

Another preferred example of a polycarbonate is based on dilinoleic acid/propanediol copolymer and has the following structure:



where R contains a cyclic or non-cyclic carbonate.

Another preferred example of a polycarbonate is based on dilinoleic acid/ dilinoleic diol copolymer and has the following structure:

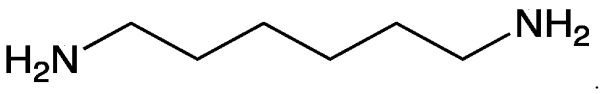


where R contains a cyclic or non-cyclic carbonate.

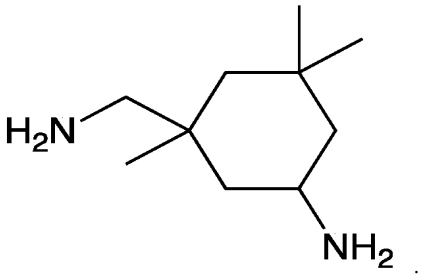
Component (A) can include one or more functional groups in its polymeric chain. In one aspect, the polycarbonate includes one or more siloxane in its polymeric chain, e.g., in the polymer backbone.

(B) A polyamine, where the amine groups are either primary or secondary.

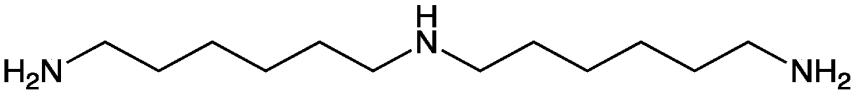
Component (B) has a molecular structure containing more than one primary or secondary amines. One preferred example of an aliphatic polyamine is hexamethylenediamine and has the structure:



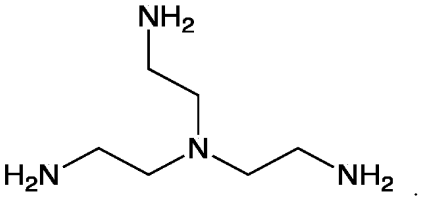
Another preferred example of an aliphatic polyamine is isophorone diamine and has the structure:



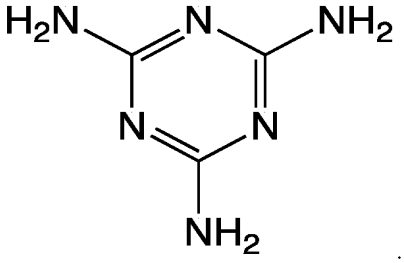
Another preferred example of an aliphatic polyamine is bis(hexamethylene)triamine and has the structure:



Another preferred example of an aliphatic polyamine is tris(aminoethyl)amine and has the structure:



One preferred example of an aromatic polyamine is melamine and has the structure:



(C) An optional reaction catalyst.

Component (C) can be optionally used to increase the rate of NIPU elastomer formation. Titanium alkoxide are preferred catalysts for the synthesis of NIPU elastomer gels due to their favorable toxicity profile and acceptable use in topical products. Preferably, titanium isopropoxide is used as the NIPU catalyst. Zinc, tin, bismuth, and amine based NIPU catalysts can also be used. Appropriate NIPU catalysts include but are not limited to:

- Triethylenediamine
- N,N,N',N",N"-Pentamethyldiethylenetriamine
- 1,2-Dimethylimidazole
- N,N,N',N'-Tetramethyl-1,6-hexanediamine
- N,N',N'-Trimethylaminoethylpiperazine
- 1,1'-[[3-(dimethylamino)propyl]imino]bispropan-2-ol
- N,N,N'-Trimethylaminoethylethanolamine
- N,N',N"-Tris(3-dimethylaminopropyl)-hexahydro-s-triazine
- 1,4-diazabicyclo[2.2.2]octane
- 1,5,7-Triazabicyclo[4.4.0]dec-5-ene
- Stannous octoate
- Stannous oxalate
- Stannous oxide
- Stannous chloride
- Dioctyltin di(2-hexylhexanoate)-solution
- Dioctyltin dithioglycolate
- Dioctyltin dilaurate
- Dioctyltin oxide blend
- Dibutyltin dilaurate
- Monobutyl tin tris-(2-ethylhexanoate)
- Dioctyltin diketanoate
- Dioctyltin diacetate
- Dioctyltin oxide
- Dibutyltin diacetate
- Modified dibutyltin diacetate

- Dibutyltin oxide
- Monobutyltin dihydroxychloride
- Organotin oxide
- Monobutyltin oxide
- Dioctyltin dicarboxylate
- Dioctyltin carboxylate
- Dioctyltin stannoxane
- Zinc neodecanoate
- Zinc octoate
- Zinc acetylacetonate
- Zinc oxalate
- Zinc acetate
- Bismuth carboxylates
- Zinc neodecanoate

(D) A Carrier Fluid.

The NIPU elastomers may be contained in an optional carrier fluid (D). Carrier fluids include any suitable solvent that can be used to prepare the NIPU elastomers. In exemplary embodiments, the carrier fluid is a "topically acceptable carrier fluid" which is a solvent for topical use on cutaneous surfaces i.e. skin, lips, mucous membranes, etc. Although it is not required, typically the carrier fluid may be the same as the solvent used for conducting the elastomer reaction as described above. The carrier fluid used for the synthesis of the NIPU elastomer rubber and gel can be fully, partially, or not biobased. The carrier fluid, including a topically acceptable carrier fluid, preferably has a viscosity between 1-65 mPas at 20 °C. The spreading value of the carrier fluid, including the topically acceptable carrier fluid, is preferably between 500-2500 $mm^2/10$ min. Appropriate topically acceptable carrier fluids for the synthesis of the NIPU elastomer rubber and processing of the NIPU elastomer gel include but are not limited to esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof, and include:

- Bis-Diglyceryl Polyacyladipate-1
- Bis-Diglyceryl Polyacyladipate-2
- Butylene Glycol Dicaprylate/Dicaprate
- Butyrospermum Parkii Butter

- Caprylic/Capric Glycerides
- Caprylic/Capric Triglyceride
- Caprylic/Capric/Myristic/Stearic Triglyceride
- Caprylic/Capric/Succinic Triglyceride
- Caprylyl Methicone
- Coco-Caprylate/Caprate
- Decamethylcyclopentasiloxane
- Decyl Oleate
- Dimethiconol
- Diphenylsilanediol
- Dodecamethylcyclohexasiloxane
- Ethyl trisiloxane
- Glyceryl Caprylate
- Glyceryl Citrate/Lactate/Linoleate/Oleate
- Glyceryl Cocoate
- Glyceryl Isostearate
- Glyceryl Oleate
- Glyceryl Ricinoleate
- Glyceryl Ricinoleate, Tocopherol
- Glyceryl Stearate
- Glyceryl Stearate Citrate
- Hexamethyldisilazane
- Hexamethyldisiloxane
- Hydrogenated Coco-Glycerides
- Hydrogenated Palm Oil
- Hydroxytrimethylsilane
- Isopropoxytrimethylsilane
- Methylheptyl Isostearate
- Octamethylcyclotetrasiloxane
- Oleyl Erucate
- Olus Oil

- Organo-modified Siloxanes
- Organosilicone Fluids
- PCA Glyceryl Oleate
- PEG-6 Caprylic/Capric Glycerides
- Phenyltrichlorosilane
- Poly(dimethyl siloxane)
- Poly(ethylene glycol)-containing siloxanes
- Polydimethylsiloxane
- Polyglyceryl-2 Caprate
- Polyglyceryl-3 Caprate
- Polyglyceryl-3 Diisostearate
- Polyglyceryl-3 Polyricinoleate
- Polyglyceryl-4 Cocoate
- Propylene Carbonate
- Propylene Glycol Dicaprylate/Dicaprate
- Silicone oil
- Stearalkonium Bentonite
- Stearalkonium Hectorite
- Triheptanoin
- TriMethyl(broModifluoroMethyl)silane
- Trimyristin
- Tristearin

(E) The Active.

Component (E) is a "pharmaceutically active ingredient," and suitably an active selected from any personal active ingredient or health care active ingredient. As used herein, a "personal care active ingredient" means any compound or mixtures of compounds that are known in the art as additives in the personal care formulations that are typically added for the purpose of treating skin, lips or to provide a cosmetic and/or aesthetic benefit. A "healthcare active ingredient" means any compound or mixtures of compounds that are known in the art to provide a pharmaceutical or medical benefit. Thus, "healthcare active ingredient" includes materials considered an active ingredient or active drug ingredient as generally used and defined by the United States Department of Health & Human

Services Food and Drug Administration, contained in Title 21, Chapter I, of the Code of Federal Regulations, Parts 200-299 and Parts 300-499. Thus, pharmaceutically active ingredient can include any component that is intended to furnish pharmacological activity or other direct effect in the diagnosis, cure, mitigation, treatment, or prevention of disease, or to affect the structure or any function of the body of a human or other animals. The phrase can include those components that may undergo chemical change in the manufacture of drug products and be present in drug products in a modified form intended to furnish the specified activity or effect.

Some representative examples of pharmaceutically active ingredients include; drugs, vitamins, minerals; hormones; topical antimicrobial agents such as antibiotic active ingredients, antifungal active ingredients for the treatment of athlete's foot, jockitch, or ringworm, and acne active ingredients; astringent active ingredients; deodorant active ingredients; wart remover active ingredients; corn and callus remover active ingredients; pediculicide active ingredients for the treatment of head, pubic (crab), and body lice; active ingredients for the control of dandruff, seborrheic dermatitis, or psoriasis; and Sunburn prevention and treatment agents.

Useful pharmaceutically active ingredients for use in processes according to the invention include Vitamins and its derivatives, including “pro-vitamins”. Vitamins useful herein include, but are not limited to, Vitamin A, retinol, C-C esters of retinol, Vitamin E, tocopherol, esters of vitamin E, and mixtures thereof. Retinol includes trans-retinol, 1.3-cis-retinol, 11-cis-retinol, 9-cis-retinol, and 3,4-didehydro-retinol, Vitamin C and its derivatives, Vitamin B, Vitamin B. Pro Vitamin B5, panthenol, Vitamin B. Vitamin B2, niacin, folic acid, biotin, and pantothenic acid. Other suitable vitamins and the INCI names for the vitamins considered included herein are ascorbyl dipalmitate, ascorbyl methylsilanol pectinate, ascorbyl palmitate, ascorbyl Stearate, ascorbyl glucoside, sodium ascorbyl phosphate, sodium ascorbate, disodium ascorbyl sulfate, potassium (ascorbyl/tocopheryl)phosphate.

Retinol, it should be noted, is an International Nomenclature Cosmetic Ingredient Name (INCI) designated by The Cosmetic, Toiletry, and Fragrance Association (CTFA), Washington D.C., for vitamin A. Other suitable vitamins and the INCI names for the vitamins considered included herein are retinylacetate, retinyl palmitate, reti nyl propionate, o-tocopherol tocopher solan, tocopheryl acetate, tocopheryl linoleate, tocopheryl nicotinate, and tocopheryl succinate.

The pharmaceutically active ingredient used in processes according to the invention can be an active drug ingredient. Representative examples of some suitable active drug ingredients which can be used are hydrocortisone, ketoprofen, timolol, pilocarpine, adriamycin, mitomycin C, morphine, hydromorphone, diltiazem, theophylline, doxorubicin, daunorubicin, heparin, penicillin G,

carbenicillin, cephalothin, cefoxitin, cefotaxime, 5-fluorouracil, cytarabine, 6-azauridine, 6-thioguanine, vinblastine, Vincristine, bleomycin sulfate, aurothioglucose, suramin, mebendazole; clonidine, scopolamine, propranolol, phenylpropanolamine hydrochloride, ouabain, atropine, haloperidol, isosorbide, nitroglycerin, ibuprofen, ubiquinones, indomethacin, prostaglandins, naproxen, Salbutamol, guanaben Z, labetalol, pheniramine, metrifonate, and steroids.

Considered to be included herein as active drug ingredients for purposes of the present invention are antiacne agents such as benzoyl peroxide and tretinoin; antibacterial agents such as chlorohexadiene gluconate; antifungal agents such as miconazole nitrate; anti-inflammatory agents; corticosteroidal drugs; non-steroidal anti-inflammatory agents such as diclofenac; antipsoriasis agents such as clobetasol propionate; anesthetic agents such as lidocaine; antipruritic agents; antidermatitis agents; and agents generally considered barrier films.

The active component E) of the present invention can be a protein, such as an enzyme. The internal inclusion of enzymes in the NIPU elastomer gel have advantages to prevent enzymes from deactivating and maintain bioactive effects of enzymes for longer time. Enzymes include, but are not limited to, commercially available types, improved types, recombinant types, wild types, variants not found in nature, and mixtures thereof. For example, suitable enzymes include hydrolases, cutinases, oxidases, transferases, reductases, hemicellulases, esterases, isomerases, pectinases, lactases, peroxidases, laccases, catalases, and mixtures thereof. Hydrolases include, but are not limited to, proteases (bacterial, fungal, acid, neutral or alkaline), amylases (alpha orbeta), lipases, mannanases, cellulases, collagenases, lisozymes, superoxide dismutase, catalase, and mixtures thereof. Said proteases include, but are not limited to, trypsin, chymotrypsin, pepsin, pancreatin and other mammalian enzymes; papain, bromelain and other botanical enzymes; subtilisin, epidermin, nisin, naringinase(L-rhammnosidase) urokinase and other bacterial enzymes. Said lipases include, but are not limited to, triacyl-glycerol lipases, monoacyl glycerol lipases, lipoprotein lipases, e.g. steapsin, erepsin, pepsin, other mammalian, botanical, bacterial lipases and purified ones. Natural papain is preferred as said enzyme. Further, stimulating hormones, e.g. insulin, can be used together with these enzymes to boost the effectiveness of them.

The pharmaceutically active ingredient may also be a sunscreen agent. The Sunscreen agent can be selected from any Sunscreen agent known in the art to protect skin from the harmful effects of exposure to sunlight. The sunscreen compound is typically chosen from an organic compound, an inorganic compound, or mixtures thereof that absorbs ultraviolet (UV) light. Thus, representative non limiting examples that can be used as the sunscreen agent include; aminobenzoic acid, cinoxate, diethanolamine methoxycinnamate, digalloyl trioleate, dioxybenzone, ethyl 4-bis(Hydroxypropyl)

aminobenzoate, glyceryl aminobenzoate, homosalate, lawsone with dihydroxyacetone, menthyl anthranilate, octocrylene, octyl methoxycinnamate, octyl salicylate, oxybenzone, padimate O, phenylbenzimidazole sulfonic acid, red petrolatum, sulisobenzone, titanium dioxide, trolamine salicylate, cetarninosalol, allatoin, PABA, benzalphthalide, benzophenone, benzophenone 1-12, 3-benzylidene camphor, benzylidenecamphor hydrolyzed collagen sulfonamide, benzylidene camphor sulfonic acid, benzyl salicylate, bomelone, bumetriozole, butyl methoxydibenzoylmethane, butyl PABA, ceria/silica, ceria/silica talc, cinoxate, DEA-methoxycinnamate, dibenzoxazol naphthalene, di-t-butyl hydroxybenzylidene camphor, digalloyl trioleate, diisopropyl methyl cinnamate, dimethyl PABA ethyl cetearyldimonium tosylate, dioctyl butamido triazone, diphenyl carbomethoxy acetoxy naphthopyran, disodium bisethylphenyl tiamminotriazine stilbenedisulfonate, disodium sistyrylbiphenyl triaminotriazine stilbenedisulfonate, disodium distyrylbi phenyl disulfonate, drometrizole, drometrizole trisiloxane, ethyl dihydroxypropyl PABA, ethyl diisopropylcinnamate, ethyl methoxycinnamate, ethyl PABA, ethyl urocanate, etrocrylene ferulic acid, glyceryl octanoate dimethoxycin namate, glyceryl PABA, glycol salicylate, homosalate, isoamyl p-methoxycinnamate, isopropylbenzyl salicylate, isopropyl dibenzolylmethane, isopropyl methoxycinnamate, menthyl anthranilate, menthyl salicylate, 4-methylbenzylidene, camphor, octocrylene, octrizole, octyl dimethyl PABA, octyl methoxycinnamate, octyl salicylate, octyl triazone, PABA, PEG-25 PABA, pentyl dimethyl, PABA, phenylbenzimidazole sulfonic acid, polyacrylamidomethyl benzylidene camphor, potassium methoxycinnamate, potassium phenylbenzimidazole sulfonate, red petrolatum, sodium phenylbenzimidazole sulfonate, sodium urocanate, TEA-phenylbenzimidazole sulfonate, TEA-salicylate, terephthalylidene dicamphor sulfonic acid, titanium dioxide, zinc dioxide, serium dioxide, TriPABA panthenol, urocanic acid, and VA/crotonates/ methacryloxybenzophenone-1 copolymer.

The Sunscreen agent can be a single one or combination of more than one. Alternatively, the Sunscreen agent is a cinnamate based organic compound, or alternatively, the Sunscreen agent is octyl methoxycinnamate, Such as Uvinul R. MC 80 an ester of para-methoxycinnamic acid and 2-ethyl hexanol.

Component (E) may also be a fragrance or perfume. The perfume can be any perfume or fragrance active ingredient commonly used in the perfume industry. These compositions typically belong to a variety of chemical classes, as varied as alcohols, aldehydes, ketones, esters, ethers, acetates, nitrites, terpenic hydrocarbons, heterocyclic nitrogen or Sulfur containing compounds, as well as essential oils of natural or synthetic origin. Many of these perfume ingredients are described

in detail in standard textbook references such as Perfume and Flavour Chemicals, 1969, S. Arctander, Mont clair, N.J.

Fragrances may be exemplified by, but not limited to, perfume ketones and perfume aldehydes. Illustrative of the perfume ketones are buccoxime; isojasmone; methyl beta naphthyl ketone; musk indanone; tonalid/musk plus; Alpha Damascone, Beta-Damascone, Delta-Damascone, Iso Damascone, Damascenone, Damarose, Methyl Dihydrojasmonate, Menthone, Carvone, Camphor, Fenchone, Alpha-lonone, Beta-lonone, Gamma-Methyl So called lonone, Fleuramone, Dihydrojasmone, Cis-Jasmone, Iso-E-Super, Methyl-Cedrenyl-ketone or Methyl-Cedrylone, Acetophenone, Methyl-Acetophenone, Para-Methoxy-Acetophenone, Methyl-Beta-Naphtyl-Ketone, Benzyl-Acetone, Benzophenone, Para-Hydroxy-Phenyl-Butanone, Celery Ketone or LiveScone, 6-Isopropyldecahydro-2-naphtone, Dimethyloctenone, Freskomenthe, 4-(1-Ethoxyvinyl)-3,3, 5.5,-tetramethyl-Cyclohexanone, Methyl heptenone, 2-(2-(4-Methyl-3-cyclohexen-1-yl)propyl)-cyclopentanone, 1-(p- Menthen-6(2)-yl)-1-propanone, 4-(4-Hydroxy-3- methoxyphenyl)-2-butanone, 2-Acetyl-3,3-Dimethyl Norbornane, 6,7-Dihydro-1,1,2,3,3-Pentamethyl-4(5H)- Indanone, 4-Damascol, Dulcinyl or Cassione, Gelsone, Hexylon, Isocyclemone E. Methyl Cyclocitrone, Methyl Lavender-Ketone, Orivon, Para-tertiary-Butyl-Cyclohexanone, Verdone, Delphone, Muscone, Neobutenone, Plica tone, Veloutone, 2,4,4,7-Tetramethyl-oct-6-en-3-one, and Tetrameran.

More preferably, the perfume ketones are selected for their odor character from Alpha Damascone, Delta Damascone, Iso Damascone, Carvone, Gamma-methyl-ionone, Iso-E-Super, 2.4.4.7-Tetramethyl-oct-6-en-3-one, Benzyl Acetone, Beta Damascone, Damascenone, methyl dihydrojasmonate, methyl cedrylone, and mixtures thereof.

Preferably, the perfume aldehyde is selected for its odor character from adoxal, anisic aldehyde, cymal, ethylvanillin, florhydral, helional, heliotropin, hydroxycitronellal, koavone, lauric aldehyde, lyral, methyl nonyl acetaldehyde, P. T. bucinal, phenyl acetaldehyde, undecylenic aldehyde, vanillin, 2,6,10-trimethyl-9-undecenal, 3-dodecen-1-al, alpha-n-amyl cinnamic aldehyde, 4-methoxybenzaldehyde, benzaldehyde, 3-(4-tert-butylphenyl)-propanal, 2-methyl-3-(para-methoxyphenyl propanal, 2-methyl-4-(2,6,6-trimethyl-2(1)-cyclohexen-1-yl) butanal, 3-phenyl-2-propenal, cis-/trans-3,7-dimethyl-2,6-octadien-1-al, 3,7-dimethyl-6-octen-1-al. (3,7-dimethyl-6-octenyl)oxyacetaldehyde, 4-isopropylbenzyaldehyde, 1,2,3,4,5,6,7,8-octahydro-8,8-dimethyl-2-naphthaldehyde, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, 2-methyl-3-(isopropylphenyl)propanal, 1-decanal; decyl aldehyde, 2,6-dimethyl-5-heptenal, 4-(tricyclo[5.2.1.0(2,6)-decylidene-8)-butanal, octahydro-4,7-methano-1H-indenecarboxaldehyde, 3-ethoxy-4-hydroxy benzaldehyde, para-ethyl-alpha,alpha-dimethyl hydrocinnamaldehyde, alpha-

methyl-3,4-(methylenedioxy)-hydrocinnamaldehyde, 3,4-methylenedioxybenzaldehyde, alpha-n-hexyl cinnamic aldehyde, m-cymene-7-carboxaldehyde, alpha-methyl phenyl acetaldehyde, 7-hydroxy-3,7-dimethyl octanal, Undecenal, 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde, 4-(3)(4-methyl-3-pentenyl)-3-cyclohexen-carboxaldehyde, 1-dodecanal, 2,4-dimethyl cyclohexene-3-carboxaldehyde, 4-(4-hydroxy-4-methylpentyl)-3-cylohexene 1-carboxaldehyde, 7-methoxy-3,7-dimethyloctan-1-al, 2-methyl undecanal, 2-methyl decanal, 1-nonanal, 1-octanal, 2,6,10-trimethyl-5.9-undecadienal, 2-methyl-3-(4-tertbutyl) propanal, dihydrocinnamic aldehyde, 1-methyl-4-(4-methyl 3-pentenyl)-3-cyclohexene-1-carbox aldehyde, 5 or 6 methoxyl-hexahydro-4,7-methanoindan-1 or 2-carboxaldehyde, 3,7-dimethyloctan-1-al, 1-undecanal, 10-undecen-1-al, 4-hydroxy-3-methoxy benzaldehyde, 1-methyl-3-(4-methylpentyl)-3-cyclhexenecarboxaldehyde, 7-hydroxy-3,7-dimethyl octanal, trans-4-decenal, 2,6-nonadienal, paratolylacetaldehyde, 4-methylphenylacetaldehyde, 2-me thyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butenal, ortho-methoxycinnamic aldehyde, 3,5,6-trimethyl-3-cyclohexene carboxaldehyde, 3,7-dimethyl-2-methylene-6-octenal, phenoxyacetaldehyde, 5,9-dimethyl-4,8-decadienal, peony aldehyde (6,10-dimethyl-3-oxa-5,9-undecadien-1-al), hexahydro-4,7-methanoindan-1-carboxaldehyde, 2-methyloctanal, alpha-methyl-4-(1-methylethyl)benzene acetaldehyde, 6,6-dimethyl-2-norpinene-2-propionaldehyde, para-methyl phenoxyacetaldehyde, 2-methyl-3-phenyl-2-propen-1-al, 3,5,5-trimethylhexanal, Hexahydro-8,8-dimethyl-2-naphthaldehyde, 3-propyl-bicyclo[2.2.1-hept-5-ene-2-carbaldehyde, 9-decenal, 3-methyl-5-phenyl-1-pentanal, methylnonyl acetaldehyde, hexanal, trans-2-hexenal, 1-pmenthene- q-carboxaldehyde and mixtures thereof. More preferred aldehydes are selected for their odor character from 1-decanal, benzaldehyde, florhydral, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, cis/trans-3,7-dim ethyl-2,6-octadien-1-al, heliotropin, 2,4,6-trimethyl-3- cyclohexene-1-carboxaldehyde, 2,6-nonadienal, alphanamyl cinnamic aldehyde, alpha-n-hexyl cinnamic aldehyde, P.T. Bucinal, lyral, cymal, methylnonyl acetaldehyde, hexanal, trans-2-hexenal, and mixture thereof. In the above list of perfume ingredients, some are commercial names conventionally known to one skilled in the art, and also includes isomers. Such isomers are also suitable for use in the present invention.

Component (E) may also be one or more plant extract. Examples of these components are as follows: Ashitaba extract, avocado extract, hydrangea extract, Althea extract, Arnica extract, aloe extract, apricot extract, apricot kernel extract, Ginkgo Biloba extract, fennel extract, turmeric Curcuma extract, oolong tea extract, rose fruit extract, Echinacea extract, Scutellaria root extract, Phellodendro bark extract, Japanese Coptis extract, Barley extract, Hyperium extract, White Nettle extract, Watercress extract, Orange extract, Dehydrated saltwater, seaweed extract, hydrolyzed

elastin, hydrolyzed wheat powder, hydrolyzed silk, Chamomile extract, Carrot extract, Artemisia extract, Glycyrrhiza extract, hibiscustea extract, Pyracantha Fortuneana Fruit extract, Kiwi extract, Cinchona extract, cucumber extract, guanocine, Gardenia extract, Sasa albomarginata extract, Sophora root extract, Walnut extract, Grapefruit extract, Clematis extract, Chlorella extract, mulberry extract, Gentiana extract, black tea extract, yeast extract, burdock extract, rice bran ferment extract, rice germ oil, comfrey extract, collagen, cowberry extract, Gardenia extract, Asiasarum root extract, Family of Bupleurum extract, umbilical cord extract, Salvia extract, Saponaria extract, Bamboo extract, Crataegus fruit extract, Zanthoxylum fruit extract, Shiitake extract, Rehmannia root extract, gromwell extract, Perilla extract, linden extract, Filipendula extract, peony extract, calamus root extract, white birch extract, Horsetail extract, Hedera Helix(Ivy) extract, hawthorn extract, Sambucus migra extract, Achillea millefolium extract, Mentha piperita extract, sage extract, mallow extract, Cnidium officinale root extract, Japanese green gen tian extract, Soybean extract, jujube extract, thyme extract, tea extract, clove extract, Gramineae imperata cyrillo extract, citrus unshiu peel extract Japanese angelica root extract, calendula extract, peach kernel extract, Bitter orange peel extract, Houttuyna cordata extract, tomato extract, natto extract, ginseng extract, green tea extract (camelliea sine sis), garlic extract, wild rose extract, hibiscus extract, Ophio pogon tuber extract, Nelumbo nucifera extract, parsley extract, honey, hamamelis extract, parietaria extract, isodonis herba extract, bisabolol extract, Loquat extract, coltsfoot extract, butterbur extract, Porid cocos wolf extract, extract of butcher's broom, grape extract, propolis extract, lufa extract, safflower extract, peppermintextract, linden tree extract, Paeonia extract, hop extract, pine tree extract, horse chestnut extract, Mizu-bashou Lysichiton camtschatcese extract, Mukurossi peel extract, Melissa extract, peach extract, corn flower extract, eucalyptus extract, saxifrage extract, citron extract, coix extract, mugwort extract, lavender extract, apple extract, lettuce extract, lemon extract, Chinese milk vetch extract, rose extract, rosemary extract, Roman Chamomile extract, and royal jelly extract.

The amount of component (E) present in the NIPU gel composition may vary, but typically range as follows: 0.05 to 50 wt %, alternatively 1 to 25 wt %, or alternatively 1 to 10 wt %, based on the amount by weight of NIPU elastomer gel present in the composition, that is total weight of components (A), (B), (C) and (D) in the NIPU gel composition.

The active, component (E), may be added to the NIPU gel composition either during the making of the NIPU elastomer (pre-load method), or added after the formation of the NIPU elastomer gel (post load method).

The pre-load method involves:

I) mixing:

A) cyclic or aliphatic carbonate polymer, which may optionally contain siloxanes in its backbone;

B) aliphatic or cycloaliphatic polyamine;

C) an optional reaction catalyst;

D) an optional carrier fluid, wherein the topically acceptable carrier fluid is a reaction solvent or wherein the carrier fluid is added after elastomer formation, optionally wherein the carrier fluid comprises a topically acceptable carrier fluid;

E) a personal care or healthcare active with the NIPU elastomer gel to form the NIPU elastomer gel containing active.

The post-load method involves;

I) mixing:

A) cyclic or aliphatic carbonate polymer, which may optionally contain siloxanes in its backbone;

B) aliphatic or cycloaliphatic polyamine;

C) an optional reaction catalyst;

D) an optional carrier fluid, wherein the topically acceptable carrier fluid is a reaction solvent or wherein the carrier fluid is added after elastomer formation, optionally wherein the carrier fluid comprises a topically acceptable carrier fluid;

II) shearing the NIPU elastomer gel into a smooth paste; and

III) admixing:

E) a personal care or healthcare active with the NIPU elastomer gel to form the NIPU elastomer gel containing active. The personal care active may also be admixed as a component of another mixture with one or more excipients.

The NIPU Elastomers

The NIPU elastomers of the present invention are obtainable as NIPU reaction products of components (A), (B), and (C) in (D). The term "NIPU reaction" means the addition of a compound containing multiple cyclic or non-cyclic carbonate groups (such as component A) to a compound containing multiple primary or secondary amine groups (such as component B), optionally in the

presence of a catalyst (such as component C). Wherein the molar ratio of carbonate to amine groups is 1/1. Alternatively, this ratio can range from 8/1 to 0.9/1. The NIPU reaction is conducted in the presence of a solvent, where the solvent is the same as the carrier fluid described as component (D) and can optionally be used without further purification.

Methods for Measuring Hardness of NIPU Elastomer Gel Compositions

The NIPU elastomers are prepared in a carrier fluid (as described above as component D) to form gelled compositions. The gelled compositions of the present invention may be characterized by their hardness or firmness. Useful tests to characterize the gels are those recommended by the Gelatin Manufacturers Institute of America such as the use of a "Texture Analyzer" (model TAXT2, Stable Micro Systems, Inc., Godalming, England). The gel sample is subjected to a compression test with the Texture Analyzer having a probe with a 5.0 kg load cell. The probe approaches the surface of the gel at a speed of 1 mm/sec and continues compression into the gel to a distance of 5.0 mm. The Texture Analyzer detects the resistance force the probe experiences during the compression test. The force exhibited by the load cell is plotted as a function of time. The hardness of the NIPU elastomers, gels and elastomer blends (SEBs) for purposes of this invention is defined as the resistance force detected by the probe of the "Texture Analyzer" during the compression test. Hardness is characterized as the force at the maximum compression point (i.e. the 5.0 mm compression point into the gel Surface). The average of a total of 3 tests are typically performed for each gel and gels were made in triplicate.

The value obtained for force (in grams) is converted into Newtons (N), by dividing the gram force value by 101.97. (i.e. 1 Newton equals 101.97g force based on the size of the probe used). The second property reported by Texture Analyzer measurement is Area F-T 1:2, in g force.sec. This is the area integration of the force vs. test time cure. This property is indicative of a gel network since it indicates ability to sustain resistance to the compression force, which is relevant to elastomers and gels. The value is reported in g force.sec and is converted to Newton.sec in SI unit by dividing the value in force.sec by 101.97.

The NIPU gels of the present invention have a compression hardness of at least 0.5 Newton/cm^2, alternatively 1 Newton/cm^2, or alternatively 2 Newton/cm^2 when measured with a 1.27 cm diameter spherical probe and a 50 g gel sample in a 4-ounce round glass jar.

Gel Paste Compositions Containing the NIPU Elastomer

The gelled compositions of the present invention can be used to prepare gel paste or gel blend compositions containing actives by:

I) shearing the NIPU elastomer gel, as described below,

II) combining the sheared NIPU elastomer gel with additional quantities of

D) the carrier fluid, as described above, and optionally

E) a personal or health care active to form a gel paste or blend composition. The personal care active may also be admixed as a component of another mixture with one or more excipients.

The NIPU elastomer gel compositions of the present invention may be considered as discrete crosslinked NIPU elastomer gel particles dispersed in carrier fluids. Thus, the NIPU elastomer compositions are effective rheological thickeners for compatible lower molecular weight solvents. As such they can be used to prepare useful gel blend compositions, such as "gel paste' compositions.

To make such NIPU elastomer gel pastes, the aforementioned NIPU elastomer gels of known initial elastomer content (IEC) are sheared to obtain small particle size and further diluted to a final elastomer content (FEC). Shearing, as used herein refers to any shear mixing process, such as obtained from homogenizing, sonolating, or any other mixing processes known in the art as shear mixing. The shear mixing of the NIPU elastomer gel composition results in a composition having reduced particle size. The subsequent composition having reduced particle size is then further combined with D) the carrier fluid. The carrier fluid may be any carrier fluid as described above, but typically is a linear ester (e.g. heptyl undecylenate), triglyceride (e.g. triheptanoin), or alkane (e.g. isododecane). The technique for combining D) the carrier fluid with the NIPU elastomer composition having reduced particle size is not critical, and typically involves simple stirring or mixing. The resulting compositions may be considered as a paste, having a viscosity greater than 100,000 cP (mPas).

Methods for Measuring Viscosity of NIPU Elastomer Gel Pastes

The Brookfield HELIPATH™ Stand, when used with a suitable Brookfield Viscometer fitted with a special T-bar type spindle, will permit viscosity/consistency measurements in centipoise values for materials having characteristics similar to paste, putty, cream, gelatin, or wax. The viscosity of NIPU elastomer blends was determined using a Brookfield Model DV-II+Pro Viscometer with HELIPATH™ stand (Brookfield Model D) and T-Bar spindles (Brookfield Helipath Spindle Set). All were purchased from Brookfield Engineering Laboratories, Inc. (11 Commerce Boulevard Middleboro, Mass., USA). A sample size of 50 g in a 4-ounce round jar was required. The following

preparation procedure was used before measurement: air bubbles were removed from samples first via centrifuge and then under vacuum for two hours. After de-airing, the sample was conditioned for a minimum of 4 hours at 25 °C. The measurement was taken according to the typical procedure for a HELIPATH™ spindle. In general, spindle 93 (T-bar spindle E) is used and the standard setting for rpm was 6.5. The spindle speed is maintained at constant 6.5 rpm.

Topical formulations comprising the gel compositions or gel pastes are also provided herein. In such formulations, the gel compositions or gel pastes are suitably used as thickeners or stabilizers for the topical formulations. Other components of the topical formulations are known in the art, and can include for example, various components such as emulsion stabilizers, emulsifiers skin conditioners, suspending agents etc. The amounts of these additional components can be on the order of about 0.01% to about 50% by weight.

As used herein an "emulsion stabilizer" refers to a composition that aids in keeping an emulsion from separating into its oil and aqueous components. In embodiments, the emulsion stabilizer utilized in the formulations described herein is a naturally derived gum or a modified gum or natural mineral. Exemplary emulsion stabilizers include, but are not limited to, acacia, cellulose, crystalline cellulose, gellan, guar, locust (carob) bean, xanthan, magnesium aluminum silicate, bentonite or hectorite clays and the like, including combinations thereof.

As used herein a "skin conditioner" refers to a composition that acts as a lubricant on the surface of the skin or a composition that increases the water content of the surface of the skin. Exemplary skin conditioners for use in the formulations include, but are not limited to, adipate esters, alkyl benzoates, fatty acid esters of C8 or greater, esterified erucates, laurates, neopentanoates, salicylates, stearates, triglycerides, carbonates, glycols, glycerin, mineral oils and the like, including combinations thereof.

As used herein an "emulsifier" refers to a composition that aids in the formation of an oil in water, or a water in oil, emulsion. Exemplary emulsifiers for use in the formulations include, but are not limited to, polysorbates, ethoxylated fatty acids, fatty acids neutralized with sodium hydroxide, potassium hydroxide or amines, substituted glucosides, sodium lauryl and lauryl ether sulfates, ethoxylated esters, lecithin and lecithin derivatives and the like, including combinations thereof.

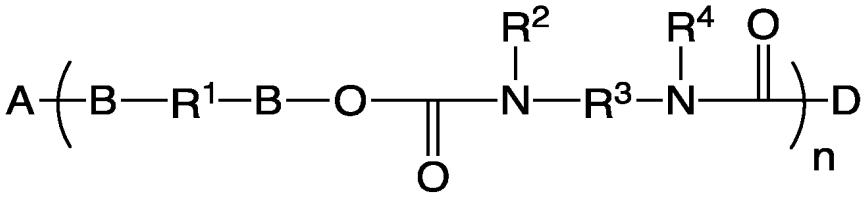
As used herein a "suspending agent" refers to a composition that modifies the interface between solid particles and a liquid medium to improve the particles' resistance to coming together and falling out of solution. Exemplary suspending agents for use in the formulations include, but are not limited to, hydroxy stearic acid, polyhydroxystearic acid, sodium polyacrylate polymers, methyl methacrylate crosspolymers and the like, including combinations thereof.

In additional embodiments, the non-isocyanate polyurethane (NIPU) elastomers can be utilized in solid-based formats, including for example, as a foot conforming shoe insert or shoe sole.

The non-isocyanate polyurethane (NIPU) elastomers can also be used as medically acceptable gels, including for example, medical implants or portions of implants, including as cartilage replacements, bone replacements, etc.

Exemplary embodiments:

Embodiment 1. A non-isocyanate polyurethane (NIPU) elastomer of Formula I:

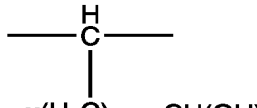


Formula I

wherein:

n is 2 to m;

A is an end group selected from a cyclocarbonate and an amine;

B is selected from  and $-(CH_2)_x-C(OH)R^5-$;

x is 0 to 4;

R1 is a C1-C30 substituted or unsubstituted linear or branched aliphatic group, cycloaliphatic group, aryl group, heterocycloaliphatic group, or heteroaryl group, optionally comprising a heteroatom;

R2, R4, and R5 are independently hydrogen or a C1-C30 substituted or unsubstituted linear or branched alkyl group, aliphatic group, cycloaliphatic group, or aryl group, optionally comprising a heteroatom;

R3 is a C1-C30 substituted or unsubstituted linear or branched aliphatic group, cycloaliphatic group, aryl group, heterocycloaliphatic group, or heteroaryl group, optionally comprising a heteroatom; and

D is an end group selected from a cyclocarbonate and an amine,

wherein m is a whole integer between 3 and 1,000,000,000,000, including 10, 100, 1,000, 10,000, 100,000, 1,000,000, 10,000,000, 100,000,000, 1,000,000,000, 10,000,000,000, 100,000,000,000 and 1,000,000,000,000, as well as other values between 3 and 1,000,000,000,000.

Embodiment 2. A gel composition comprising a non-isocyanate polyurethane (NIPU) elastomer prepared from the reaction of:

A) a polycarbonate or a mixture of polycarbonates comprising two or more carbonate functional groups;

B) a polyamine or mixture of polyamines comprising two or more amine functional groups, where the amine functional groups are either primary or secondary;

C) an optional NIPU reaction catalyst; and

D) an optional topically acceptable carrier fluid, wherein the topically acceptable carrier fluid is a reaction solvent or wherein the topically acceptable carrier fluid is added after elastomer formation, at a concentration of between 50% (w/w) and 99.9% (w/w) of the gel composition.

Embodiment 3. The gel composition of embodiment 2, wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof.

Embodiment 4. The gel composition of embodiment 2, wherein the topically acceptable carrier fluid is selected from the group consisting of diisooctyl succinate, heptyl undecylenate, neopentyl glycol diheptanoate, and coco caprylate.

Embodiment 5. The gel composition of embodiment 2, further comprising a pharmaceutically active ingredient dissolved in the topically acceptable carrier fluid.

Embodiment 6. The gel composition of embodiment 2, further comprising a pharmaceutically active ingredient incorporated in the gel.

Embodiment 7. The gel composition of embodiment 2 wherein the polycarbonate or mixture of polycarbonates is a low molecular weight polycarbonate or mixture of polycarbonates containing two or more hydroxyl groups and wherein the polyamine or mixture of polyamines is a low molecular weight polyamine or mixture of polyamines containing two or more primary or secondary amines.

Embodiment 8. A method of making a non-isocyanate polyurethane (NIPU) elastomer gel comprising:

i) mixing a polycarbonate reactant and a polyamine reactant, wherein the polycarbonate comprises two or more carbonate functional groups and the polyamine comprises two or more primary or secondary amines; and

ii) optionally adding a topically acceptable carrier fluid, wherein the topically acceptable carrier fluid is a reaction solvent or wherein the topically acceptable carrier fluid is added after

elastomer formation, to form a polymer gel mixture with a polymer concentration of about 80% (w/w); and

iii) optionally adding a NIPU reaction catalyst; and

iv) optionally heating the reaction mixture to about 100°C to form the NIPU elastomer.

Embodiment 9. The method of embodiment 8, wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof.

Embodiment 10. The method of embodiment 8, wherein the topically acceptable carrier fluid is selected from the group consisting of diisooctyl succinate, heptyl undecylenate, neopentyl glycol diheptanoate, and coco caprylate.

Embodiment 11. The method of embodiment 8, further comprising dissolving a pharmaceutically active ingredient in the topically acceptable carrier fluid.

Embodiment 12. The method of embodiment 8, wherein the polycarbonate reactant comprises two or more hydroxyl groups.

Embodiment 13. The method of embodiment 8, further comprising preparing the polycarbonate reactant from a vegetable oil or mixture of vegetable oils containing two or more hydroxyl groups.

Embodiment 14. The method of embodiment 8, further comprising preparing the polycarbonate reactant from a copolymer of dilinoleic acid or mixture of copolymers of dilinoleic acid.

Embodiment 15. A method of making a NIPU elastomer gel paste comprising the steps of:

i) shearing the NIPU elastomer of claim 8;

ii) optionally adding additional quantities of the topically acceptable carrier fluid during shearing to produce a gel paste composition; and

iii) optionally adding a pharmaceutically active ingredient.

Embodiment 16. An NIPU elastomer gel paste prepared by the embodiment of claim 15.

Embodiment 17. A topical formulation comprising:

the gel composition of embodiment 5 or embodiment 6, wherein the pharmaceutically active ingredient is a personal care active ingredient or a healthcare active ingredient.

Embodiment 18. A topical formulation comprising:

the NIPU elastomer gel paste of embodiment 15, comprising a personal care active ingredient or a healthcare active ingredient.

Embodiment 19. A gel composition comprising a non-isocyanate polyurethane (NIPU) elastomer prepared from the reaction of:

A) a polycarbonate or a mixture of polycarbonates comprising two or more carbonate functional groups;

B) a polyamine or mixture of polyamines comprising two or more amine functional groups, where the amine functional groups are either primary or secondary;

C) an optional NIPU reaction catalyst; and

D) a carrier fluid, wherein the carrier fluid is a reaction solvent or wherein the carrier fluid is added after elastomer formation, at a concentration of between 60% (w/w) and 99.9% (w/w) of the gel composition.

Embodiment 20. A foot conforming shoe insert or shoe sole comprising:

the non-isocyanate polyurethane (NIPU) elastomer of embodiment 1 or the gel composition of embodiment 19.

Embodiment 21. A medical medically acceptable gel comprising:

the non-isocyanate polyurethane elastomer (NIPU) of embodiment 1 or the gel composition of embodiment 19.

Embodiment 22. A topical formulation comprising:

the NIPU elastomer of embodiment 1.

Embodiment 23. A gel composition comprising the non-isocyanate polyurethane (NIPU) elastomer of embodiment 1 and a topically acceptable carrier fluid, at a concentration of between 60% (w/w) and 99.9% (w/w) of the gel composition.

Embodiment 24. A method of making a NIPU elastomer gel paste comprising the steps of:

i) shearing the gel paste of embodiment 23;

ii) optionally adding quantities of the topically acceptable carrier fluid during shearing to produce a gel paste composition; and

iii) optionally adding a pharmaceutically active ingredient.

Embodiment 25. A NIPU elastomer gel paste prepared by the method of embodiment 24.

Embodiment 26. A topical formulation comprising the gel composition of embodiment 24 or the NIPU elastomer gel paste of embodiment 25.

Examples

Example 1 – Preparation of Castor Oil / Isophorone diamine NIPU elastomer.

To a stainless steel or glass reaction vessel add a topically acceptable carrier fluid that can dissolve castor oil like diisooctyl succinate, (400 grams), castor oil (71.1 grams) with hydroxyl value of 166.87 mg/g, and dimethyl carbonate (20.97 grams, 1.1 equivalent with respect to moles of hydroxyl groups). Stir the reaction mixture at a temperature between 25 °C to about 100 °C for up to 8 hours before the addition of isophorone diamine (36.08 grams) with stirring. Once a homogenous mixture is obtained, pour 50 grams of the mixture into a 4-ounce glass jar. Cover the remainder of the reaction mixture and the 50-gram sample and heat to 75 °C for up to about 23 hours, at which point a translucent gel will form. The hardness of the 50-gram sample of gel is expected to be about 0.87 N/cm^2, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

Break the NIPU elastomer gel into smaller pieces, place in a metal container, and add a topically acceptable carrier fluid which may or may not be heptyl undecylenate before homogenization into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 2 – Preparation of Castor Oil / Hexemethylenediamine NIPU elastomer.

To a stainless steel or glass reaction vessel add a topically acceptable carrier fluid that can dissolve castor oil like diisooctyl succinate (400 grams), castor oil (71.1 grams) with hydroxyl value of 166.87 mg/g, and dimethyl carbonate (20.97 grams, 1.1 equivalent with respect to moles of hydroxyl groups). Stir the reaction mixture at about 75 °C for up to 8 hours before the addition of hexamethylenediamine (24.62 grams) with stirring. Once a homogenous mixture is obtained, pour 50 grams of the mixture into a 4-ounce glass jar. Cover the remainder of the reaction mixture and the 50-gram sample and heat to 75 °C for up to 23 hours, at which point a translucent gel will form. The hardness of the 50-gram sample of gel is expected to be about 0.87 N/cm^2, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

Break the NIPU elastomer gel into smaller pieces, place in a metal container, and add a topically acceptable carrier fluid which may or may not be heptyl undecylenate before homogenization into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 3 – Preparation of Castor Oil / diamine NIPU elastomer.

To a stainless steel or glass reaction vessel add a topically acceptable carrier fluid that can dissolve castor oil like diisooctyl succinate (400 grams), castor oil (71.1 grams) with hydroxyl value of 166.87 mg/g, and dimethyl carbonate (20.97 grams, 1.1 equivalent with respect to moles of hydroxyl groups). Stir the reaction mixture at a temperature between 25°C to about 100 °C for up to 8 hours before the addition of a diamine with stirring. Once a homogenous mixture is obtained, pour 50 grams of the mixture into a 4-ounce glass jar. Cover the remainder of the reaction mixture and the 50-gram sample and heat to 75 °C for up to 23 hours, at which point a translucent gel will form. The hardness of the 50-gram sample of gel is expected to be about 0.87 N/cm^2, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

Break the NIPU elastomer gel into smaller pieces, place in a metal container, and add a topically acceptable carrier fluid which may or may not be heptyl undecylenate before homogenization into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 4 – Preparation of Castor Oil / triamine NIPU elastomer gel.

To a stainless steel or glass reaction vessel add a topically acceptable carrier fluid that can dissolve castor oil like diisooctyl succinate (400 grams), castor oil (71.1 grams) with hydroxyl value of 166.87 mg/g, and dimethyl carbonate (20.97 grams, 1.1 equivalent with respect to moles of hydroxyl groups). Stir the reaction mixture at a temperature between 25°C to about 100 °C for up to 8 hours before the addition of a triamine with stirring. Once a homogenous mixture is obtained, pour 50 grams of the mixture into a 4-ounce glass jar. Cover the remainder of the reaction mixture and the 50-gram sample and heat up to 75 °C for up to about 23 hours,

at which point a translucent gel will form. The hardness of the 50-gram sample of gel is expected to be about 0.87 N/cm^2, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

Break the NIPU elastomer gel into smaller pieces, place in a metal container, and add a topically acceptable carrier fluid which may or may not be heptyl undecylenate before homogenization into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 5 – Preparation of dilinoleic acid / propane diol copolymer diamine NIPU elastomer gel.

To a stainless steel or glass reaction vessel add a topically acceptable carrier fluid that can dissolve dilinoleic acid/propane diol copolymer triheptanoin (up to about 400 grams), and dimethyl carbonate (1.1 equivalent with respect to moles of hydroxyl groups of the diol copolymer). Stir the reaction mixture at a temperature between 25 °C to about 100 °C for up to 8 hours before the addition of a diamine with stirring. Once a homogenous mixture is obtained, pour 50 grams of the mixture into a 4-ounce glass jar. Cover the remainder of the reaction mixture and the 50-gram sample and heat up to 75 °C for up to about 23 hours, at which point a translucent gel will form. The hardness of the 50-gram sample of gel is expected to be about 0.87 N/cm^2, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

Break the NIPU elastomer gel into smaller pieces, place in a metal container, and add a topically acceptable carrier fluid which may or may not be heptyl undecylenate before homogenization into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 6 - Preparation of dilinoleic acid/ dilinoleic diol copolymer diamine NIPU elastomer gel.

To a stainless steel or glass reaction vessel add a topically acceptable carrier fluid that can dissolve dilinoleic acid/propane diol copolymer like triheptanoin (up to about 400 grams), and

dimethyl carbonate (1.1 equivalent with respect to moles of hydroxyl groups of the diol copolymer). Stir the reaction mixture at a temperature between 25 °C to about 100 °C for up to 8 hours before the addition of a diamine with stirring. Once a homogenous mixture is obtained, pour 50 grams of the mixture into a 4-ounce glass jar. Cover the remainder of the reaction mixture and the 50-gram sample and heat up to 75 °C for up to about 23 hours, at which point a translucent gel will form. The hardness of the 50-gram sample of gel is expected to be about 0.87 N/cm^2, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

Break the NIPU elastomer gel into smaller pieces, place in a metal container, and add a topically acceptable carrier fluid which may or may not be heptyl undecylenate before homogenization into a smooth gel paste with a desired viscosity using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 4500 to 8000 revolutions per minute.

Example 7 – Preparation of a serum containing an NIPU elastomer.

Add an NIPU elastomer gel (700 g) from one of the Examples 1 to 6 to a stainless steel reaction vessel that is equipped with an overhead stirrer. Add to this gel up to 300 g of argan oil and stir the mixture in the presence or absence of heat for up to 1 h to yield an argan serum

Example 8 – Preparation of an oil in water emulsion with the NIPU elastomer

An oil in water emulsion may be formed by adding a topically acceptable oil to the water phase with gentle heating to 75 °C. Once cooled to room temperature, the NIPU elastomer may be post-added to a concentration between 5 and 90% to yield an elegant cream

Example 9 – Preparation of sunscreen composition containing Castor Oil / Isophorone diamine NIPU elastomer.

Add Avobenzone (30g; 3% w/w) + Octocrylene (100 g; 10% w/w) + Homosalate (150 g; 15% w/w) + Octylsalicylate (50 g; 5% w/w) + Sunboost (50 g; 5% w/w; Kobo) + Halbrite (50 g; 5% w/w; Hallstar), Vegelight (270 g; 27% w/w) and Castor Oil / Isophorone diamine NIPU elastomer gel paste (300 g; 30% w/w) to a stainless steel vessel and mix with an overhead mixer fitted with a paddle blade for 20 min to provide a homogenous sunscreen formulation.

Example 10 – Preparation of a dilinoleic diol / polyoxypropylenetriamine NIPU elastomer

To a 4 ounce glass jar was added dilinoleic diol dimethyl dicarbonate (25.0 g), which was previously synthesized by the reaction of dilinoleic diol and dimethyl carbonate, and Jeffamine T-403 (12.65 g; Huntsman International LLC, The Woodlands, TX). The reaction mixture was stirred at room temperature until homogenous, at which time triazabicyclodecene (753 mg) was added. The colorless and clear reaction mixture was heated overnight at to 120 °C to yield a slightly tinted clear non-pourable elastomer rubber with a hardness of 180 N/cm^2, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

Example 11 – Preparation of a castor oil / isophorone diamine NIPU elastomer

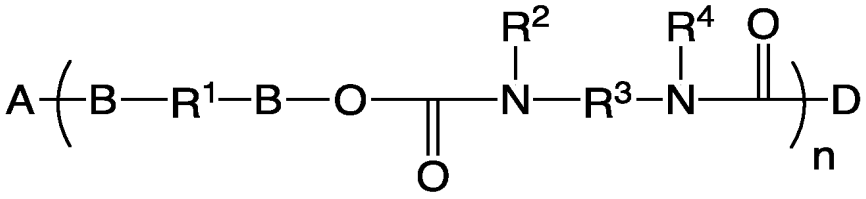
To a test tube was added castor oil carbonate (500 mg), which was previously synthesized by the reaction of castor oil and dimethyl carbonate, and isophorone diamine (247 mg). The reaction mixture was vortexted at room temperature until homogenous, at which time triazabicyclodecene (12.47 mg) was added. The reaction mixture was heated to 120 °C in a heat block and vortexed to ensure homogenous mixture. The reaction mixture was heated overnight at 120 °C to yield a slightly non-pourable elastomer rubber with a hardness of 250 N/cm^2, as determined using a Stable Micro Systems Texture Analyzer with a 5-kilogram load cell, fitted with a TA-18B Stable Micro Systems probe, and inserted 5 mm into the gel surface.

Example 12 – Preparation of a dilinoleic diol / polyoxypropylenetriamine NIPU elastomer gel paste

The dilinoleic diol / polyoxypropylenetriamine NIPU elastomer of Example 10 was broken into small pieces using a hand tool and 24.65 g of the elastomer solids was added to a stainless steel reaction vessel followed by the addition of 24.65 g of diisooctyl succinate. The slurry was homogenized into a smooth gel paste after 5 minutes of mixing using a Silverson L5M-A homogenizer with a 30 mm diameter rotor, Square Hole High Shear Screen, and operating at 5000 revolutions per minute. The viscosity of the resultant smooth gel was 62,333 cps as measured using a spindle Brookfield Model DV-II+Pro Viscometer with Helipath stand (Brookfield Model D) and Spindle TC. The measurement was taken according to the typical procedure for a Helipath spindle with a constant spindle speed maintained at 6.5 rpm and torque of 37.4%.

Claims

1. A non-isocyanate polyurethane (NIPU) elastomer of Formula I:

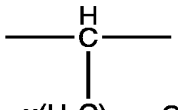


Formula I

wherein:

n is 2 to 100000;

A is an end group selected from a cyclocarbonate and an amine;

B is selected from  and $-(CH_2)_x-C(OH)R^5-$;

x is 0 to 4;

R^1 is a C_1-C_{30} substituted or unsubstituted linear or branched aliphatic group, cycloaliphatic group, aryl group, heterocycloaliphatic group, or heteroaryl group, optionally comprising a heteroatom;

R^2, R^4, and R^5 are independently hydrogen or a C_1-C_{30} substituted or unsubstituted linear or branched alkyl group, aliphatic group, cycloaliphatic group, or aryl group, optionally comprising a heteroatom;

R^3 is a C_1-C_{30} substituted or unsubstituted linear or branched aliphatic group, cycloaliphatic group, aryl group, heterocycloaliphatic group, or heteroaryl group, optionally comprising a heteroatom; and

D is an end group selected from a cyclocarbonate and an amine.

2. A gel composition comprising a non-isocyanate polyurethane (NIPU) elastomer prepared from the reaction of:

A) a polycarbonate or a mixture of polycarbonates comprising two or more carbonate functional groups;

B) a polyamine or mixture of polyamines comprising two or more amine functional groups, where the amine functional groups are either primary or secondary;

C) an optional NIPU reaction catalyst; and

D) an optional topically acceptable carrier fluid, wherein the topically acceptable carrier fluid is a reaction solvent or wherein the topically acceptable carrier fluid is added after elastomer formation, at a concentration of between 50% (w/w) and 99.9% (w/w) of the gel composition.

3. The gel composition of claim 2, wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof.

4. The gel composition of claim 2, wherein the topically acceptable carrier fluid is selected from the group consisting of diisooctyl succinate, heptyl undecylenate, neopentyl glycol diheptanoate, and coco caprylate.

5. The gel composition of claim 2, further comprising a pharmaceutically active ingredient dissolved in the topically acceptable carrier fluid.

6. The gel composition of claim 2, further comprising a pharmaceutically active ingredient incorporated in the gel.

7. The gel composition of claim **2** wherein the polycarbonate or mixture of polycarbonates is a low molecular weight polycarbonate or mixture of polycarbonates containing two or more hydroxyl groups and wherein the polyamine or mixture of polyamines is a low molecular weight polyamine or mixture of polyamines containing two or more primary or secondary amines.

8. A method of making a non-isocyanate polyurethane (NIPU) elastomer comprising:
i) mixing a polycarbonate reactant and a polyamine reactant, wherein the polycarbonate comprises two or more carbonate functional groups and the polyamine comprises two or more primary or secondary amines; and
ii) optionally adding a topically acceptable carrier fluid, wherein the topically acceptable carrier fluid is a reaction solvent or wherein the topically acceptable carrier fluid is added after elastomer formation, to form a polymer gel mixture with a polymer concentration of about 80% (w/w);
iii) optionally adding a NIPU reaction catalyst; and
iv) optionally heating the reaction mixture to about 100°C to form the NIPU elastomer.

9. The method of claim 8, wherein the topically acceptable carrier fluid is selected from the group consisting of esters, triglycerides, hydrocarbons, silicone fluids, and combinations thereof.

10. The method of claim 8, wherein the topically acceptable carrier fluid is selected from the group consisting of diisooctyl succinate, heptyl undecylenate, neopentyl glycol diheptanoate, and coco caprylate.

11. The method of claim 8, further comprising dissolving a pharmaceutically active ingredient in the topically acceptable carrier fluid.

12. The method of claim 8, wherein the polycarbonate reactant comprises two or more hydroxyl groups.

13. The method of claim 8, further comprising preparing the polycarbonate reactant from a vegetable oil or mixture of vegetable oils containing two or more hydroxyl groups.

14. The method of claim 8, further comprising preparing the polycarbonate reactant from a copolymer of dilinoleic acid or mixture of copolymers of dilinoleic acid.

15. A method of making a NIPU elastomer gel paste comprising the steps of:
i) shearing the NIPU elastomer of claim 8;
ii) optionally adding additional quantities of the topically acceptable carrier fluid during shearing to produce a gel paste composition; and
iii) optionally adding a pharmaceutically active ingredient.

16. An NIPU elastomer gel paste prepared by the method of claim 15.

17. A topical formulation comprising:
the gel composition of claim 5 or claim 6, wherein the pharmaceutically active ingredient is a personal care active ingredient or a healthcare active ingredient.

18. A topical formulation comprising:
the NIPU elastomer gel paste of claim 15, comprising a personal care active ingredient or a healthcare active ingredient.

19. A gel composition comprising a non-isocyanate polyurethane (NIPU) elastomer prepared from the reaction of:
    A) a polycarbonate or a mixture of polycarbonates comprising two or more carbonate functional groups;
    B) a polyamine or mixture of polyamines comprising two or more amine functional groups, where the amine functional groups are either primary or secondary;
    C) an optional NIPU reaction catalyst; and
    D) a carrier fluid, wherein the carrier fluid is a reaction solvent or wherein the carrier fluid is added after elastomer formation, at a concentration of between 50% (w/w) and 99.9% (w/w) of the gel composition.

20. A foot conforming shoe insert or shoe sole comprising:
    the non-isocyanate polyurethane (NIPU) elastomer of claim 1 or the gel composition of claim 19.

21. A medical medically acceptable gel comprising:
    the non-isocyanate polyurethane elastomer (NIPU) of claim 1 or the gel composition of claim 19.

22. A topical formulation comprising the NIPU elastomer of claim 1.

23. A gel composition comprising the non-isocyanate polyurethane (NIPU) elastomer of claim 1 and a topically acceptable carrier fluid, at a concentration of between 60% (w/w) and 99.9% (w/w) of the gel composition.

24. A method of making a NIPU elastomer gel paste comprising the steps of:
    i) shearing the gel paste of claim 23;
    ii) optionally adding quantities of the topically acceptable carrier fluid during shearing to produce a gel paste composition; and
    iii) optionally adding a pharmaceutically active ingredient.

25. A NIPU elastomer gel paste prepared by the method of claim 25.

26. A topical formulation comprising the gel composition of claim 23 or the NIPU elastomer gel paste of claim 25.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 21/31916

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C08J 9/12; C08J 9/18; C08J 9/232 (2021.01)

CPC - A43B 13/187; A43B 13/40; B29C 44/3453; B29D 35/122

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KE et al. "Non-isocyanate polyurethane/epoxy hybrid materials with different and controlled architectures prepared from a CO2-sourced monomer and epoxy via an environmentally friendly route", RSC Adv., 2017, 7, pp 28841-28852, especially: pg 28842, col 1, para 1; pg 28843, Scheme 2, pre-polymer product.	1,20-21,22-23
A	BENIAH et al. "Novel Thermoplastic Polyhydroxyurethane Elastomers as Effective Damping Materials over Broad Temperature Ranges", European Polymer Journal. 2016. Volume 84, Pages 770-783, especially: abstract; pg 7, Scheme 1, product.	1,20-21,22-23
A	CN 105001400 A (BEIJING UNIVERSITY OF CHEMICAL TECHNOLOGY) 30 March 2018 (30.03.2018), especially: translated document, abstract; original document, pg 2, formula (II).	1,20-21,22-23
P/A	WO 2021/007489 A1 (NANOMETICS LLC) 14 January 2021 (14.01.2021), entire document.	1,20-21,22-23

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 August 2021 (25.08.2021)	SEP 30 2021
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Kari Rodriquez Telephone No. PCT Helpdesk: 571-272-4300

Form PCT/ISA/210 (second sheet) (July 2019)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 21/31916

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
(see extra sheet)

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1,20-21,22-23

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

--BOX III - LACK OF UNITY--

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1, 20-21(in part) and 22-23, directed to a non-isocyanate polyurethane (NIPU) elastomer of Formula I.

Group II: Claims 2-19, 20-21(in part), and 24-26 directed to a gel composition comprising a non-isocyanate polyurethane (NIPU) elastomer prepared from the reaction of: A) a polycarbonate or a mixture of polycarbonates comprising two or more carbonate functional groups; B) a polyamine or mixture of polyamines comprising two or more amine functional groups, where the amine functional groups are either primary or secondary; C) an optional NIPU reaction catalyst; and D) an optional topically acceptable carrier fluid, wherein the topically acceptable carrier fluid is a reaction solvent or wherein the topically acceptable carrier fluid is added after elastomer formation, at a concentration of between 50% (w/w) and 99.9% (w/w) of the gel composition.

Special Technical Features

The inventions listed as Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group I requires a non-isocyanate polyurethane (NIPU) elastomer of Formula I, which is not required by Group II.

Group II requires a gel composition comprising a non-isocyanate polyurethane (NIPU) elastomer prepared from the reaction of: A) a polycarbonate or a mixture of polycarbonates comprising two or more carbonate functional groups; B) a polyamine or mixture of polyamines comprising two or more amine functional groups, where the amine functional groups are either primary or secondary; C) an optional NIPU reaction catalyst; and D) an optional topically acceptable carrier fluid, wherein the topically acceptable carrier fluid is a reaction solvent or wherein the topically acceptable carrier fluid is added after elastomer formation, at a concentration of between 50% (w/w) and 99.9% (w/w) of the gel composition, which is not required by Group I.

Shared Common Features

The only feature shared by Groups I and II that would otherwise unify the groups is a non-isocyanate polyurethane (NIPU) elastomer. However, this shared technical feature does not represent a contribution over prior art, because the shared technical feature is anticipated by the article entitled "Nôn-isocyanate polyurethane/epoxy hybrid materials with different and controlled architectures prepared from a CO2-sourced monomer and epoxy via an environmentally friendly route" by Ke et al. (hereinafter 'KE').

Ke teaches a non-isocyanate polyurethane (NIPU) elastomer (pg 28842, col 1, para 1, In addition, several groups have reported the preparation of analogous NIPU elastomer which is derived from the
modifed amine).

As the technical features were known in the art at the time of the invention, this cannot be considered a special technical feature that would otherwise unify the groups. Groups I and II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.

Note:
claim 25 is self dependent claim. For the purposes of completing this ISR, claim 25 is assumed to depend from claim 24.

PTO/AIA/14 (01-22)
Approved for use through 05/31/2024. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	GRAN-1012-U-D
	Application Number	
Title of Invention	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2:

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Anna	K.	CROOM	

Residence Information (Select One) ● US Residency ○ Non US Residency ○ Active US Military Service

City	State/Province	Country of Residence
Brooklyn	NY	US

Mailing Address of Inventor:

Address 1	557 Atlantic Avenue
Address 2	
City	Brooklyn
State/Province	NY
Postal Code	11217
Country	US

Inventor 2 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Ronald	V.	LERUM	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

City	State/Province	Country of Residence
Leonia	NJ	US

Mailing Address of Inventor:

Address 1	212 Glenwood Avenue
Address 2	
City	Leonia
State/Province	NJ
Postal Code	07605
Country	US

Inventor 3 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	John		GORMLEY	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

PTO/AIA/14 (01-22)
Approved for use through 05/31/2024. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	GRAN-1012-U-D
	Application Number	
Title of Invention	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE	

City	Midland Park	State/Province	NJ	Country of Residence	US

Mailing Address of Inventor:

Address 1	52 Hillside Avenue		
Address 2			
City	Midland Park	**State/Province**	NJ
Postal Code	07432	**Country**	US

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	20311		
Email Address	info@lmiplaw.com	Add Email	Remove Email

Application Information:

Title of the Invention	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE		
Attorney Docket Number	GRAN-1012-U-D	**Small Entity Status Claimed**	☒
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	1	**Suggested Figure for Publication (if any)**	

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	GRAN-1012-U-D
	Application Number	
Title of Invention	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE	

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	● Customer Number	US Patent Practitioner	◯ Limited Recognition (37 CFR 11.9)
Customer Number	20311		

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, 365(c), or 386(c) or indicate National Stage entry from a PCT application. Providing benefit claim information in the Application Data Sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the "Application Number" field blank.

Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
	Division of	16992831	2020-08-13
Prior Application Status	Expired		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
16992831	Claims benefit of provisional	62893968	2019-08-30
Prior Application Status	Expired		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
16992831	Claims benefit of provisional	62976015	2020-02-13

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button. Add

Foreign Priority Information:

PTO/AIA/14 (01-22)
Approved for use through 05/31/2024. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	GRAN-1012-U-D
	Application Number	
Title of Invention	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE	

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55. When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)[i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(i)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button. Add

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	GRAN-1012-U-D
	Application Number	
Title of Invention	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE	

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant **must opt-out** of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is **ONLY** reviewed and processed with the **INITIAL** filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

1. Authorization to Permit Access by a Foreign Intellectual Property Office(s)

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ A. Applicant **DOES NOT** authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.

☐ B. Applicant **DOES NOT** authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

PTO/AIA/14 (01-22)
Approved for use through 05/31/2024. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	GRAN-1012-U-D
	Application Number	
Title of Invention	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE	

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant 1 Remove

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

● Assignee	Legal Representative under 35 U.S.C. 117	Joint Inventor
Person to whom the inventor is obligated to assign.	Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor:

If the Applicant is an Organization check here. ☒

Organization Name	Grant Industries, Inc.		
Mailing Address Information For Applicant:			
Address 1	103 Main Avenue		
Address 2			
City	Elmwood Park	**State/Province**	NJ
Country	US	Postal Code	07407
Phone Number		Fax Number	
Email Address			

Additional Applicant Data may be generated within this form by selecting the Add button. Add

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

PTO/AIA/14 (01-22)
Approved for use through 05/31/2024. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	GRAN-1012-U-D
	Application Number	
Title of Invention	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE	

Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication. An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

Remove

If the Assignee or Non-Applicant Assignee is an Organization check here. ☒

Organization Name	Grant Industries, Inc.

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1	103 Main Avenue		
Address 2			
City	Elmwood ParK	**State/Province**	NJ
Country i	US	Postal Code	07407
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button. Add

Signature:

Remove

NOTE: This Application Data Sheet must be signed in accordance with 37 CFR 1.33(b). **However, if this Application Data Sheet is submitted with the INITIAL filing of the application and either box A or B is not checked in subsection 2 of the "Authorization or Opt-Out of Authorization to Permit Access" section, then this form must also be signed in accordance with 37 CFR 1.14(c).**

This Application Data Sheet **must** be signed by a patent practitioner if one or more of the applicants is a **juristic entity** (e.g., corporation or association). If the applicant is two or more joint inventors, this form must be signed by a patent practitioner, **all** joint inventors who are the applicant, or one or more joint inventor-applicants who have been given power of attorney (e.g., see USPTO Form PTO/AIA/81) on behalf of **all** joint inventor-applicants.

See 37 CFR 1.4(d) for the manner of making signatures and certifications.

Signature	/Michael N. Mercanti/			Date (YYYY-MM-DD)	2022-12-14
First Name	Michael N.	Last Name	Mercanti	Registration Number	33966

Additional Signature may be generated within this form by selecting the Add button. Add

PTO/AIA/14 (01-22)
Approved for use through 05/31/2024. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	GRAN-1012-U-D
	Application Number	
Title of Invention	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE	

This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1 The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3 A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent CooperationTreaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Espacenet

JP3631542B2 null

Applicants: DAI ICHI KOGYO SEIYAKU CO LTD

Inventors: KATAOKA HIRONORI,MURATA MASARU

Classifications:

IPC ***C08G18/32; C08G18/36; C08G18/81; C08K5/36; C08L75/00; C08L75/04;*** (IPC1-7): C08G18/36; C08L75/04; C08G18/81; C08K5/36;

Priorities: JP31281395A 1995-11-30

Application: JP31281395A·1995-11-30

Publication: JP3631542B2·2005-03-23

Published as: JP3631542B2;**JPH09151317A**

null

Abstract

PROBLEM TO BE SOLVED: To obtain a molding material capable of exhibiting action effects such as antimicrobial and antifungal properties and prevention of decay for a long period by directly including allyl isothiocyanate in a polyurethane resin molding material itself. SOLUTION: (A) Allyl isothiocyanate alone or a hydrophobic medium containing allyl isothiocyanate is subjected to resinification reaction with (B) a polyfunctional isocyanate (e.g. hexamethylene diisocyanate), (C) a polyol (e.g. castor oil) and (D) a catalyst (e.g. tri-n-butyltin acetate). Furthermore, the reaction is carried out at 10-30 deg.C for 0.1-10hr and the components C and D are preferably blended respectively in amounts of 50-200 pts.wt. and 0.05-0.5 pts.wt. based on 100 pts.wt. component B.

(19)日本国特許庁(JP)　(12)特　許　公　報(B2)　(11)特許番号
特許第3631542号
(P3631542)
(45)発行日　平成17年3月23日(2005.3.23)　(24)登録日　平成16年12月24日(2004.12.24)

(51)Int.Cl.[7]	F I
C08L 75/04	C08L 75/04
C08G 18/36	C08G 18/36
C08G 18/81	C08G 18/81
C08K 5/36	C08K 5/36

請求項の数 1　(全 8 頁)

(21)出願番号　特願平7-312813
(22)出願日　平成7年11月30日(1995.11.30)
(65)公開番号　特開平9-151317
(43)公開日　平成9年6月10日(1997.6.10)
審査請求日　平成14年5月15日(2002.5.15)

(73)特許権者　000003506
第一工業製薬株式会社
京都府京都市下京区西七条東久保町５５番地
(74)代理人　100079382
弁理士　西藤　征彦
(72)発明者　片岡　裕紀
奈良県生駒郡三郷町夕陽ケ丘７－７
(72)発明者　村田　勝
滋賀県近江八幡市篠原町１－１０－１０

審査官　松浦　新司

最終頁に続く

(54)【発明の名称】ポリウレタン樹脂成形体の製法

(57)【特許請求の範囲】
【請求項1】
下記の（Ａ）～（Ｄ）成分を樹脂化反応させることによりイソチオシアン酸アリルを含有するフィルム状もしくはシート状のポリウレタン樹脂成形体を製造するポリウレタン樹脂成形体の製法であって、（Ｄ）成分の配合割合が（Ｂ）成分１００重量部に対して０．０１～１重量部となるよう設定されていることを特徴とするポリウレタン樹脂成形体の製法。
（Ａ）イソチオシアン酸アリル単独もしくはイソチオシアン酸アリルを含有する疎水性媒体。
（Ｂ）多官能性イソシアネート。
（Ｃ）ヒマシ油。
（Ｄ）触媒。

【発明の詳細な説明】
【０００１】
【発明の属する技術分野】
本発明は、長期にわたり殺菌性、抗菌性を有するポリウレタン樹脂成形体の製法に関するものである。
【０００２】
【従来の技術】
わさびの主成分であるイソチオシアン酸アリルが、従来から抗菌作用や防黴作用、腐敗防

止作用を有することは経験上知られている。
【０００３】
そして、このイソチオシアン酸アリルの上記作用を利用した様々な製品が提案されている。例えば、上記イソチオシアン酸アリルを合成樹脂フィルム表面上に吸着させ、その表面から微量のイソチオシアン酸アリルの蒸気を放出させてなる殺菌性を有する合成樹脂フィルムが提案されている（特開平３－１５１９７２号公報）。また、フィルム等の高分子成形品中に吸着剤を含有させ、この吸着剤にイソチオシアン酸アリルを吸着させて、上記高分子成形品表面からイソチオシアン酸アリルの蒸気を放散させることにより抗菌性を発揮させることが提案されている（特開平３－２２３５号公報）。
【０００４】
【発明が解決しようとする課題】
しかしながら、このイソチオシアン酸アリルは、その揮散性が顕著であり、短時間で消失するという性質がある。このため、上記提案されているイソチオシアン酸アリルを表面吸着した合成樹脂フィルムは、その吸着当初は殺菌性を有しているが、イソチオシアン酸アリルが徐々に揮散してしまい、長期間にわたってその殺菌性を維持できないという問題を有している。また、上記吸着剤にイソチオシアン酸アリルを吸着させた高分子成形品においても同様の問題がある。
【０００５】
本発明は、このような事情に鑑みなされたもので、殺菌性および抗菌性を長期間にわたって奏することのできるポリウレタン樹脂成形体の製法の提供をその目的とする。
【０００６】
【課題を解決するための手段】
上記の目的を達成するため、本発明は、下記の（Ａ）～（Ｄ）成分を樹脂化反応させることによりイソチオシアン酸アリルを含有するフィルム状もしくはシート状のポリウレタン樹脂成形体を製造するポリウレタン樹脂成形体の製法であって、（Ｄ）成分の配合割合が（Ｂ）成分１００重量部に対して０．０１～１重量部となるよう設定されているポリウレタン樹脂成形体の製法を要旨とする。
（Ａ）イソチオシアン酸アリル単独もしくはイソチオシアン酸アリルを含有する疎水性媒体。
（Ｂ）多官能性イソシアネート。
（Ｃ）ヒマシ油。
（Ｄ）触媒。
【０００７】
本発明において、ポリウレタン樹脂成形体自体に、直接、イソチオシアン酸アリルを含有させるとは、従来のように、吸着剤等の第三物質を介在させることなく、上記ポリウレタン樹脂成形体内部に、直接、イソチオシアン酸アリル自身を含有させることをいう。
【０００８】
すなわち、本発明者らは、樹脂成形体からのイソチオシアン酸アリルの揮散抑制方法を中心に検討し、どのような形態をとることがイソチオシアン酸アリルの揮散抑制に効果的であるか研究を重ねた。その結果、ポリウレタン樹脂成形体自体に、直接、イソチオシアン酸アリルを含有させることによって上記目的を達成することができ、長期にわたるイソチオシアン酸アリルの揮散が可能となることを見出し本発明に到達した。
【０００９】
そして、上記イソチオシアン酸アリルを含有するポリウレタン樹脂成形体は、前記（Ａ）～（Ｄ）成分を用い、かつ（Ｄ）成分の配合を特定量に設定して樹脂化反応させることにより得られることを突き止めた。
【００１０】
【発明の実施の形態】
つぎに、本発明の実施の形態を説明する。
【００１１】

本発明にかかるポリウレタン樹脂成形体は、イソチオシアン酸アリル単独もしくはイソチオシアン酸アリルを含有する疎水性媒体（Ａ成分）と、多官能性イソシアネート（Ｂ成分）と、特定のポリオール（Ｃ成分）と、触媒（Ｄ成分）から構成された反応成分を混合し所定の条件で反応させることにより得られる。上記反応条件としては、１０～３０℃、０．１～１０時間に設定され、これら条件で反応は完了する。

【００１２】

上記Ａ成分において、イソチオシアン酸アリルを単独で用いてもよいが、上記のように疎水性媒体中に含有させてもよい。好ましくはポリウレタン樹脂による包接を完全にするという点から、イソチオシアン酸アリル単独で用いることである。

【００１３】

上記イソチオシアン酸アリルの使用量は、単独であるいは疎水性媒体中に含有させる場合のいずれにおいても、得られるポリウレタン樹脂成形体において、イソチオシアン酸アリルの含有量が０．１～２０重量％（以下「％」と略す）の範囲となるよう設定される。

【００１４】

上記疎水性媒体としては、イソチオシアン酸アリルの揮発性防止剤として用いられるものであって、例えば、安息香酸ベンジル、フタル酸ジオクチル等のエステル類、鉱物油類、綿実油類等の植物油類があげられる。

【００１５】

上記多官能性イソシアネート（Ｂ成分）としては、フェニレンジイソシアネート、トリレンジイソシアネート、ヘキサメチレンジイソシアネート、ジフェニルメタンジイソシアネート、ナフタレンジイソシアネート、キシリレンジイソシアネート、ポリメリックジフェニルメタンジイソシアネート、イソホロンジイソシアネート、トリフェニルメタントリイソシアネート等があげられる。さらに、これら多官能性イソシアネートのイソシアヌレート変性体やビュレット変性体、トリメチロールプロパン、ヘキサントリオールのようなポリオールとの付加物であるジイソシアネートプレポリマー等があげられる。これらは単独でもしくは２種以上併せて用いられる。

【００１６】

上記トリメチロールプロパン、ヘキサントリオール以外のポリオールとしては、例えば、エチレングリコール、プロピレングリコール、ヘキサンジオール等の脂肪族ポリオール、キシリレングリコール等の芳香族ポリオール、ハイドロキノン、カテコール等の多価フェノール、あるいはこれら多価フェノールとアルキレンオキシドとの縮合物、ポリエステルポリオール、ポリエーテルポリオール等のポリオールプレポリマー等があげられる。これらは単独でもしくは２種以上併せて用いられる。そして、これらポリオールのなかでも、強固なポリウレタン樹脂成形体を得るという点からトリメチロールプロパンを用いることが好ましい。

【００１７】

そして、これら多官能性イソシアネート（Ｂ成分）のなかでも、光に反応して黄変し、商品価値を低下させないという点から、ヘキサメチレンジイソシアネート、イソホロンジイソシアネートを用いることが好ましい。

【００１８】

上記多官能性イソシアネート（Ｂ成分）とともに用いられる特定のポリオール（Ｃ成分）としては、反応性という点からヒマシ油が用いられる。

【００１９】

上記特定のポリオール（Ｃ成分）の配合量は、上記多官能性イソシアネート（Ｂ成分）１００重量部（以下「部」と略す）に対して１０～３００部に設定することが好ましく、特に好ましくは５０～２００部である。この特定のポリオール（Ｃ成分）の配合量が１０部未満あるいは３００部を超えると、すなわち、上記配合量の範囲外では、強固なポリウレタン樹脂成形体を得ることが困難となる傾向がみられるからである。

【００２０】

さらに、上記Ａ～Ｃ成分とともに用いられる触媒（Ｄ成分）としては、有機スズ化合物が

用いられ、例えば、トリ－ｎ－ブチルチンアセテート、ｎ－ブチルチントリクロライド、ジメチルチンジクロライド、ジブチルチンジクロライド、トリメチルチンハイドロオキサイド等があげられる。これら触媒はそのまま用いてもよいし、酢酸エチル等の溶媒に、濃度が０．１～２０％となるように溶解して、イソシアネート成分である上記多官能性イソシアネート（Ｂ成分）１００部に対して、固形分として０．０１～１部となるよう添加する必要がある。このように、上記触媒（Ｄ成分）の配合量は、そのまま、あるいは溶剤に溶解した状態のいずれの場合においても、固形分として、多官能性イソシアネート（Ｂ成分）１００部に対して０．０１～１部となるよう添加する必要があり、特に好ましくは０．０５～０．５部である。すなわち、触媒（Ｄ成分）の配合量が０．０１部未満のように少な過ぎると、ポリウレタン樹脂成形体の形成が遅く、樹脂状に硬化せず成形が困難となる。逆に、１部を超えると、樹脂の形成が極端に速くなり、シート状あるいはフィルム状の形状に形成しにくいからである。

【００２１】

本発明にかかるポリウレタン樹脂成形体は、上記Ａ～Ｄ成分を用い混合し反応させて、次第に樹脂化反応が始まり、ポリウレタン樹脂が得られるが、このポリウレタン樹脂が完全に固化する前にフィルム状もしくはシート状の成形体に成形することが行われる。

【００２２】

このようにして得られる本発明にかかるポリウレタン樹脂成形体は、ポリウレタン樹脂成形体内部に、直接、イソチオシアン酸アリルを含有した成形体である。

【００２３】

本発明にかかるポリウレタン樹脂成形体において、その成形体の形状としてはフィルム状、シート状があげられる。

【００２４】

上記フィルム状あるいはシート状に成形する場合、その厚みは特に限定するものではなく、その用途に応じて適宜に設定される。例えば、上記フィルム状あるいはシート状に成形する場合は、二本ロール、ドクターブレード等を用いた公知の方法により成形することができ、具体的には、厚み１～１００μｍのフィルムあるいはシートに成形できる。

【００２５】

このようにして得られる本発明にかかるポリウレタン樹脂成形体の、含有するイソチオシアン酸アリルの有する抗菌性効果、殺菌性効果等の特性を利用してなる用途の一例をあげる。すなわち、ポリウレタン樹脂成形体を、イソチオシアン酸アリル透過可能なポリオレフィン等の密封袋に入れて、これを食品容器内や冷蔵庫内に配置する。また、本発明にかかるポリウレタン樹脂成形体がフィルム状の場合、このポリウレタン樹脂フィルムの両面にイソチオシアン酸アリル透過可能なポリオレフィン樹脂フィルムを積層してなる多層構造のフィルムを作製し、これをみかん箱等の食品保存用箱、食品トレー、コンテナー等に入れる、あるいはその内壁面に張り付けるという用途があげられる。

【００２６】

つぎに、実施例について比較例と併せて説明する。

【００２７】

【実施例１】

イソチオシアン酸アリルを１部、ヘキサメチレンジイソシアネートとトリメチロールプロパンの付加物（日本ポリウレタン社製、コロネートＨＬ）を４９部（多官能性イソシアネート）、ジブチルチンジラウレート（触媒）の１０％酢酸エチル溶液を１部、ヒマシ油を５０部（ポリオール）を２５℃で混合溶解し、樹脂化反応させながらロールコーターにより厚み４０μｍのフィルム状に成形した。そして、２時間経過後に厚み４０μｍのフィルムに固化した。このポリウレタン樹脂フィルムは１ヶ月放置した後においてもわさび臭を発していた。

【００２８】

また、上記混合液をポリエチレンフィルム上に配置し、ロールコーターでフィルム状に成形して二層構造のフィルム（ポリエチレンフィルム＋ポリウレタン樹脂フィルム）を形成

した。ついで、この二層構造のフィルムを略中心部分から、ポリウレタン樹脂フィルム層（厚み５０μｍ）面が対峙するよう素早く半分に折り曲げることにより、内層にポリウレタン樹脂フィルム層が位置し、そのポリウレタン樹脂フィルム層の外周面にポリエチレンフィルム層が位置した、いわば、ポリウレタン樹脂フィルムをポリエチレンフィルムで密封した積層体を作製した。その後、この積層体のポリウレタン樹脂フィルム層部分（厚み５０μｍ×２）の反応が進行して、１時間後に完全固化して、厚み１００μｍの積層体を得た。上記積層体は、製造後、１ヶ月経過した後もわさび臭を発していた。

【００２９】

また、得られた上記ポリウレタン樹脂フィルム（積層体のポリウレタン樹脂フィルム層も同じ）のイソチオシアン酸アリルの含有量は１％であった。

【００３０】

【実施例２～４、比較例１，２】

イソチオシアン酸アリル、多官能性イソシアネート、触媒およびポリオールとして、下記の表１に示す材料を同表に示す割合で用い、実施例１と同様にして目的とする厚み４０μｍのポリウレタン樹脂フィルムを製造した。また、実施例１と同様にして厚み１００μｍの積層体（ポリウレタン樹脂フィルムをポリエチレンフィルムで密封した）を製造した。なお、上記ポリウレタン樹脂フィルムのみの単層フィルム（ポリウレタン樹脂フィルムａ）、および、上記積層体のポリウレタン樹脂フィルム層部分（ポリウレタン樹脂フィルムｂ）の製造時の固化時間を下記の表１に示す。

【００３１】

そして、上記ポリウレタン樹脂フィルムのみの単層フィルム（ポリウレタン樹脂フィルムａ）、および積層体の双方とも、製造後、１ヶ月を経過してもわさび臭を発していた。

【００３２】

【表１】

	実施例２	比較例１	実施例３	比較例２	実施例４
ｲｿﾁｵｼｱﾝ酸ｱﾘﾙ配合量（部）	１部	３部	３部	５部	１０部
イソシアネート成分	HMDＩ(*1)系イソシアヌレート型ポリイソシアネート（旭化成社製、デュラネートＴＰＡ）	ＴＤＩ(*2)とＴＭＰ(*3)の付加物（日本ポリウレタン社製、コロネートＬ）	HMDＩ系ビュレット型ポリイソシアネート（住友バイエル社製、スミジュールＮ－３２００）	ＸＤＩ(*4)とＴＭＰの付加物（武田薬品工業社製、タケネートＤ－１１０Ｎ）	ＩＰＤＩ(*6)とＴＭＰの付加物（武田薬品工業社製、タケネートＤ－１４０Ｎ）
配合量（部）	５０部	４５部	４０部	５５部	５２部
触媒	トリメチルチンハイドロオキサイド	トリーｎ－ブチルチンアセテート	トリメチルチンハイドロオキサイド	ジメチルチンジクロライド	ｎ－ブチルチントリクロライド
配合量（部）	０．２部	０．１部	０．４部	０．１部	０．２部
ポリオール配合量（部）	ヒマシ油 ４８．８部	ポリテトラメチレンエーテルグリコール*7　51.9 部	ヒマシ油 ５６．６部	ブチレンアジペート*5 ３９．９部	ヒマシ油 ３７．８部
ﾎﾟﾘｳﾚﾀﾝ樹脂ﾌｨﾙﾑａの固化時間	１時間	２時間	０．５時間	２時間間	１時間
ﾎﾟﾘｳﾚﾀﾝ樹脂ﾌｨﾙﾑｂの固化時間	１時間	２時間	０．５時間	２時間間	１時間

＊１：ヘキサメチレンジイソシアネート
＊２：トリレンジイソシアネート
＊３：トリメチロールプロパン
＊４：キシリレンジイソシアネート
＊５：重量平均分子量１０００
＊６：イソホロンジイソシアネート
＊７：重量平均分子量６５０

【００３３】
また、実施例２～４および比較例１，２で得られたポリウレタン樹脂フィルム（積層体のポリウレタン樹脂フィルム層も同じ）のイソチオシアン酸アリルの含有量を下記の表２に示す。
【００３４】
【表２】

	実施例			比較例	
	2	3	4	1	2
イソチオシアン酸アリルの含有量（%）	1	3	１０	3	5

【００３５】
【比較例３】
市販の、大きさ１００×１００ｍｍで厚み５０μｍのポリプロピレンフィルム面に、イソチオシアン酸アリル１．０ｇを塗布した。このフィルムに関して３日後にはわさび臭は完全に消失していた。
【００３６】
【比較例４】
吸着剤（セピオライト微粉末）を４０部と、ポリエチレン６０部を溶解混合した後、フィルム状に成形して吸着剤を含有する厚み５０μｍのポリエチレンフィルムを製造した。つぎに、このポリエチレンフィルムを、液状イソチオシアン酸アリルを入れたシャーレとともに、密閉性容器にいれて密封し、温度４０℃の恒温槽に入れ、２４時間放置した。放置した後、上記密閉容器を開放し、なかからイソチオシアン酸アリルを吸着したポリエチレンフィルムを取り出した。このポリエチレンフィルムは、取り出してから１０日経過した後にはわさび臭が完全に消失していた。
【００３７】
【発明の効果】
以上のように、本発明は、前記Ａ～Ｄ成分を用い、かつＤ成分の配合を特定量に設定して樹脂化反応させることによりイソチオシアン酸アリルを含有するフィルム状もしくはシート状のポリウレタン樹脂成形体を製造する。そして、得られたイソチオシアン酸アリルを含有するフィルム状もしくはシート状のポリウレタン樹脂成形体は、例えば、従来の、単にイソチオシアン酸アリルがフィルム表面に吸着されたものや、吸着剤を利用してこれにイソチオシアン酸アリルを吸着させ、この吸着剤を含有した成形品に比べて、イソチオシアン酸アリルの揮散が長期にわたってなされる。その結果、イソチオシアン酸アリルに起因する殺菌性、抗菌性等の効果が長期間にわたり発現することとなる。したがって、本発明にかかるポリウレタン樹脂成形体は、抗菌、防黴および腐敗防止等の作用効果を長期間発揮する、フィルム状あるいはシート状の成形体として各種用途に有用である。

(56)参考文献　特開平０４－２６５２５９（ＪＰ，Ａ）
特開平０４－２８０８４７（ＪＰ，Ａ）
実開平０３－１２６４８９（ＪＰ，Ｕ）
特開昭６０－０５８４３９（ＪＰ，Ａ）

(58)調査した分野(Int.Cl.^{7}，ＤＢ名)
C08L75/04～75/16

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 May 2013 (23.05.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/074655 A1

(51) International Patent Classification:
A61Q 5/12 (2006.01)

(21) International Application Number:
PCT/US2012/065052

(22) International Filing Date:
14 November 2012 (14.11.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/559,266 14 November 2011 (14.11.2011) US

(71) Applicant: **INOLEX INVESTMENT CORPORATION** [US/US]; 103 Springer Building, 3411 Silverside Road, Wilmington, DE 19810 (US).

(72) Inventors: **BURGO, Rocco**; 604 Widgeon Court, Mullica Hill, NJ 08062 (US). **WINN, Daniel**; 14 Euclid Avenue, Kingston, NJ 08528 (US). **BURCH, Kimbery**.

(74) Agents: **BULLOCK, Kristyne, A.** et al.; Flaster/Greenberg PC, Four Penn Center, Suite 200, 1600 John F. Kennedy Boulevard, Philadelphia, PA 19103 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

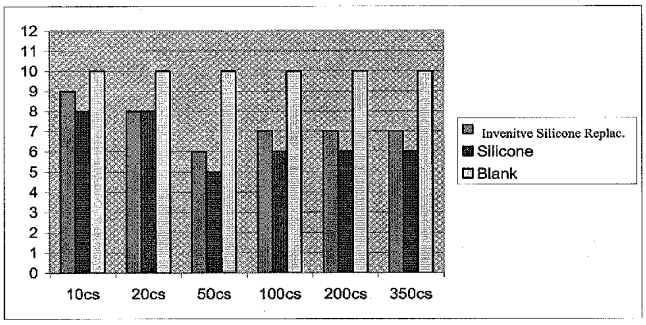
Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) **Title**: NATURAL SILICONE REPLACEMENTS FOR SILICONE FLUIDS IN PERSONAL CARE FORMULATIONS

FIGURE 9



(57) **Abstract**: Described herein is a silicone replacement for use in a personal care formulation comprising a mixture of at least one polymeric ester and at least one non-polymeric ester. The polymeric ester is an esterification reaction product of (i) at least one first dicarboxylic acid, (ii) at least one first monoiunctional alcohol or monoiunctional carboxylic acid and (iii) glycerin or derivatives thereof. The non-polymeric ester is an esterification reaction product of (i) at least one second dicarboxylic acid and (ii) at least one second monoiunctional alcohol, wherein the replacement is substantially free of silicone. As described is a personal care formulation that is substantially free of silicone, wherein the formulation comprises a silicone replacement consisting substantially of a mixture of at least one polymeric ester as described above, and a non-polymeric ester as described above. Related methods are alse described.

WO 2013/074655 A1

TITLE OF THE INVENTION

[0001] Natural Silicone Replacements for Silicone Fluids In Personal Care Formulations

CROSS-REFERENCE TO RELATED APPLICATIONS

[0002] This application claims the benefit under 35 U.S.C. §119(e) to U.S. Provisional Patent Application No. 61/559,266, filed November 14, 2011, the entire disclosure of which is incorporated herein by reference

BACKGROUND OF THE INVENTION

[0003] Silicone fluids are widely used in toiletry, cosmetic, and personal care formulations. Most frequently used are the dimethicones, the cyclomethicones, and phenyl trimethicone (hereinafter all silicone materials collectively refereed to as "silicones"). Incorporated into a skin care formulation, silicone fluids provide a variety of benefits such as improved slip, reduction of tack, impartation of emolliency, and other modifications of the "feel" characteristics of the formulation, as well as other benefits. Incorporated into hair care formulations such as conditioners, they can reduce wet combing force and increase shine of hair

[0004] Silicone fluids have been considered to be particularly useful as they tend to provide the aforementioned benefits without contributing to oiliness or greasiness and give what many consider to be a "dry" skin feel. This attribute is highly desired in toiletry, cosmetic, and other personal care formulations such as creams, lotions, antiperspirants, shaving formulations, and make-up formulations. Additional benefits are that silicones are excellent dispersing and spreading agents, are generally water white in color, low in odor, and are resistant to chemical and oxidative attack. These attributes make them particularly suitable for personal care applications. However, the use of silicones in personal care formulation comes with drawbacks.

DESCRIPTION OF RELATED ART

[0005] For example, there has been concern about the safety of the use of silicone fluids on the skin. In light of potential links between silicone and silicone degradation products to the development of autoimmune system deficiencies in women with silicone breast implants and/or individuals with other disorders, these materials have recently come under higher scrutiny by the Food and Drug Administration (FDA). Although definitive links have not been confirmed, many cosmetic formulators have acted to attempt to reduce and or

eliminate silicone ingredients from formulations. The downside of not using silicones is of course that the skin feel and formulation benefits are lost.

[0006] In addition, silicones have also been implicated as potentially being harmful to the environment. For example, Environment Canada has published a documents indicating that dimethiciones are suspected to be environmental toxins and biocumulative.

[0007] Accordingly, there exists a need in the art to identify alternative non-silicone fluids that provide silicone-like benefits in formulation but do not bring with the real or perceived health and environmental risks.

[0008] The industry has made efforts to respond to this need. For example, U.S. Patent Application Publication 2005/0260150 describes low viscosity esters that may be used as replacements for low viscosity silicone fluids. United States Patent Application Publication 2004/0241200 describes blends of certain synthetic esters with volatile hydrocarbons that are useful for the replacement of volatile tetramer and pentamer cyclomethicones. United States Patent Application Publication 2009/0123398 describes blends of hydrocarbon fluids useful for the replacement of volatile tetramer and pentamer cyclomethicones. United States Patent Application Publication 2011/0064685 describes personal care compositions comprising an aqueous dispersion comprising a metallocene catalyzed polyolefin and an ethylene acrylic acid copolymer; a cationic polymer; and a least one cosmetically acceptable surfactant, emollient, or cosmetic active, provided that the personal care composition contains less than 0.09 wt % of 15 silicone, and preferably is substantially free of silicone.

[0009] As the population becomes more aware of the potential adverse effects to the body and to the environment associated with the use ingredients derived from fossil fuels, the personal care industry has rapidly advanced their search for "natural" ingredients for use in virtually all cosmetic formulation types and forms. Media has driven this growth by popularizing the idea that there may be potential adverse effects to the body and to the environment associated with the use ingredients derived from fossil fuels. The personal care industry has rapidly advanced its attempts to identify "natural" ingredients for use in virtually all cosmetic product types and forms. Notably, although used in marketing materials, the term "natural" has not yet been clearly defined within this context; efforts are under way by industry trade organizations to give the term a more concise and consistent meaning.

[0010] It may be some time before an industry accepted universal definition of natural is provided; however, it is generally recognized that materials derived from renewable and/or sustainable, or otherwise non-fossil fuel sources are considered to be natural.

Petrochemicals are derived from fossil fuels and are not considered to be natural. Any derivatives of petrochemicals are not considered to be natural. As such, silicones are not classified as natural, as they are petrochemically derived. Accordingly, there is a need in the art for natural silicone replacements that can be used in lieu of silicones in personal care formulations and which provide to the consumer the advantageous end properties of silicones.

BRIEF SUMMARY OF THE INVENTION

[0011] Described herein is a silicone replacement for use in a personal care formulation comprising a mixture of at least one polymeric ester and at least one non-polymeric ester. The polymeric ester is an esterification reaction product of (i) at least one first dicarboxylic acid, (ii) at least one first monofunctional alcohol or monofunctional carboxylic acid and (iii) glycerin or derivatives thereof. The non-polymeric ester is an esterification reaction product of (i) at least one second dicarboxylic acid and (ii) at least one second monofunctional alcohol, wherein the replacement is substantially free of silicone.

[0012] Also described is a personal care formulation that is substantially free of silicone, wherein the formulation comprises a silicone replacement consisting substantially of a mixture of at least one polymeric ester as described above, and a non-polymeric ester as described above. Related methods are also described.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0013] The foregoing summary may be better understood when read in conjunction with the appended drawings. For the purpose of illustrating aspects of the invention, there is shown in the drawings data and embodiments of the invention. It should be understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown. In the drawings:

[0014] Fig. 1 shows the infrared spectrum of an exemplary non-polymeric ester of the invention, deheptyl succinate;

[0015] Fig. 2 shows that infrared spectrum of an exemplary polymeric ester of the invention, GSC Type 4;

[0016] Fig. 3 shows spread rate of the silicone replacement as compared to that of the conventional silicone material in graphic form;

[0017] Fig. 4 is a table showing the reactant amounts of various sample and comparative sample formulations provided to human test subjects in a panel evaluation of comparative skin feel properties;

[0018] Fig. 5 is a copy of the survey used by the panel in evaluating the sample and comparative sample formulations;

[0019] Fig. 6 (containing Figs. 6A to 6E) shows the results the results of the panel evaluation in graphic form;

[0020] Fig. 7 is a photographic record of the data demonstrating the comparative stickiness (tack) of the silicone replacement and the silicone containing conventional formulation;

[0021] Fig. 8 shows the results of a pigment grind evaluation; and

[0022] Fig. 9 shows the results of a shine (gloss) evaluation of hair to which the silicone replacements were applied.

DETAILED DESCRIPTION OF THE INVENTION

[0023] The invention described herein encompasses silicone replacements for use in personal care formulations (such as, without limitation, shampoos, cleansers, conditioners, cosmetics and lotions) that are substantially free of silicone(s) but have substantially equivalent tactile and/or end use characteristics. Specifically, the applicants have made the surprising discovery that by mixing certain types of natural (i.e., non-petrochemically-derived) ester fluids, certain desirable characteristics ordinarily imparted to personal care formulations by silicone fluids can be realized, including, for example, spreading rate, skin feel, tack reduction, pigment dispersancy, and hair shine. Using the silicone replacements of the invention, one can formulate personal care formulations, including skin and hair products, that contain natural ingredients, are substantially free of silicone, and are perceived by the human end users as having the same or similar aesthetic, tactile and/or skinfeel properties of conventional silicone containing formulations.

[0024] By "substantially free of silicone," it is meant that the personal care formulations are formulated without the inclusion of any initial compounds containing silicone groups. For example, the formulations of the invention contain less than 0.09 wt % of 15 silicone, and preferably 08.% by weight or less.

[0025] The invention includes a natural silicone replacement for use in personal care formulations that is a mixture of at least one polymeric ester and at least one non-polymeric ester. The term "natural," as used herein describing any acids, alcohols and/or esters, means that all atoms contained in the structure(s) of the acid, ester or alcohol that are used to prepare the esters are obtained from renewable and/or sustainable sources. By "renewable and sustainable," it is meant that the carbon is not obtained from petrochemical sources.

Exemplary carbon sources that are not petrochemical may include, but are not limited to, plant, agricultural or forestry waste biomass.

[0026] Particularly useful in the invention are mixtures or blends of non-polymeric and polymeric esters derived from the esterification of natural acids and alcohols. The term "esterification" is used herein to describe a condensation reaction between a carboxylic acid group and/or a carboxylic acid ester group with an hydroxyl group. An "esterification reaction product" is a resultant product of this event. The silicone replacements included in the invention are a blend of polymeric and non-polymeric esters formed from esterification reactions.

[0027] Each of the esters present in the silicone replacement fluid is derived from the esterification of at least one dicarboxylic acid. In the practice of the invention, the polymeric ester is an esterification reaction product of at least one first dicarboxylic acid, at least one first monofunctional alcohol or monofunctional carboxylic acid and glycerin and/or a derivative thereof. The polymeric esters in a given silicone replacement may be made from the same first dicarboxylic acid, first monofunctional alcohol or monofunctional carboxylic acid, and glycerin or glycerin derivative or it may be prepared from a mixture of first dicarboxylic acids, first monofunctional alcohols and/or monofunctional carboxylic acids, and glycerin or glycerin derivatives or any permutation of these materials, such that the "polymeric ester" included in the blend/silicone replacement is itself a blend or mixture of various polymeric esters.

[0028] The non-polymeric ester of the silicone replacement is a reaction product of at least one second dicarboxylic acid and at least one second monofunctional alcohol. As with the polymeric esters, the non-polymeric ester in a given silicone replacement may be made from the same second dicarboxylic acid and a second monofunctional alcohol or it may be prepared from a mixture of second dicarboxylic acids and second monofunctional alcohols or any permutation of these materials, such that the "non-polymeric ester" included in the blend/silicone replacement is itself a blend or mixture of various non-polymeric esters.

[0029] In the case of each of the polymeric ester and the non-polymeric ester, suitable dicarboxylic acids and/or monofunctional alcohols may independently contain carbon chains of medium or short lengths (although the polymeric and non-polymeric esters need not be prepared from initial materials having the same number of carbon atoms). By "short" chain length, it is meant that the compound contains about one to about six carbon atoms. By "medium" chain length, it is meant that the compound contains about seven to about twelve carbon atoms.

[0030] In some embodiments, the dicarboxylic acids and/or monofunctional alcohols may independently contain chains of about 1, about 2, about 3, about 4, about 5, about 6, about 7, about 8, about 9, about 10, about 11, about 12, about 13, about 14, or about 15 carbon atoms. In other embodiments, the dicarboxylic acids and/or monofunctional alcohols may independently contain chains of about 10 to about 25 carbon atoms and/or about 1 to about 10 carbon atoms. In any of the embodiments of the invention, one or more of the dicarboxylic acids and/or monofunctional alcohols may independently have carbon chains that are independently linear and/or branched and/or carbon atoms that are independently saturated and/or unsaturated and/or functionalized or unfunctionalized. In some embodiments, at least one of the carbon atoms of the chain is saturated and the others are unsaturated.

[0031] Particularly useful acids and/or alcohols may be those that contain linear, saturated chains containing about three to about ten carbon atoms.

[0032] Any dicarboxylic acids known or developed in the art may be independently selected for use in the esterification reactions, including, without limitation, 1,4-butanedioic acid (succinic acid,) 1,5-pentanedioic acid (glutaric acid,) 1,6-hexanedioic acid (adipic acid), 9-nonanedioic acid (azelaic acid) and 1,10-decanedioic acid. In some circumstances, sebacic acid may be preferred.

[0033] Any monofunctional dicarboxylic acids known or developed in the art may be independently selected for use in the esterification reaction, including, without limitation hexanoic acid (caproic acid,) heptanoic acid, octanoic acid (caprylic acid) nonanoic acid, decanoic acid (capric acid,) and dodecanoic acid (lauric acid.) It some circumstances, caprylic acid and capric acid may be preferred.

[0034] Glycerin or glycerin derivatives are used in the preparation of the polymeric ester. Glycerin derivatives include, but are not limited to, those derived from the condensation of glycerol with itself to from higher glycerol ether derivatives, known as polyglycols.

[0035] Any monofunctional alcohols known or developed in the art may be used, including, without limitation 1-hexanol, 1-heptanol, 1-octanol, 2-octanol, and 1-decanol. Under some conditions, 1-heptanol may be preferred.

[0036] In each case, it may be preferred that the acid(s), alcohol(s) and/or polyols (glycerin or is derivatives) are natural as defined above.

[0037] In the formation of the esters that make up the silicone replacements included in the invention from natural reactants, one or more dicarboxylic acids are esterified with one

or more monofunctional alcohols and/or one or more monofunctional carboxylic acid. The esters may be formed by any esterification technique known in the art. For example, in a first reaction, a non-polymeric ester derived from the esterification of one or more monofunctional alcohols with one or more dicarboxylic acids is prepared. In a second reaction, a polymeric ester derived from one or more dicarboxylic acids, one or more monofunctional carboxylic acids, and glycerol and/or polyglycerol is prepared.

[0038] To prepare the silicone replacement, non-polymeric and polymeric esters are then blended in an identified ratio such that the replacement imparts to a personal care formulation performance characteristics that correspond the silicone fluid that the mixture is intended to replace, such as a cyclomethicone and/or dimethicone fluids. "Performance characteristics" means the desirable end properties experienced by the consumer and/or the product formulator that silicone fluids impart to personal care formulations, such as spread rate, skin feel and other tactile properties (slip or drag, feeling of oiliness, residual afterfeel, absorption rate into skin, gloss/shine of hair, light- versus heavy-feeling), tackiness (stickiness), and the ability to disperse pigments.

[0039] The polymeric and non-polymeric esters may be present in the silicone replacement in any ratio desired, so long as the performance characteristics are achieved or retained. Evaluation of a given blend to ensure it demonstrates adequate and desired performance characteristics as a silicone replacement (as dictated by the end personal care formulation) is a matter of routine testing, well within the skill of an ordinary formulator. In some cases the ratio by weight of polymeric ester to non-polymeric ester may be about 1 to about 1 to about 1: to about 50 (that is, ~1:~1 to ~1:~50).

[0040] In some circumstances, as a matter of formulation convenience, it may be desirable to use an identified ratio of polymeric polymer to non-polymeric polymer in the silicone replacement that is adjusted so that the silicone replacement has a specific viscosity. (That way, a personal care product formulator seeking to substitute a silicone replacement into his/her formulation in place of a silicone of a specific viscosity will not have to modify his/her formulation in other ways, increasing the convenience of the silicone replacement.) In such circumstances, the indentified ratio may determined by measuring the viscosity of the end product (the silicone replacement), and adjusting the ratio as necessary to arrive at the target viscosity. For example, one may desire a silicone replacement that has a viscosity of about 1 to about 1000 cSt, about 10 to about 500 cSt, about 20 to about 350 cSt, about 50 to about 200 cSt and/or about 70 to about 100 cSt. In some circumstances, for ease of handling by personal care formulators, it may be desirable to prepare silicone replacements

having an identified ratio of polymeric to non-polymeric esters that results in viscosities of about 10, about 20, about 50, about 100, about 200, and/or about 350 (all cSt).

[0041] The invention also includes personal care formulations that are natural and are substantially free of silicone. The personal care formulations include the silicone replacement of the invention and at least one more ingredient (that is not a silicone). Any ingredient that can be applied to hair, skin or nails may be included, including pharmacological agents. Exemplary ingredients may include, without limitation, a surfactant, a flavorant, a fragrance, an opacifier, a colorant, a wax, an emulsifier, a fat, an oil, a preservative, a UV absorbing compound, a detergent, foaming agents, stabilizers, pH modifiers, foaming agents, moisturizers, water, an alcohol, a urea, a cosmetic active, a pigment, a wetting agent, a skin or hair conditioner and a solvent. Others may include acetone, water, alcohol, parabens, mineral oil, vegetable oil, olive oil, paraffin, PEG, polyethylene, polyethylene glycol, polyoxyethylene, oxynol, petrolatum, sodium lauryl sulfate, sodium laureth sulfate, sodium myreth sulfate, sodium oleth sulfate, sodium ceteareth sulfate, DMDM hydantoin, sodium hydroxymethylglycinate, triethanolamine, cocamide diethanolamine, laurimide diethanolamine, linoleamide diethanolamine, oleamide diethanolamine, oxybenzone, essential oils, an emollient, octylmethoxycinnamate, titanium dioxide, and zinc oxide.

[0042] The personal care formulation may be prepared by any means known in the art and the methods will necessary vary depending on the specific type of personal care formulation being prepared (e.g., underarm antiperspirant formulation versus a skin cleanser formulation). The personal care formation itself make take the form of a solid, semi-solid, liquid, gel, aerosolized or aerosolizable material, film, paste, cream, lotions, emulsion, suspension, and/or powder.

[0043] The silicone replacement may be present in the personal care formulation in any amount; the amount will vary depending on a variety of factors, including specific type of personal care formulation being prepared. In may circumstances it may be preferred that the silicone replacement is present in the personal care formulation in an amount of about 1% to about 95% by weight, about 5% to about 80% by weight, about 10% to about 70% by weight, about 15% to about 60% by weight, about 20% to about 50% by weight, or about 30% to about 40% by weight of the total composition. It may be preferred that the silicone replacement is present in the amount of about 1%, about 2%, about 3%, about 4%, about 5%, about 6%, about 7%, about 8%, about 9% by weight of the total composition.

[0044] Both the silicone replacements and personal care formulations included in the invention as described herein exhibit similar or the same end properties as compared to their convention silicone containing counterparts. In particular, the difference between a spread value of either a silicone blend of the invention or of a personal care formulation of the invention ("invention spread value") and a spread value of a corresponding conventional silicone or conventional silicone containing personal care formulation ("conventional spread value") is less than about 10%, less than about 5%, less than about 1% of the total conventional spread value. Additionally, the skinfeel properties, the tackiness (stickiness) and the pigment dispersion capabilities of the silicone replacements and that of the convention silicone containing counterpart are similar or statistically identical.

[0045] Example 1: Preparation of an Exemplary Non-Polymeric Ester of the Invention

[0046] The reaction product of 1-heptanol and succinic acid ("diheptyl succinate") was prepared. To a five liter four neck flask equipped with a stirrer, heating mantle, nitrogen gas sparge, vapor column, and total condenser, 2813 grams (24.25 gram moles) of n-heptanol were added. 938 grams (7.94 gram moles) of succinic acid were added. To this, 7.5 grams of ethanesulfonic acid (70% aqueous solution) was added as a catalyst.

[0047] The mixture was heated to about 150°C, and vacuum was slowly staged in. At the completion of this step, the acid value of the material was measured to be 0.90 mg KOG/g. The mixture was then cooled to about 90°C and a solution of sodium carbonate was added to neutralize the residual acidity.

[0048] The ester was then batch distilled followed by steam stripping. The stripped ester was treated with activated charcoal, and filtered yielding an essentially odorless and colorless fluid.

[0049] Analytical properties of the ester are shown below in Table 1.

Table 1

Property	Units	Result
Color	APHA	23
Acid Value	mg KOH/g	0.035
Hydroxyl Value	mg KOH/g	0.25
Odor	Organoleptic	Mild
Viscosity at 25° C	cSt	8.6
Viscosity at 40° C	cSt	5.8
Sp. Gr. 25/25	---	0.9338
Flash Point	°C	186
Moisture	% wt/wt	0.01

[0050] Figure 1 shows the infrared spectrum of the non-polymeric ester prepared as described above.

[0051] Example 2: Preparation of Exemplary Polymeric Esters of the Invention

[0052] Variants of the reaction product of decanedioic acid ("sebacic acid," derived from 5 castor oil) 1,2,3-propanetriol ("glycerol," derived from coconut oil) and octanoic acid ("caprylic acid," derived from coconut oil) were prepared. Reactant amounts for each variant are given in Table 2.1, below.

[0053] The esterification/polyesterifications were carried out in a four neck flask equipped with a stirrer, heating mantle, nitrogen gas sparge, vapor column, and total condenser. In each case, the reactants were charged to the vessel and heated to about 215°C.

[0054] Pressure was then reduced to drive off the water of reaction and the acid value was monitored to follow the course of the reaction. When the reaction was sufficiently complete (acid value of 5 or lower mg KOH/g,) the reactor contents were cooled to about 180°C and were steam stripped under hard vacuum 15 for about four hours. Steam stripping was stopped, and the reaction product was cooled and discharged into containers. Table 2.2 shows the properties obtained.

[0055] Figure 2 shows the infrared spectrum of the exemplary polymeric ester GSC Type 4.

Table 2.1

Product	Octanoic Acid (grams)	Glycerol (grams)	Sebacic Acid (grams)
GSC Type 1	1440	960	1600
GSC Type 2	1462	769	1269
GSC Type 3	1416	786	1298
GSC Type 4	1392	774	1334
GSC Type 5	1558	733	1209
GSC Type 6	1492	737	1271

Table 2.2

Product	Octanoic Acid (grams)	Glycerol (grams)	Sebacic Acid (grams)
GSC Type 1	1440	960	1600
GSC Type 2	1462	769	1269
GSC Type 3	1416	786	1298
GSC Type 4	1392	774	1334
GSC Type 5	1558	733	1209
GSC Type 6	1492	737	1271

[0056] Example 3: Preparation of Exemplary Silicone Replacement of the Invention

[0057] The esters of Examples 1 and 2 were blended to make a total of about 1000 grams of test blend by mixing in a glass beaker of suitable size with mechanical stirrer until a clear, homogeneous solution was obtained. Six test blends were prepared (N10, N20, N50, N100, N200, N350) to have the approximate viscosities of 10 cSt, 20 cSt, 50 cSt, 100 cSt, 200 cSt, and 350cSt, respectively, as measured at 25°C.

Table 3.1 shows the properties obtained for exemplary silicone replacement of the invention.

Table 3.1

Blend ID	GSC Type 4 (wt.%)	DHS (wt.%)	Viscosity at 25° C (cSt)	Flash Point (°C)	Refractive Index	Sp.G.r. 25/25
N10	2.0	98.0	10.0	195	1.4395	0.9356
N20	11.3	88.7	19.7	198	1.4417	0.9443
N50	27.5	72.5	53.8	206	1.4456	0.584
N100	32.5	67.5	109	200	1.4480	0.9691
N200	44.0	56.0	206	208	1.4507	0.9798
N350	52.5	47.5	351	204	1.4529	0.9892

[0058] Example 4: Evaluation of Spread Rate of Silicone Replacement

[0059] An evaluation of the spread rates of the silicones replacements included in the invention as compared to the spread rate of various dimethicones commonly used in personal care formulations was carried out. As is understood in the art, the rate of spreading or spreading value is indicative of the ability of the formulation to flow over the skin upon application, and is regarded as a significant measurement in determining the attributes of a final personal care formulation.

[0060] Six samples of the silicone replacement of the invention (S1-S6) prepared in example 3 and six comparative samples of dimethicone fluid (CS1-CS6) were evaluated, each of varying viscosity, as shown in the table below:

Samples Blend ID Comparative Samples

S1 N10 CS1 Dimethicone 10cst

S2 N20 CS2 Dimethicone 20cst

S3 N50 CS 3 Dimethicone 50cst

S4 N100 CS4 Dimethicone 100cst

S5 N200 CS5 Dimethicone 200cst

S6 N350 CS6 Dimethicone 350cst

[0061] Samples S1-S6 (Blend IDS N10, N20, N50, N100, N200, N350) were prepared using the method set forth in Example 3. Each sample S1-S6 and CS1-CS6 was handled as follows: A piece of filter paper was placed over a Petri dish. Using a pipeter, 50L of the sample was applied to the approximate center of the filter paper. After the lapse of each of 1 minute, 3 minutes and 5 minutes, the circumference of the sample was traced onto the paper. The diameter of each of the circles created was measured. Two measurements were taken for each sample at each time interval. The measurements are shown below. As plotted, the measurements are shown in Figure 3, by viscosity.

Figure 3

Samples	Blend ID		Comparative Samples
S1	N10	CS1	Dimethicone 10cst
S2	N20	CS2	Dimethicone 20cst
S3	N50	CS3	Dimethicone 50cst
S4	N100	CS4	Dimethicone 100cst
S5	N200	CS5	Dimethicone 200cst
S6	N350	CS6	Dimethicone 350cst

[0062] Example 5: Comparison of Skin Feel Properties Between Mixtures of the Invention and Silicone Fluids

[0063] Samples were prepared as follows, using the reactant amounts as shown in the table of Figure 4. Water in the amount shown for phase A was heated to 78 - 80C. Using a propeller, the remainder of phase A ingredients were combined together into a slurry, then mixed into the heated water. The combined phase "B" ingredients were heated to 80C and added to the phase "A" with continued mixing. The entire mixture was allowed to cool to 60C. Phase "C" was added to each batch and the entire mixture was cooled to room temperature.

[0064] Four ounces of each formulation was packaged in a glass jar. Study participants were directed to apply 0.10 – 0.20g of lotion to hid or her inner forearm (one formulation to 15 each arm). Participants were then asked to complete a survey. The survey is attached hereto as Figure 5. Data generated from the surveys are plotted in Figure 6 (6A to 6D).

[0065] The results of this study indicate that the silicone replacements perform similar to the dimethicone counterparts.

[0066] Six sample blends (S1-S6) were created by combining 20% by weight of Lexorex 200 (a proprietary blend of trimethylpentanediol/adipic acid/glycerine

crosspolymer; available from Inolex Chemical Company, Philadelphia, PA USA) and 80% by weight of each of the samples S1-S6, as shown below:

Sample No.	Sample Blend ID
S1	N10
S2	N20
S3	N50
S4	N100
S5	N200
S6	N350

[0067] Lexorex 200 is a viscous polyester having a viscosity of approximately 25,000 cP at 25°C. Samples S1-S6 were prepared as set art in Example 7. Using a disposable transfer pipet, 0.20g of Lexorez 200 was applied to the left side of a Petri dish and 0.20g of each of S1-S6 was applied to the right side of the dish. Each sample was manually spread to cover a circle having a diameter of 2 centimeters. A standard cotton ball (purchased from a beauty supply store) was placed over each sample circle. The cotton ball was pressed into the sample, and then pulled away using an upward motion. The amount of cotton fiber remaining on each sample circle was visually assessed and recorded by photographic means.

[0068] The photos created are shown in Figure 7. In each case, the silicone replacements of the invention exhibit decreased or low tackiness (dry skin feel), a characteristic associated with silicones.

[0069] Example 7: Evaluation of Pigment Grind

[0070] The capability of the silicone replacements to act as pigment dispersant was assessed by evaluation of viscosity and appearance of pigment grinds. This capability is significant, since high concentration, low viscosity pigment dispersions are used in color cosmetics.

[0071] Nine test formulations were prepared by combining the ingredients as shown in the table below:

	A	B	C	D	E	F	G	H	I
N10	50.00								
N20		50.00							
N50			50.00						
N100				50.00					
N200					50.00				
N350						50.00			
Dimenthicone 50cst							50.00		
Castor Oil								50.00	
LexFeel 700									50.00

Red 7 Lake	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00

[0072] LexFeel 700 is a blend of pentaenthrity/heptanoate/caprylate/caprate available from Inolex Chemical Company, Philadelphia, PA, USA. Blends N10, N20, N50, N100, N200, N350 were prepared as set out in Example 3. The test selected dimethicone/silicone replacement was mixed slowly with the red lake pigment until pigment is wetted out to avoid losing pigment in a dust cloud. Mixing was continued until the pigment was completely dispersed. The viscosity of each test blend A to I was measured using Brookfield viscometer using spindle T-D and helipath stand. The results are shown in Figure 8.

[0073] The data indicate that the series silicone replacements are comparative to the silicone blend, and facilitate acceptable pigment dispersant. The silicone replacement blends were easy to mix and the resulting viscosities were low.

[0074] Example 8: Evaluation of Shine

[0075] The ability of the silicone replacements to impart shine as compared to dimethicone counterparts was evaluated, specifically on human hair. Silicones, both dimethicone and cyclomethicone, are routinely used to add shine capabilities to hair styling products, but often build up on hair and do not decompose once washed away into the environment. Test formulations A to L were prepared by mixing the ingredients for each as shown in the table below:

	A	B	C	D	E	F	G	H	I	J	K	L
Isododecane	80	80	80	80	80	80	80	80	80	80	80	80
N10	20	--	--	--	--	--	--	--	--	--	--	--
Dimethicone 10 cst	--	20	--	--	--	--	--	--	--	--	--	--
N20	--	--	20	--	--	--	--	--	--	--	--	--
Dimethicone 20cst				20								
N50					20							
Dimethicone 50cst						20						
N100							20					

Blends N10, N20, N50, N100, N200 and N350 where prepared as set forth in Example 3.

[0076] Virgin human hair tresses were cut into thirteen strips of 8 cm. Each tress was

[0077] shampooed and rinsed with deionized water for one minute. Each tress was sprayed with one of the test formulations A to L, with one tress remaining untreated. Each tress was wrapped around a 28 cm cylinder and allowed to air dry. To evaluate shine, the

cylinder was place on a flat surface 1 meter away from power-light work light. All other light sources were eliminated. The cylinder with tresses was illuminated with the power light. A photo of the hair was taken and the bandwidth of the shine was measured. The data collected is graphically shown in Figure 9. Based upon these data, it can be concluded that the silicone replacements are comparable to the dimethicone counterparts as they contribute similar shine to the hair, leaving a high gloss finish.

[0078] Example 9: Natural Skin Moisturizing Lotion:

[0079] A natural skin moisturizing lotion is prepared using the silicone replacement of the invention. The ingredients used in the formulation are set forth in the table below:

Phase	Ingredient	Amount (wt%)
A	Water	70.15
A	Panthenol	0.1
B	Glycerin	5.0
B	Microcrystalline cellulose and cellulose gum	1.0
B	Xanthan gum	0.2
C	Cetearyl alcohol and cetearyl glucoside	5.0
C	N100 (Example 3)	10.0
C	Jojoba esters	2.0
C	Cetyl alcohol	2.0
C	Helianthus annus oil	3.0
C	Tocopheryl acetate	0.1
C	Caprylhydroxamic acid and glyceryl caprylate and glycerin	1.0

[0080] The ingredients of phase A are mixed and heated to 80◦C. The ingredients of phase C are premixed with one another, then are added to the heated phase A mixture with propeller mixing. The A/C mixture is heated to 80◦C. The ingredients of phase B are premixed. Once the A/C mixture is at 80◦C, the A?C mixture is added to the phase B premix with propeller mixing. Mixing is continued until the entire formulation is uniformly mixed. The formulation is cooled to room temperature while mixing is maintained.

[0081] Upon evaluation, it is determined that the lotion has a pH of 5.82 at 25°C and a Brookfield viscosity of 39,000 cps at 25°C and that the lotion has both a dry skin feel and a pigment dispersion capability similar to that to a lotion that contains dimethicone.

[0082] Example 10: Antiperspirant Stick

[0083] An antiperspirant stick formulation is prepared suing the replacement of the invention. The ingredients used in the preparation are set forth below:

Phase	Ingredient	Amount (wt%)
A	N5 (Example 3)	56.0
A	Hydroxystearic acid	10.0
B	Talc	6.0
B	Silica	4.0
B	Aluminum zirconium tetrachlorohydrex/glycine	26.0

[0084] The ingredients of phase A are mixed using moderate propeller agitation and heated to 80°C. Subsequently, each phase B ingredient is added individually to the phase A mixture while temperature is maintained. Mixing is accomplished using moderate propeller agitation. The final mixture is cooled to room temperature.

[0085] The resulting antiperspirant product contains no silicones, but exhibits the dry skin feel and smooth application properties of cyclomethicone-containing formulations.

[0086] Example 11: Natural Lip Stain

[0087] A natural lip stain formulation is prepared suing the replacement of the invention. The ingredients used in the preparation are set forth below:

Phase	Ingredient	Amount (wt %)
A	N350 (Example 3)	37.30
A	N5 (Example 3)	20.0
A	Distarch Phosphate	5.0
A	Argnia Spinosa (Argan) Kernel Oil	1.5
A	Triticum Vulgare (Wheat) Germ Oil	3.0
A	Prunus Armeniaca (Apricot) Kernel Oil	2.0
A	Copernica Cerifera (Carnauba) Wax	12.0

A	Euprorbia Cerifera (Candelilla) Wax	4.0
A	Maqnifera Indica (Manqo) Seed Butter	2.0
A	Butyrosperum Parkii (Shea) Butter	1.0
A	Glyceryl Caprylate (and) Glyceryl Undecylenate	0.8
B	Mica Sericite	6.0
B	Titanium Dioxide	2.0
B	Yellow 6 Lake	0.8
B	Red 6 Lake	0.2
B	Mica (and) Titanium Dioxide	1.5
C	Tocopheryl Acetate Vitamin E Acetate	0.3
C	Retinyl Palmitate Vi tamin A Palmitate	0.3
C	Fragrance	0.3

[0088] The ingredients of phase A are combined and heated to about 80°C to 85°C while undergoing propeller mixing. The phase B pigments are ground, then added to phase A. The mixture is mixed until it appears visually uniform. The heat is removed, and the ingredients of phase C are added. The final mixture is cooled and packaged.

[0089] Upon evaluation it is demonstrated that the formulation has a pH of 5.25 at 25°C and a Brookfield viscosity of 82,000 cps. Moreover, it is found that the lip stain formulation provides spreadability and skin feel properties like those of dimethicone-containing formulations.

[0090] Example 12: Silicone-Free Natural Hair Conditioner&

[0091] A natural silicone-free hair conditioner is prepared suing the replacement of the invention. The ingredients used in the preparation are set forth below:

Phase	Ingredient	Amount (wt%)
A	Water	
A	Glycerine	
A	Arginine	
B	Brassicyl Isoleucinate Esylate (and) Brassica	

	Alcohol	
B	N350 (Example 3)	8.0
B	Glyceryl Caprylate (and) Glyceryl Undecylenate	1.0
B	Orbignya Speciosa Kernel Oil (and) Astrocaryum Murumuru Seed Butter	1.0

[0100] To prepare the conditioner, one combines the ingredients of phase A, and heats them to 75°C with propeller mixing. Separately, one combines the ingredients of phase A also heating them to 75°C with propeller mixing. The heat is removed and phase B is added to phase A. When the mixture has cooled to 35°C, the ingredients of phase C are added. The entire formulation is cooled to room temperature while mixing.

[0101] Evaluation of the formulation demonstrates that it has a pH of 3.85 at 25°C and a Brookfield viscosity of 35,000 cps at 25°C. In addition, the conditioner provides a feel and a shine to hair comparable to silicone-containing formulations.

[0102] It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the present invention as defined by the appended claims.

CLAIMS

We claim:

1. A silicone replacement for use in a personal care formulation comprising a mixture of at least one polymeric ester and at least one non-polymeric ester, wherein the polymeric ester is an esterification reaction product of (i) at least one first dicarboxylic acid, (ii) at least one first monofunctional alcohol or monofunctional carboxylic acid and (iii) glycerin or derivatives thereof; and the non-polymeric ester is an esterification reaction product of (i) at least one second dicarboxylic acid and (ii) at least one second monofunctional alcohol, wherein the replacement is substantially free of silicone.

2. The replacement of claim 1, wherein at least one of the polymeric ester and the nonpolymeric ester is natural.

3. The replacement of claim 1, wherein at least one of the first or the second monofunctional alcohols is independently chosen from monofunctional alcohols having about 1 carbon atom to about 25 carbon atoms.

4. The replacement of claim 1, wherein at least one of the first or the second monofunctional alcohols is independently chosen from monofunctional alcohols having about 1 carbon atom to about 10 carbon atoms.

5. The replacement of claim 1, wherein at least one of the first or the second monofunctional alcohols is independently chosen from a monofunctional alcohol having about 1 carbon atom, a monofunctional alcohol having about 2 carbon atoms, a monofunctional alcohol having about 3 carbon atoms, having about 4 carbon atoms, a monofunctional alcohol having about 5 carbon atoms, having about 6 carbon atoms, a monofunctional alcohol having 25 about 7 carbon atoms, a monofunctional alcohol having about 8 carbons atoms, a monofunctional alcohol having about 9 carbon atoms, a monofunctional alcohol having about
10 carbon atoms, a monofunctional alcohol having about 11 carbon atoms, and a monofunctional alcohol having about 12 carbon atoms.

6. The replacement of claim 1, wherein at least one of the first or the second monofunctional alcohols is independently a linear chain monofunctional alcohol.

7. The replacement of claim 1, wherein at least one of the first or the second monofunctional alcohols contains saturated carbon atoms.

8. The replacement of claim 7, wherein all of the carbon atoms present in the at least one of the first or the second monofunctional alcohols are saturated.

9. The replacement of claim 1, wherein at least one of the first dicarboxylic acid or the second dicarboxylic acid is independently chosen from dicarboxylic acids having about 15 carbon atom to about 25 carbon atoms.

10. The replacement of claim 1, wherein at least one of the first dicarboxylic acid or the second dicarboxylic acid is independently chosen from dicarboxylic acids having about 5 carbon atoms to about 10 carbon atoms.

11. The replacement of claim 1 having a viscosity of about 10 cSt.

12. The replacement of claim 1, having a viscosity of about 20 sSt.

13. The replacement of claim 1, having a viscosity of about 50 cSt.

14. The replacement of claim 1, having a viscosity of about 100 cSt.

15. The replacement of claim 1, having a viscosity of about 200 cSt.

16. The replacement of claim 1, having a viscosity of about 350 cSt.

17. The replacement of any of claims 1 to 16, wherein the replacement exhibits a spread rate that is substantially equivalent to a spread rate of a counterpart silicone fluid.

18. The replacement of any of claims 1 to 16, wherein the replacement exhibits a pigment dispersion capability that is substantially equivalent to pigment dispersion capability of a counterpart silicone fluid.

19. The replacement of any of claims 1 to 16, wherein the replacement exhibits skinfeel properties that are substantially equivalent to skinfeel properties of a counterpart silicone fluid.

20. The replacement of any of claims 1 to 16, wherein the replacement exhibits a tack (stickiness) that is substantially equivalent to a tack (stickiness) of a counterpart silicone fluid.

21. A personal care formulation that is substantially free of silicone, wherein the formulation comprises a silicone replacement consisting substantially of a mixture of at least one polymeric ester and at least one non-polymeric ester, wherein the polymeric ester is an esterification reaction product of (i) at least one first dicarboxylic acid, (ii) at least one first monofunctional alcohol or monofunctional carboxylic acid and (iii) glycerin or derivatives thereof; and the non-polymeric ester is an esterification reaction product of (i) at least one second dicarboxylic acid and (ii) at least one second monofunctional alcohol, and at least one additional personal care ingredient.

22. The personal care formulation of claim 21, wherein at least one of the polymeric ester and the non-polymeric ester is natural.

23. The personal care formulation of claim 21, wherein at least one of the first or the second monofunctional alcohols is independently chosen from monofunctional alcohols having about 1 carbon atom to about 25 carbon atoms.

24. The personal care formulation of claim 21, wherein at least one of the first or the second monofunctional alcohols is independently chosen from monofunctional alcohols having about 1 carbon atom to about 10 carbon atoms.

25. The personal care formulation of claim 21, wherein at least one of the first or the second monofunctional alcohols is independently chosen from a monofunctional alcohol having about 1 carbon atom, a monofunctional alcohol having about 2 carbon atoms, a monofunctional alcohol having about 3 carbon atoms, having about 4 carbon atoms, a monofunctional alcohol having about 5 carbon atoms, having about 6 carbon atoms, a 15 monofunctional alcohol having about 7 carbon atoms, a monofunctional alcohol having about 8 carbons atoms, a monofunctional alcohol having about 9 carbon atoms, a monofunctional alcohol having about 10 carbon atoms, a monofunctional alcohol having about 11 carbon atoms, and a monofunctional alcohol having about 12 carbon atoms.

26. The personal care formulation of claim 21, wherein at least one of the first or the second monofunctional alcohols is independently a linear chain monofunctional alcohol.

27. The personal care formulation of claim 21, wherein at least one of the first or the second monofunctional alcohols contain at least one saturated carbon atom.

28. The personal care formulation of claim 21, wherein all of the carbon atoms present in the at least one of the first or the second monofunctional alcohols are saturated.

29. The personal care formulation of claim 21, wherein at least one of the first dicarboxylic acid or the second dicarboxylic acid is independently chosen from dicarboxylic acids having about 1 carbon atom to about 25 carbon atoms.

30. The personal care formulation of claim 21, wherein at least one of the first dicarboxylic acid or the second dicarboxylic acid is independently chosen from dicarboxylic acids having about 5 carbon atom to about 10 carbon atoms.

31. The personal care formulation of claim 21, wherein all of the carbon atoms present in the at least one of the first or the second dicarboxylic acids are saturated.

32. The personal care formulation of claim 21, wherein the silicone replacement of has a viscosity of about 10 cSt.

33. The personal care formulation of claim 21, wherein the silicone replacement of has a viscosity of about 20 sSt.

34. The personal care formulation of claim 21, wherein the silicone replacement of has a viscosity of about 50 cSt.

35. The personal care formulation of claim 21, wherein the silicone replacement of has a viscosity of about 100 cSt.

36. The personal care formulation of claim 21, wherein the silicone replacement of has a viscosity of about 200 cSt.

37. The personal care formulation of claim 21, wherein the silicone replacement of has a viscosity of about 350 cSt.

38. The personal care formulation of claim 21, wherein the at least one personal care ingredient is selected from a surfactant, a flavorant, a fragrance, an opacifier, a colorant, a wax, an emulsifier, a fat, an oil, a preservative, a UV absorbing compound, a detergent, foaming agents, stabilizers, pH modifiers, foaming agents, moisturizers, water, an alcohol, a urea, a wetting agent, a skin or hair conditioner and a solvent.

39. The personal care formulation of claim 21, wherein the at least one personal care ingredient is selected from parabens, mineral oil, vegetable oil, olive oil, paraffin, PEG, polyethylene, polyethylene glycol, polyoxyethylene, oxynol, petrolatum, sodium lauryl sulfate, sodium laureth sulfate, sodium myreth sulfate, sodium oleth sulfate, sodium ceteareth sulfate, DMDM hydantoin, sodium hydroxymethylglycinate, triethanolamine, cocamide diethanolamine, laurimide diethanolamine, linoleamide diethanolamine, oleamide diethanolamine, oxybenzone, essential oils, an emollient, octylmethoxycinnamate, titanium dioxide, and zinc oxide.

40. The personal care formulation of claim 21, wherein the silicone replacement is present in an amount of about 1% to about 95% by total weight of the formulation.

41. The personal care formulation of claim 21, wherein the silicone replacement is present in an amount of about 5% to about 80% by total weight of the formulation.

42. The personal care formulation of claim 21, wherein the silicone replacement is present in an amount of about 10% to about 30% by total weight of the formulation.

43. The personal care formulation of claim 21, wherein the silicone replacement is present in an amount of about 3% by total weight of the formulation.

44. The personal care formulation of any of claims 21 to 43, wherein the formulation exhibits a pigment dispersion capability that is substantially equivalent to pigment dispersion capability of a counterpart silicone-containing formulation.

45. The personal care formulation of any of claims 21 to 43, wherein the formulation exhibits skinfeel properties that are substantially equivalent to skinfeel properties of a counterpart silicone-containing formulation.

46. The personal care formulation of any of claims 21 to 43, wherein the formulation exhibits a tack (stickiness) that is substantially equivalent to a tack (stickiness) of a silicone containing formulation.

47. A method of preparing a personal care formulation that is substantially free of silicone comprising preparing a base formulation and incorporating into the base formulation a silicone replacement consisting substantially of at least one polymeric ester and at least one non-polymeric ester, wherein the polymeric ester is an esterification reaction product of (i) at least one first dicarboxylic acid, (ii) at least one first monofunctional alcohol or monofunctional carboxylic acid and (iii) glycerin or derivatives thereof,; and the non-polymeric ester is an esterification reaction product of (i) at least one second dicarboxylic acid and (ii) at least one second monofunctional alcohol, wherein the base formulation comprises at least one of a surfactant, a flavorant, a fragrance, an opacifier, a solvent, a colorant, a wax, an emulsifier, a fat, an oil, a preservative, a UV absorbing compound, a detergent, a foaming agent, a stabilizer, a pH modifier, a moisturizer, water, an alcohol, a urea, a wetting agent, and a skin or hair conditioner.

48. The method of claim 47, wherein at least one of the polymeric ester and the nonpolymeric ester is natural.

49. The method of claim 47, wherein at least one of the first or the second monofunctional alcohols is independently chosen from monofunctional alcohols having about 30 carbon atoms to about 25 carbon atoms.

50. The method of claim 47, wherein at least one of the first or the second monofunctional alcohols is independently chosen from monofunctional alcohols having about 1 carbon atom to about 10 carbon atoms.

51. The method of claim 47, wherein at least one of the first or the second monofunctional alcohols is independently chosen from a monofunctional alcohol having about 1 carbon atom, a monofunctional alcohol having about 2 carbon atoms, a monofunctional alcohol having about 3 carbon atoms, having about 4 carbon atoms, a monofunctional alcohol having about 5 carbon atoms, having about 6 carbon atoms, a monofunctional alcohol having about 7 carbon atoms, a monofunctional alcohol having about 8 carbons atoms, a monofunctional alcohol having about 9 carbon atoms, a

monofunctional alcohol having about 10 carbon atoms, a monofunctional alcohol having about 11 carbon atoms, and a monofunctional alcohol having about 12 carbon atoms.

52. The method of claim 47, wherein at least one of the first or the second monofunctional alcohols is independently a linear chain monofunctional alcohol.

53. The method of claim 47, wherein at least one of the first or the second monofunctional alcohols contains at least one saturated carbon atom.

54. The method of claim 47, wherein all of the carbon atoms present in the at least one of the first or the second monofunctional alcohols are saturated.

55. The method of claim 47, wherein at least one of the first dicarboxylic acid or the second dicarboxylic acid is independently chosen from dicarboxylic acids having about 1 carbon atom to about 25 carbon atoms.

56. The method of claim 47, wherein at least one of the first dicarboxylic acid or the second dicarboxylic acid is independently chosen from dicarboxylic acids having about 5 carbon atom to about 10 carbon atoms.

57. The method of claim 47, wherein all of the carbon atoms present in the at least one of the first or the second dicarboxylic acids are saturated.

58. The method of claim 47, wherein at least one of the carbon atoms present in the at least one of the first or the second dicarboxylic acids are saturated.

FIGURE 1

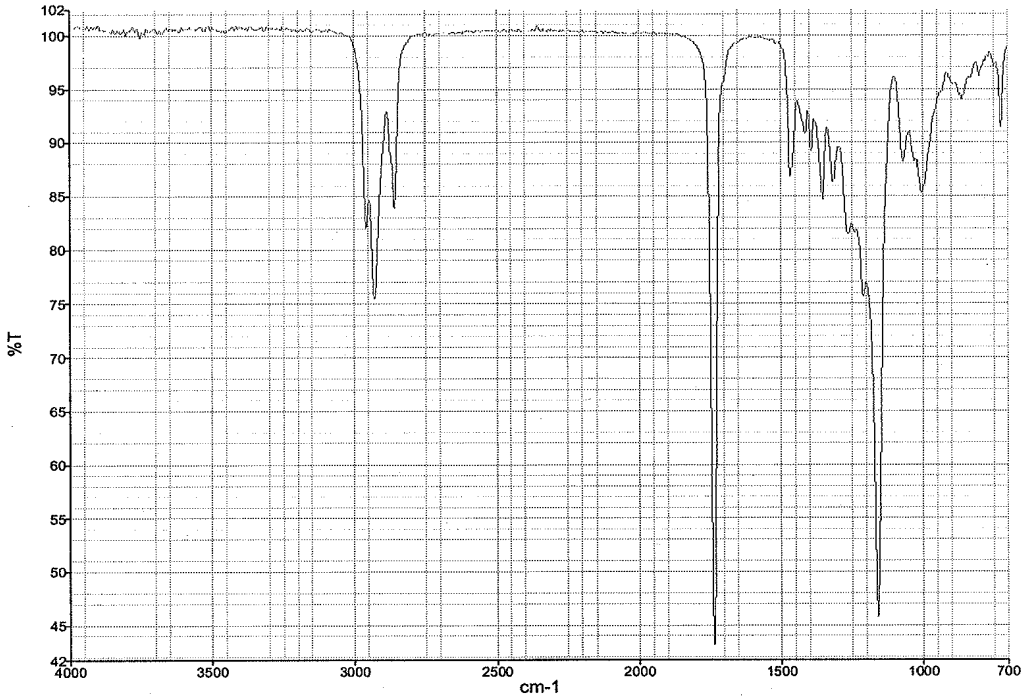

%T
102
100
95
90
85
80
75
70
65
60
55
50
45
42
4000
3500
3000
2500
2000
1500
1000
700
cm-1

FIGURE 2

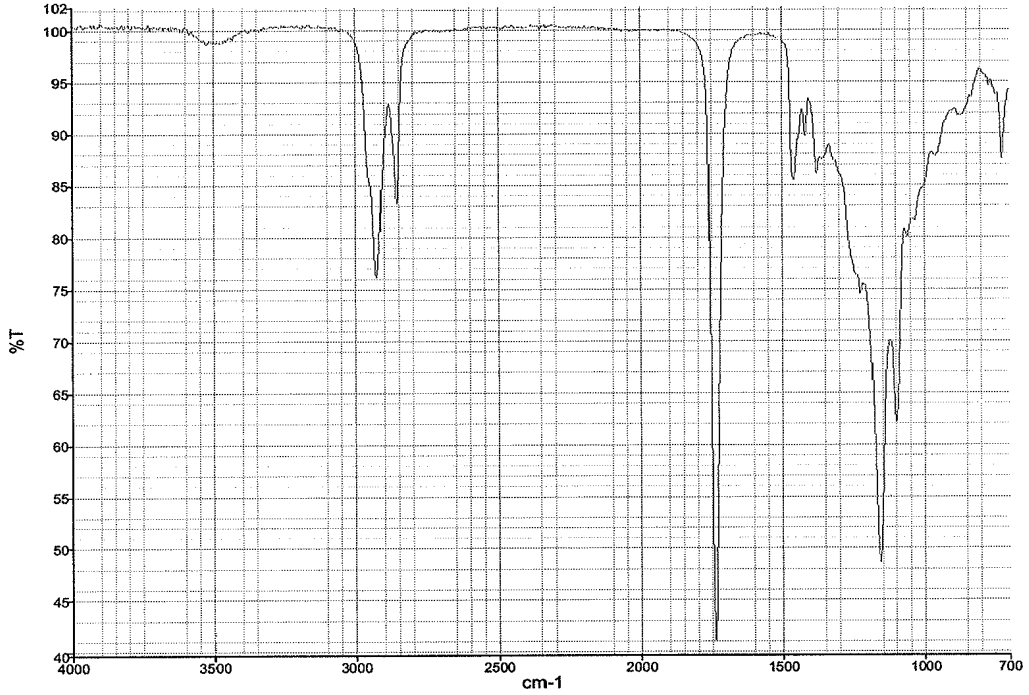

%T
102
100
95
90
85
80
75
70
65
60
55
50
45
40
4000
3500
3000
2500
2000
1500
1000
700
cm-1

FIGURE 3

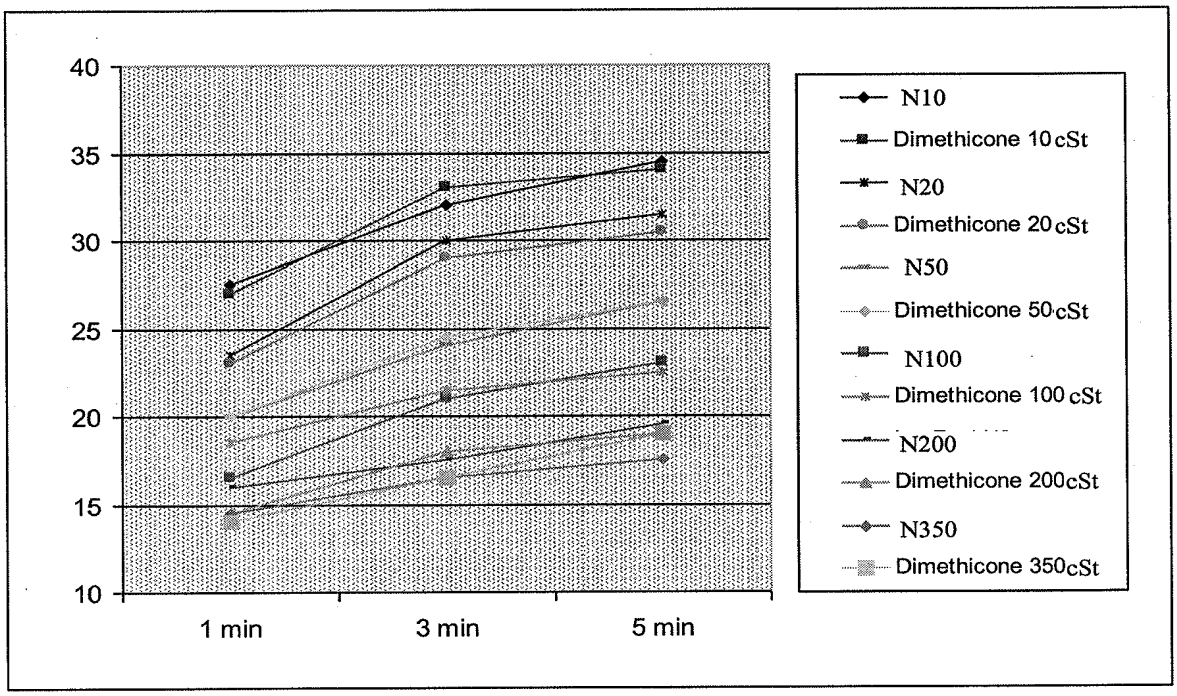

40
35
30
25
20
15
10
1 min
3 min
5 min
N10
Dimethicone 10 cSt
N20
Dimethicone 20 cSt
N50
Dimethicone 50 cSt
N100
Dimethicone 100 cSt
N200
Dimethicone 200 cSt
N350
Dimethicone 350 cSt

FIGURE 4

	INGREDIENTS		582-177A %w/w	582-177B %w/w	582-177C %w/w	582-177D %w/w	582-177E %w/w	586-093F %w/w	586-093G %w/w
A	Deionized Water		76.15	76.15	76.15	76.15	76.15	76.15	76.15
	Xanthan Gum	Keltrol CG-T	0.25	0.25	0.25	0.25	0.25	0.25	0.25
	Microcrystalline Cellulose (and) Cellulose Gum	Avicel PC611	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	Glycerin		4.00	4.00	4.00	4.00	4.00	4.00	4.00
	Trisodium EDTA		0.10	0.10	0.10	0.10	0.10	0.10	0.10
B	Glyceryl Stearate SE	**Lexemul T**[1]	5.00	5.00	5.00	5.00	5.00	5.00	5.00
	Cetyl Alcohol		2.50	2.50	2.50	2.50	2.50	2.50	2.50
	Dimethicone	DC 200/10	10.00	----	----	----	----	----	----
		N10	----	10.00	----	----	----	----	----
	Dimethicone	DC200/20	----	----	10.00	----	----	----	----
		N20	----	----	----	10.00	----	----	----
	Dimethicone	DC200/100	----	----	----	----	10.00	----	----
		LexFeel N100	----	----	----	----	----	10.00	----
	Dimethicone	DC200/200	----	----	----	----	----	----	10.00
		N200	----	----	----	----	----	----	----
	Dimethicone	DC200/350	----	----	----	----	----	----	----
		N350	----	----	----	----	----	----	----
C	Caprylhydroxamic Acid (and) Caprylyl Glycol (and) Glycerin	**Spectrastat**$^{TM\ 1}$	1.00	1.00	1.00	1.00	1.00	1.00	1.00
		Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00

	INGREDIENTS		582-177A %w/w	582-177B %w/w	582-177C %w/w	582-177D %w/w	582-177E %w/w	586-093F %w/w	586-093G %w/w
A	Deionized Water		76.15	76.15	76.15	76.15	76.15	76.15	76.15
	Xanthan Gum	Keltrol CG-T	0.25	0.25	0.25	0.25	0.25	0.25	0.25
	Microcrystalline Cellulose (and) Cellulose Gum	Avicel PC611	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	Glycerin		4.00	4.00	4.00	4.00	4.00	4.00	4.00
	Trisodium EDTA		0.10	0.10	0.10	0.10	0.10	0.10	0.10
B	Glyceryl Stearate SE	**Lexemul T**[1]	5.00	5.00	5.00	5.00	5.00	5.00	5.00
	Cetyl Alcohol		2.50	2.50	2.50	2.50	2.50	2.50	2.50
	Dimethicone	DC 200/10	10.00	----	----	----	----	----	----
		N10	----	10.00	----	----	----	----	----
	Dimethicone	DC200/20	----	----	10.00	----	----	----	----
		N20	----	----	----	10.00	----	----	----
	Dimethicone	DC200/100	----	----	----	----	10.00	----	----
		N100	----	----	----	----	----	10.00	----
	Dimethicone	DC200/200	----	----	----	----	----	----	10.00
		N200	----	----	----	----	----	----	----
	Dimethicone	DC200/350	----	----	----	----	----	----	----
		N350	----	----	----	----	----	----	----
C	Caprylhydroxamic Acid (and) Caprylyl Glycol (and) Glycerin	**Spectrastat**^{TM} [1]	1.00	1.00	1.00	1.00	1.00	1.00	1.00
		Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00

FIGURE 5

SURVEY:

We are studying the attributes of a series of new natural emollients. Each participant will receive a set of two samples for evaluation twice a day for the next three days.
Please apply sample to forearm as directed and record evaluation of products below.

Name:_____

Product A:_____

Product B:_____

1. Product A

   a. How does lotion feel when applied?
   Light ..... Rich
   1 2 3 4 5

   b. How does your skin feel during rub-in (mid-application)?
   Slippery ..... Sticky
   1 2 3 4 5

   c. How long does it take for the product to be absorbed?
   Quick ..... Long
   1 2 3 4 5

   d. How does your skin feel immediately after application? Is there a residue?
   Not Oily ..... Very Oily
   1 2 3 4 5

   e. After 5 minutes, how does your skin feel?
   No Residual ..... Rich Residual (waxy, greasy, silky, etc,)
   1 2 3 4 5

2. Repeat evaluation with product B

   Record feedback:
   Product B

   a. How does lotion feel when applied?
   Light ..... Rich
   1 2 3 4 5

   b. How does your skin feel during rub-in (mid-application)?
   Slippery ..... Sticky
   1 2 3 4 5

   c. How long does it take for the product to be absorbed?
   Quick ..... Long
   1 2 3 4 5

   d. How does your skin feel immediately after application? Is there a residue?
   Not Oily ..... Very Oily
   1 2 3 4 5

   e. After 5 minutes, how does your skin feel?
   No Residual ..... Rich Residual (waxy, greasy, silky, etc,)
   1 2 3 4 5

FIGURE 6A

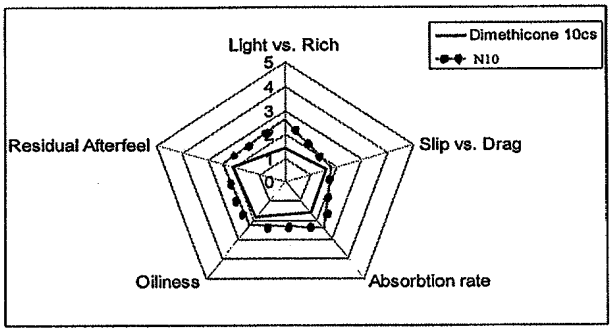


FIGURE 6B

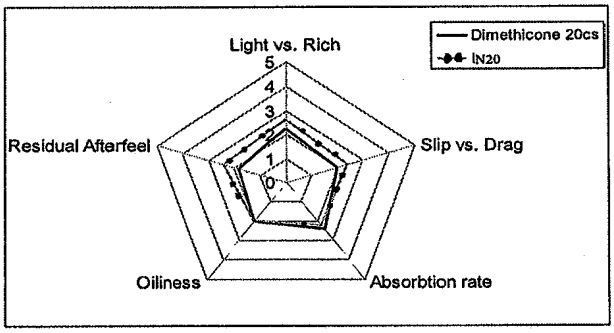


FIGURE 6C

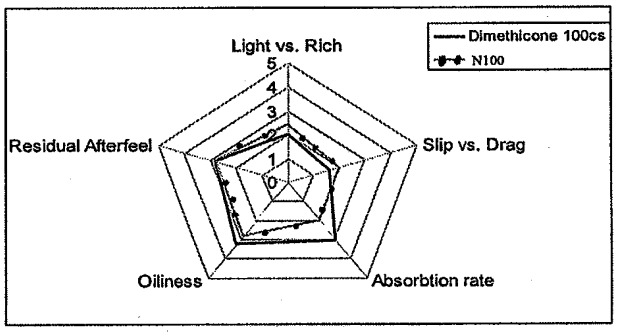


FIGURE 6D

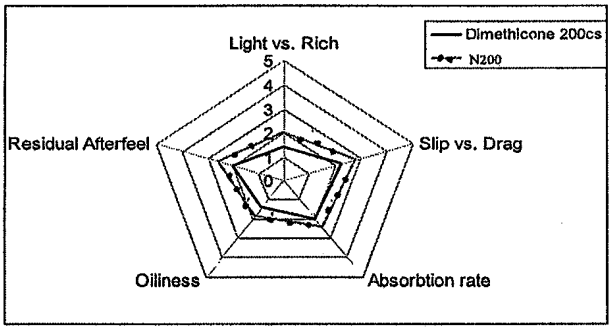


FIGURE 6E

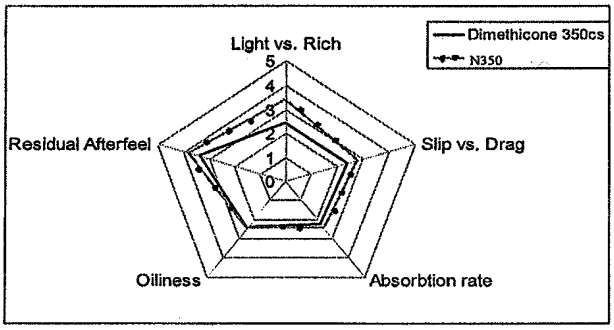
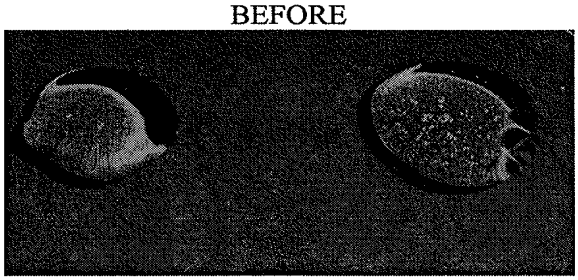


FIGURE 7A

BEFORE



AFTER
80% Lexorez200 + 20% N10

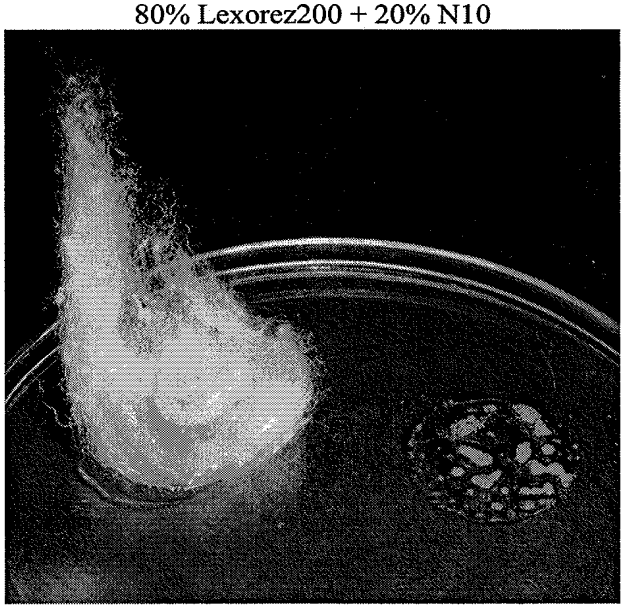


FIGURE 7B

BEFORE



AFTER
80% Lexorez200 + 20% N20

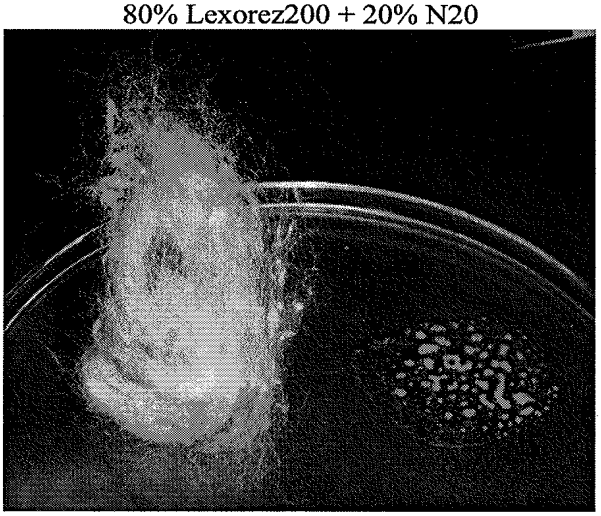
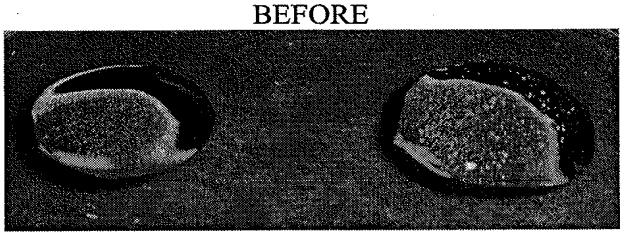


FIGURE 7C

BEFORE



AFTER
80% Lexorez200 + 20% N50

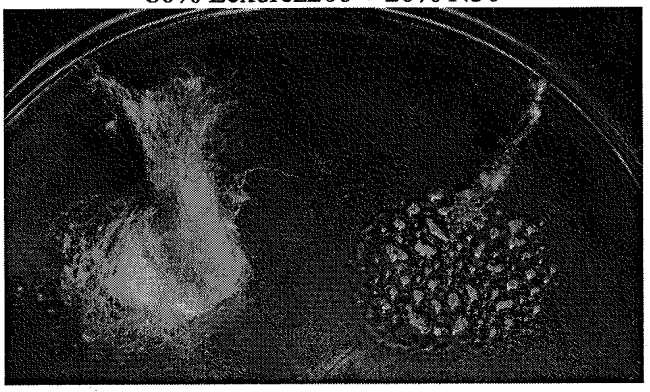
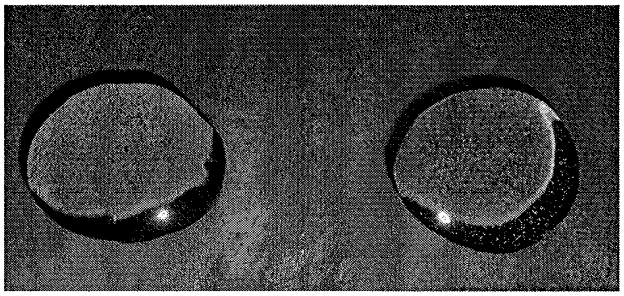


FIGURE 7D

BEFORE



AFTER
80% Lexorez200 + 20% N100

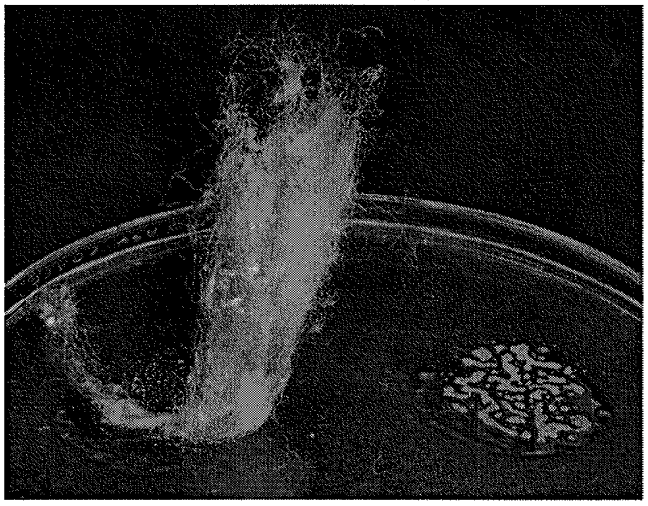
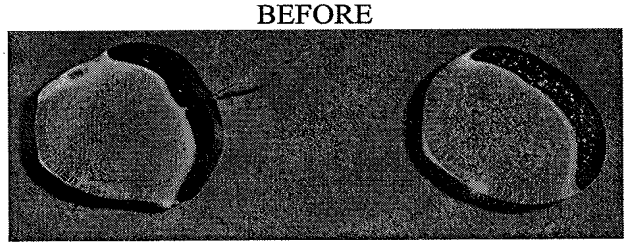


FIGURE 7E

BEFORE



AFTER
80% Lexorez200 + 20% N200

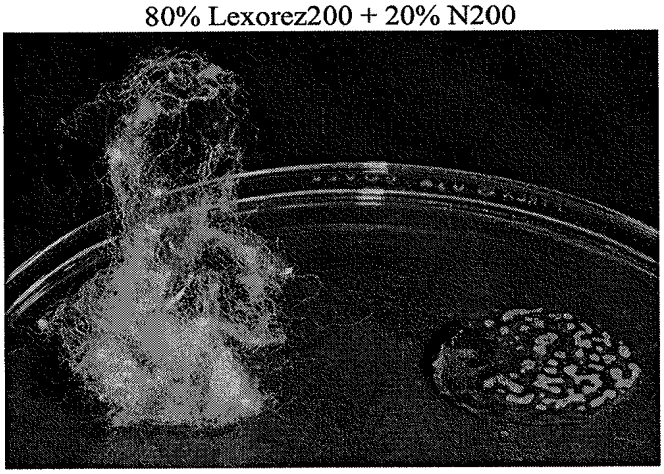
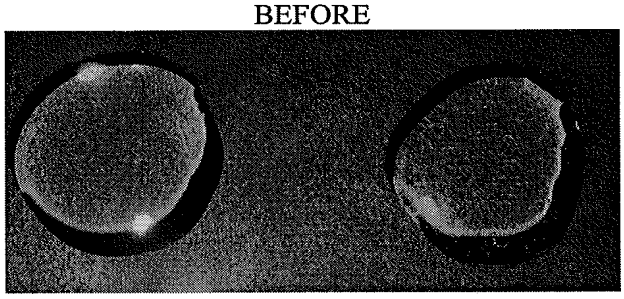


FIGURE 7F

BEFORE



AFTER
80% Lexorez200 + 20% N350

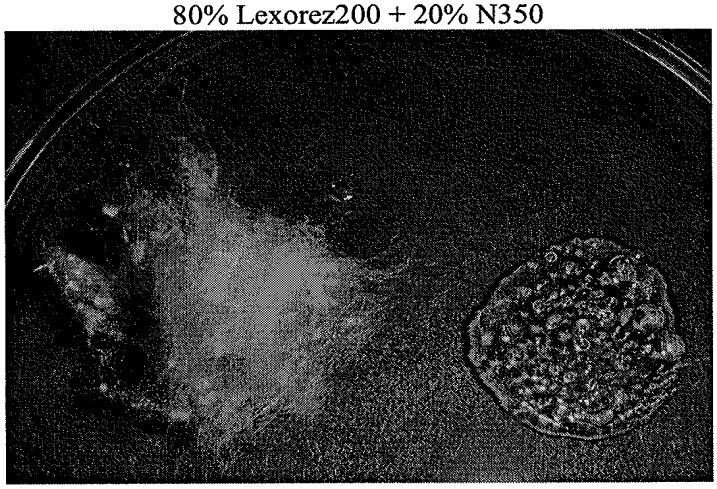


FIGURE 8

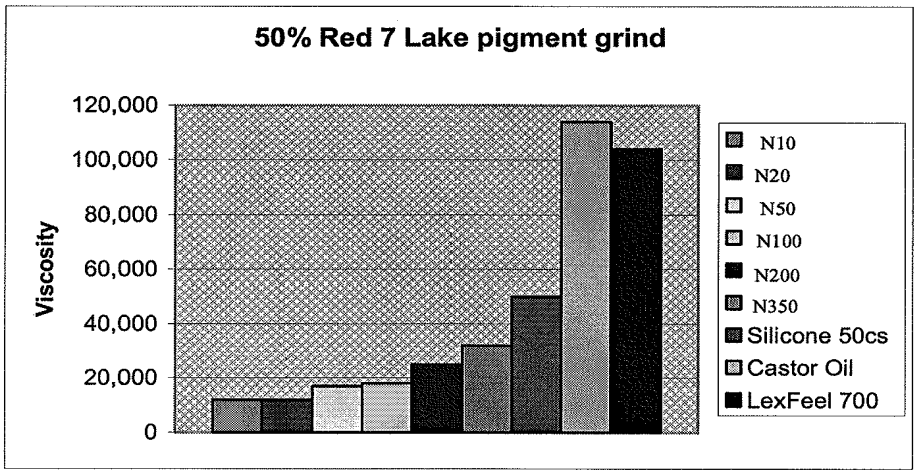
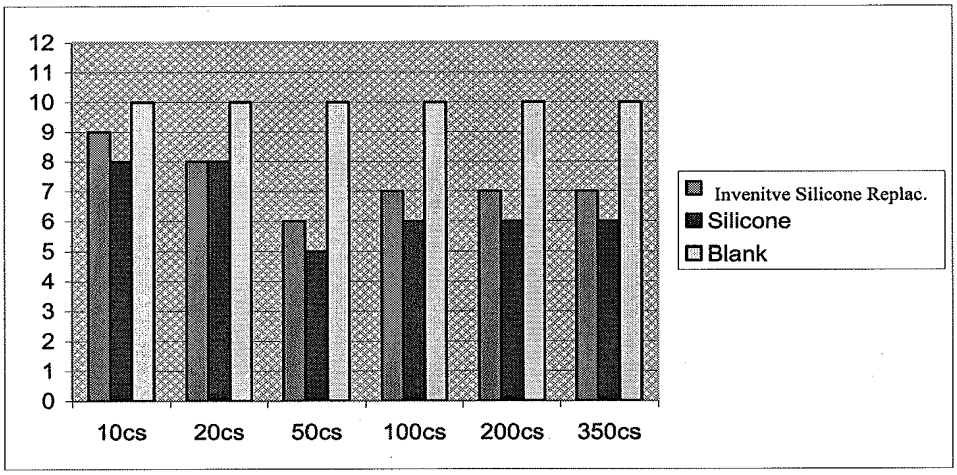

50% Red 7 Lake pigment grind
Viscosity
120,000
100,000
80,000
60,000
40,000
20,000
0
N10
N20
N50
N100
N200
N350
Silicone 50cs
Castor Oil
LexFeel 700

FIGURE 9


12
11
10
9
8
7
6
5
4
3
2
1
0
10cs
20cs
50cs
100cs
200cs
350cs
Invenitve Silicone Replac.
Silicone
Blank

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/65052

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - A61Q 5/12 (2012.01)
USPC - 424/70.12
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC -- 424/70.12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC -- 424/70.11

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST (USPT,PGPB,JPAB,EPAB); Google
Search Terms: NATURAL SILICONE REPLACEMENTS SILICONE FLUIDS PERSONAL CARE FORMULATIONS ester polyester polymeric ester carboxylic dicarboxylic acid alcohol saturated (oxalic or succinic or malonic or glutaric or adipic or pimelic or suberic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2005/0260150 A1 (Burgo) 24 Nov 2005 (24.11.2005), entire document especially Abstract, para [0010], [0044]-[0045], [0013], [0040] and [0018]; Examples 1-12	1-20
Y	US 2004/0258642 A1 (Calello et al.) 23 Dec 2004 (23.12.2004), entire document especially Abstract, para [0005], [0171] and [0187]-[0190]	1-20
A	US 2010/0068162 A1 (Greenberg et al.) 18 Mar 2010 (18.03.2010), entire document	1-20
A	US 2004/0241200 A1 (Winn et al) 04 Dec 2004 (04.12.2004), entire document	1-20
A	US 2001/0006652 A1 (Kahre et al.) 05 Jul 2001 (05.07.2001), entire document	1-20

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 Feb 2013 (27.02.2013)	12 MAR 2013
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/65052

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

---PLEASE SEE SUPPLEMENTAL BOX---

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-20

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/65052

Box III: Observations where unity of invention is lacking:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: claims 1-20: directed to a silicone replacement for use in a personal care formulation.

Group II: claims 21-58: directed to a personal care formulation that is substantially free of silicone, wherein the formulation comprises a silicone replacement and at least one additional personal care ingredient/ base formulation.

The inventions listed as Groups I - II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group I does not include the inventive concept of at least one additional base formulation selected from a surfactant, a flavorant, a fragrance, an opacifier, a solvent, a colorant, a wax, an emulsifier, a fat, an oil, a preservative, a UV absorbing compound, a detergent, a foaming agent, a stabilizer, a pH modifier, a moisturizer, water, an alcohol, a urea, a wetting agent, and a skin or hair conditioner, as required by Group II.

Group II does not include the inventive concept of solely a silicone replacement for use in a personal care formulation, as required by Group I.

Groups I and II share the technical feature of a silicone replacement for use in a personal care formulation comprising a mixture of at *least one polymeric ester and at least one non-polymeric ester, wherein the polymeric ester is an esterification reaction product of (i) at* least one first dicarboxylic acid, (ii) at least one first monofunctional alcohol or monofunctional carboxylic acid and (iii) glycerin or derivatives thereof; and the non-polymeric ester is an esterification reaction product of (i) at least one second dicarboxylic acid and (ii) at least one second monofunctional alcohol, wherein the replacement is substantially free of silicone.

However, this shared technical feature does not represent a contribution over the prior art of US 2005/0260150 A1 to Burgo (24 Nov 2005), which teaches a formulation comprising a mixture of at least one polymeric ester and at least one non-polymeric ester, wherein the polymeric ester is an esterification reaction product of (i) at least one first dicarboxylic acid, (ii) at least one first monofunctional alcohol or monofunctional carboxylic acid and (iii) glycerin or derivatives thereof; and the non-polymeric ester is an esterification reaction product of (i) at least one second dicarboxylic acid and (ii) at least one second monofunctional alcohol, wherein the replacement is substantially free of silicone. (see Abstract, para [0010], [0014]-[0016], [0026], Examples 1-2 and 12, silicone free formulations comprising polyester component derived from polyol and carboxylic acids and high and low molecular weight ester component).

As the above formulation was known at the time, as evidenced by the teaching of Burgo, this cannot be considered a special technical feature that would otherwise unify the groups.

Groups I and II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.

Electronic Patent Application Fee Transmittal

Application Number:	18066105
Filing Date:	
Title of Invention:	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE
First Named Inventor/Applicant Name:	Anna K. CROOM
Filer:	Michael Nicholas Mercanti/Carla Curado
Attorney Docket Number:	GRAN-1012-U-D

Filed as Small Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
CLAIMS IN EXCESS OF 20	2202	3	50	150
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**150**

Electronic Acknowledgement Receipt

EFS ID:	47209669
Application Number:	18066105
International Application Number:	
Confirmation Number:	1563
Title of Invention:	BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE
First Named Inventor/Applicant Name:	Anna K. CROOM
Customer Number:	20311
Filer:	Michael Nicholas Mercanti/Carla Curado
Filer Authorized By:	Michael Nicholas Mercanti
Attorney Docket Number:	GRAN-1012-U-D
Receipt Date:	14-DEC-2022
Filing Date:	
Time Stamp:	17:27:00
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$150
RAM confirmation Number	E2022BDH27360380
Deposit Account	
Authorized User	

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Fee Worksheet (SB06)	fee-info.pdf	37629 28c3737f3acfb0e27662cd9bbdb8599402ca918e	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	37629		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
18/066,105	12/14/2022		980	GRAN-1012-U-D	23	1

CONFIRMATION NO. 1563

FILING RECEIPT

20311
LUCAS & MERCANTI, LLP
30 BROAD STREET
21st FLOOR
NEW YORK, NY 10004

Date Mailed: 01/13/2023

Receipt is acknowledged of this non-provisional utility patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF FIRST INVENTOR, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection.

Please verify the accuracy of the data presented on this receipt. If an error is noted on this Filing Receipt, please submit a written request for a corrected Filing Receipt, including a properly marked-up ADS showing the changes with strike-through for deletions and underlining for additions. If you received a "Notice to File Missing Parts" or other Notice requiring a response for this application, please submit any request for correction to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections provided that the request is grantable.

Inventor(s)

Anna K. CROOM, Brooklyn, NY;
Ronald V. LERUM, Leonia, NJ;
John GORMLEY, Midland Park, NJ;

Applicant(s)

Grant Industries, Inc., Elmwood Park, NJ;

Assignment For Published Patent Application

Grant Industries, Inc., Elmwood ParK, NJ

Power of Attorney: The patent practitioners associated with Customer Number 20311

Domestic Priority data as claimed by applicant

This application is a DIV of 16/992,831 08/13/2020 PAT 11,534,389
which claims benefit of 62/893,968 08/30/2019
and claims benefit of 62/976,015 02/13/2020

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.) - None.
Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

If Required, Foreign Filing License Granted: 01/12/2023
The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 18/066,105**
Projected Publication Date: 04/20/2023
Non-Publication Request: No
Early Publication Request: No
**** SMALL ENTITY ****
Title

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Preliminary Class

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific

countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

SelectUSA

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The U.S. offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to promote and facilitate business investment. SelectUSA provides information assistance to the international investor community; serves as an ombudsman for existing and potential investors; advocates on behalf of U.S. cities, states, and regions competing for global investment; and counsels U.S. economic development organizations on investment attraction best practices. To learn more about why the United States is the best country in the world to develop

technology, manufacture products, deliver services, and grow your business, visit http://www.SelectUSA.gov or call +1-202-482-6800.

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 18/066,105

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	80		N/A	
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	350		N/A	
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	400		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	23 minus 20 =	* 3	x 50 =	150	OR		
INDEPENDENT CLAIMS (37 CFR 1.16(h))	1 minus 3 =	*	x =	0			
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			0			
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				0			
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	830		TOTAL	

APPLICATION AS AMENDED - PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)	OR	RATE($)	ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
18/066,105	12/14/2022	Anna K. CROOM	GRAN-1012-U-D

CONFIRMATION NO. 1563

20311
LUCAS & MERCANTI, LLP
30 BROAD STREET
21st FLOOR
NEW YORK, NY 10004

PUBLICATION NOTICE



Title:BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Publication No.US-2023-0122072-A1
Publication Date:04/20/2023

NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Public Records Division. The Public Records Division can be reached by telephone at (571) 272-3150 or (800) 972-6382, by facsimile at (571) 273-3250, by mail addressed to the United States Patent and Trademark Office, Public Records Division, Alexandria, VA 22313-1450 or via the Internet.

In addition, information on the status of the application, including the mailing date of Office actions and the dates of receipt of correspondence filed in the Office, may also be accessed via the Internet through the Patent Electronic Business Center at www.uspto.gov using the public side of the Patent Application Information and Retrieval (PAIR) system. The direct link to access this status information is currently https://portal.uspto.gov/pair/PublicPair. Prior to publication, such status information is confidential and may only be obtained by applicant using the private side of PAIR.

Further assistance in electronically accessing the publication, or about PAIR, is available by calling the Patent Electronic Business Center at 1-866-217-9197.

Office of Data Managment, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

Espacenet

JP2018090662A POLYURETHANE GEL AND PRODUCTION PROCESS THEREFOR

Applicants: MITSUI CHEMICALS INC

Inventors: NAKAGAWA AYA,NAKAGAWA TOSHIHIKO,YAMASHITA TATSUYA,MORITA KOICHI,YAMAZAKI SATOSHI

Classifications:
IPC ***C08G18/08; C08G18/73; C08G18/79;***

Priorities: JP2016232583A 2016-11-30

Application: JP2016232583A·2016-11-30

Publication: JP2018090662A·2018-06-14

Published as: JP2018090662A;**JP6892253B2**

POLYURETHANE GEL AND PRODUCTION PROCESS THEREFOR

Abstract

PROBLEM TO BE SOLVED: To provide a polyurethane gel that is excellent in transparency, and is excellent in tactile sensation, absorbency, holding power and volatility, and furthermore is excellent in shape retention, heat resistance and quick curability, and to provide a production process therefor.SOLUTION: In a polyurethane gel containing a reaction product of a polyisocyanate component containing a polyfunctional aliphatic polyisocyanate having an average functional group number of more than 2.0 and not more than 3.5 and a polyol component containing a bifunctional polyol by 80 mass% or more, and a solvent, the content ratio of the solvent is set to 50 mass% or more and 95 mass% or less with respect to the total amount of polyurethane gel.SELECTED DRAWING: None

(19)日本国特許庁(JP)　(12)公開特許公報(A)　(11)特許出願公開番号
特開2018-90662
(P2018-90662A)
(43)公開日　平成30年6月14日(2018.6.14)

(51)Int.Cl.		F I			テーマコード（参考）
C08G 18/08	(2006.01)	C08G	18/08	042	4J034
C08G 18/73	(2006.01)	C08G	18/73		
C08G 18/79	(2006.01)	C08G	18/79	020	

審査請求 未請求　請求項の数 8　ＯＬ　（全 24 頁）

(21)出願番号　特願2016-232583 (P2016-232583)
(22)出願日　平成28年11月30日 (2016.11.30)

(71)出願人　000005887
三井化学株式会社
東京都港区東新橋一丁目５番２号
(74)代理人　100103517
弁理士　岡本　寛之
(72)発明者　中川　亜弥
千葉県袖ヶ浦市長浦５８０番地３２　三井化学株式会社内
(72)発明者　中川　俊彦
千葉県袖ヶ浦市長浦５８０番地３２　三井化学株式会社内
(72)発明者　山下　達也
千葉県袖ヶ浦市長浦５８０番地３２　三井化学株式会社内

最終頁に続く

(54)【発明の名称】ポリウレタンゲルおよびその製造方法

(57)【要約】
【課題】透明性に優れ、また、触感、吸収性、保持力および揮散性に優れ、さらには、保型性、耐熱性および速硬化性に優れるポリウレタンゲル、および、その製造方法を提供すること。
【解決手段】平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有するポリイソシアネート成分と、２官能性ポリオールを８０質量％以上含有するポリオール成分との反応生成物と、溶媒とを含有するポリウレタンゲルにおいて、溶媒の含有割合を、ポリウレタンゲルの総量に対して、５０質量％以上９５質量％以下とする。
【選択図】なし

【特許請求の範囲】
【請求項１】
平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有するポリイソシアネート成分と、２官能性ポリオールを８０質量％以上含有するポリオール成分との反応生成物と、
溶媒と
を含有するポリウレタンゲルであって、
前記溶媒の含有割合は、前記ポリウレタンゲルの総量に対して、５０質量％以上９５質量％以下である
ことを特徴とする、ポリウレタンゲル。
【請求項２】
前記２官能性ポリオールが、ポリエーテルジオールである
ことを特徴とする、請求項１に記載のポリウレタンゲル。
【請求項３】
前記ポリウレタンゲルがウレタン化触媒を含有し、
前記ウレタン化触媒の含有割合が、前記ポリイソシアネート成分および前記ポリオール成分の総量１００質量部に対して、０．１質量部を超過し１質量部以下である
ことを特徴とする、請求項１または２に記載のポリウレタンゲル。
【請求項４】
前記多官能性脂肪族ポリイソシアネートが、イソシアヌレート誘導体を含有する
ことを特徴とする、請求項１～３のいずれか一項に記載のポリウレタンゲル。
【請求項５】
前記多官能性脂肪族ポリイソシアネートが、ペンタメチレンジイソシアネートの誘導体である
ことを特徴とする、請求項１～４のいずれか一項に記載のポリウレタンゲル。
【請求項６】
ポリウレタンと溶媒とを含有するポリウレタンゲルの製造方法であって、
平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有するポリイソシアネート成分と、２官能性ポリオールを８０質量％以上含有するポリオール成分と、ウレタン化触媒と、前記ポリウレタンゲルの総量に対して５０質量％以上９５質量％以下の溶媒とを配合する工程と、
それらを室温で反応させる工程と
を備えることを特徴とする、ポリウレタンゲルの製造方法。
【請求項７】
前記ウレタン化触媒の配合割合が、前記ポリイソシアネート成分および前記ポリオール成分の総量１００質量部に対して、０．１質量部を超過し１質量部以下である
ことを特徴とする、請求項６に記載のポリウレタンゲルの製造方法。
【請求項８】
前記ポリオール成分の水酸基に対する、前記ポリイソシアネート成分のイソシアネート基の当量比（ＮＣＯ／ＯＨ）が、０．７以上１未満である
ことを特徴とする、請求項６または７に記載のポリウレタンゲルの製造方法。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は、ポリウレタンゲルおよびその製造方法に関する。
【背景技術】
【０００２】
従来、香料、防虫剤、殺虫剤、抗菌剤、殺菌剤、忌避剤、農薬などの揮散性有効成分と、溶剤とが、ポリウレタンなどの樹脂中に内包されてなるゲル状物質が、提案されている。

【０００３】
このようなゲル状物質では、揮散性有効成分が徐々に樹脂から放出（揮散）されるため、揮散性有効成分の効果を長期間にわたって継続的に発現させることができる。
【０００４】
このようなゲル状物質としては、例えば、揮散性薬剤とポリウレタンとを含有するゲル状樹脂成形体組成物が提案されており、より具体的には、イソシアヌレート型ヘキサメチレンジイソシアネートと、ヒマシ油（グリセリルトリリシノレート）と、イソチオシアン酸アリル、薄荷油、ジャスミンオイルなどの揮散性薬剤とを種々の比率で配合し、ジブチル錫ジラウレートの存在下で反応させることにより、ポリウレタン樹脂のゲル状樹脂成形体組成物を得ることが、提案されている（例えば、特許文献１（表１～１３）参照。）。
【先行技術文献】
【特許文献】
【０００５】
【特許文献１】特開２００６－２６５５５８号公報
【発明の概要】
【発明が解決しようとする課題】
【０００６】
しかし、特許文献１に記載のゲル状樹脂成形体組成物では、ポリウレタン樹脂の原料としてヒマシ油（グリセリルトリリシノレート）が用いられている。そのため、ゲル状樹脂成形体組成物が変色し易く、透明性が十分ではない場合がある。
【０００７】
また、ポリウレタン樹脂の原料として上記のヒマシ油（グリセリルトリリシノレート）が用いられていると、ポリウレタン樹脂のネットワークが過度に強固になるため、ゲル状樹脂成形体組成物の触感（柔軟性、弾力）、デザイン性（透明感、潤い感、ぷるぷる感など）や、揮散性薬剤の吸収性および保持力が十分ではなく、また、揮散性薬剤の揮散性に劣る場合がある。
【０００８】
また、このようなゲル状樹脂成形体組成物としては、さらに、保型性（形状保持性）、耐熱性などが要求され、さらに、生産効率の観点から、速硬化性も要求される。
【０００９】
本発明の目的は、透明性に優れ、また、触感、デザイン性、吸収性、保持力および揮散性に優れ、さらには、保型性、耐熱性および速硬化性に優れるポリウレタンゲル、および、その製造方法を提供することにある。
【課題を解決するための手段】
【００１０】
本発明［１］は、平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有するポリイソシアネート成分と、２官能性ポリオールを８０質量％以上含有するポリオール成分との反応生成物と、溶媒とを含有するポリウレタンゲルであって、前記溶媒の含有割合は、前記ポリウレタンゲルの総量に対して、５０質量％以上９５質量％以下である、ポリウレタンゲルを含んでいる。
【００１１】
本発明［２］は、前記２官能性ポリオールが、ポリエーテルジオールである、上記［１］に記載のポリウレタンゲルを含んでいる。
【００１２】
本発明［３］は、前記ポリウレタンゲルがウレタン化触媒を含有し、前記ウレタン化触媒の含有割合が、前記ポリイソシアネート成分および前記ポリオール成分の総量１００質量部に対して、０．１質量部を超過し１質量部以下である、上記［１］または［２］に記載のポリウレタンゲルを含んでいる。
【００１３】
本発明［４］は、前記多官能性脂肪族ポリイソシアネートが、イソシアヌレート誘導体

を含有する、上記［１］～［３］のいずれか一項に記載のポリウレタンゲルを含んでいる。

【００１４】

本発明［５］は、前記多官能性脂肪族ポリイソシアネートが、ペンタメチレンジイソシアネートの誘導体である、上記［１］～［４］のいずれか一項に記載のポリウレタンゲルを含んでいる。

【００１５】

本発明［６］は、ポリウレタンと溶媒とを含有するポリウレタンゲルの製造方法であって、平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有するポリイソシアネート成分と、２官能性ポリオールを８０質量％以上含有するポリオール成分と、ウレタン化触媒と、前記ポリウレタンゲルの総量に対して５０質量％以上９５質量％以下の溶媒とを配合する工程と、それらを室温で反応させる工程とを備える、ポリウレタンゲルの製造方法を含んでいる。

【００１６】

本発明［７］は、前記ウレタン化触媒の配合割合が、前記ポリイソシアネート成分および前記ポリオール成分の総量１００質量部に対して、０．１質量部を超過し１質量部以下である、上記［６］に記載のポリウレタンゲルの製造方法を含んでいる。

【００１７】

本発明［８］は、前記ポリオール成分の水酸基に対する、前記ポリイソシアネート成分のイソシアネート基の当量比（ＮＣＯ／ＯＨ）が、０．７以上１未満である、上記［６］または［７］に記載のポリウレタンゲルの製造方法を含んでいる。

【発明の効果】

【００１８】

本発明のポリウレタンゲルは、平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有するポリイソシアネート成分と、２官能性ポリオールを８０質量％以上含有するポリオール成分とが反応してなり、また、特定割合で溶媒を含有するため、透明性に優れ、また、触感（柔軟性、弾力）、デザイン性（透明感、潤い感、ぷるぷる感など）、吸収性、保持力および揮散性に優れ、さらには、保型性、耐熱性および速硬化性に優れる。

【００１９】

また、本発明のポリウレタンゲルの製造方法によれば、透明性に優れ、また、触感、デザイン性、吸収性、保持力および揮散性に優れ、さらには、保型性、耐熱性および速硬化性に優れるポリウレタンゲルを、得ることができる。

【発明を実施するための形態】

【００２０】

本発明のポリウレタンゲルは、ポリイソシアネート成分とポリオール成分との反応生成物であるポリウレタン（分散質）と、溶媒（分散媒）とを含有し、ポリウレタンの３次元ネットワークにより、高い粘性を有し、溶媒がポリウレタン中に内包されることにより流動性を失い、系全体としては固体状となっているものである。

【００２１】

ポリウレタンゲルの２５℃における剪断弾性率は、1×10^{3}～1×10^{7}Ｐａである。剪断弾性率は、固体粘弾性測定装置により測定される。

【００２２】

なお、以下において、ポリイソシアネート成分の官能基とは、イソシアネート基を示し、ポリオール成分の官能基とは、水酸基を示す。

【００２３】

ポリイソシアネート成分は、必須成分として、多官能性脂肪族ポリイソシアネートを含有しており、具体的には、平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有している。

【００２４】

平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートとしては、例えば、脂肪族ジイソシアネート（２官能性モノマー）の誘導体が挙げられる。

【００２５】
すなわち、多官能性脂肪族ポリイソシアネートとして、具体的には、平均官能基数が上記の特定範囲となるように脂肪族ジイソシアネート（２官能性モノマー）を変性して得られる誘導体が挙げられる。
【００２６】
脂肪族ジイソシアネート（２官能性モノマー）としては、例えば、１，３－トリメチレンジイソシアネート、１，２－プロピレンジイソシアネート、１，４－ブチレンジイソシアネート、１，５－ペンタメチレンジイソシアネート（ＰＤＩ）、１，６－ヘキサメチレンジイソシアネート（ＨＤＩ）、２，４，４－または２，２，４－トリメチルヘキサメチレンジイソシアネート、２，６－ジイソシアネートメチルカプエートなどが挙げられる。
【００２７】
これら脂肪族ジイソシアネート（２官能性モノマー）は、単独使用または２種類以上併用することができる。
【００２８】
脂肪族ジイソシアネートとして、透明性の向上を図る観点から、好ましくは、１，５－ペンタメチレンジイソシアネート（ＰＤＩ）、１，６－ヘキサメチレンジイソシアネート（ＨＤＩ）が挙げられ、さらに、保型性、耐熱性および速硬化性の向上を図る観点から、より好ましくは、１，５－ペンタメチレンジイソシアネート（ＰＤＩ）が挙げられる。換言すれば、脂肪族ジイソシアネートとして、１，５－ペンタメチレンジイソシアネート（ＰＤＩ）を用いれば、透明性に優れ、さらには、速硬化性に優れるポリウレタンゲルを得ることができる。
【００２９】
脂肪族ジイソシアネートの誘導体は、平均官能基数が上記の特定範囲となるように、上記の脂肪族ジイソシアネートを公知の方法で変性することにより、得ることができる。
【００３０】
脂肪族ジイソシアネートの誘導体としては、例えば、脂肪族ジイソシアネートの３量体（例えば、イソシアヌレート誘導体、イミノオキサジアジンジオン誘導体など）、アロファネート誘導体（例えば、上記した脂肪族ジイソシアネートと２価アルコール（後述）とをアロファネート化触媒存在下で反応させることにより生成するアロファネート誘導体など。）、ビウレット誘導体（例えば、上記した脂肪族ジイソシアネートと、水やアミン類との反応により生成するビウレット誘導体など。）、オキサジアジントリオン誘導体（例えば、上記した脂肪族ジイソシアネートと炭酸ガスとの反応により生成するオキサジアジントリオン誘導体など。）、ウレトンイミン誘導体、ポリオール誘導体（例えば、上記した脂肪族ジイソシアネートと３価以上のポリオール（好ましくは、トリメチロールプロパンなどの３価アルコール（後述））との反応より生成するポリオール誘導体（アルコール付加体）などが挙げられ、好ましくは、脂肪族ジイソシアネートの３量体が挙げられ、より好ましくは、脂肪族ジイソシアネートのイソシアヌレート誘導体が挙げられる。
【００３１】
脂肪族ジイソシアネートのイソシアヌレート誘導体は、例えば、脂肪族ジイソシアネートを、公知のイソシアヌレート化触媒（例えば、Ｎ－（２－ヒドロキシプロピル）－Ｎ，Ｎ，Ｎ－トリメチルアンモニウム－２－エチルヘキサノエートなど）の存在下において反応させ、３量化反応させることにより、得ることができる。
【００３２】
なお、３量化反応における反応条件は、特に制限されず、適宜設定される。
【００３３】
また、脂肪族ジイソシアネートのイソシアヌレート誘導体は、必要により、アルコール類により変性される。

【００３４】
アルコール類としては、特に制限されないが、例えば、脂肪族アルコール、芳香族アルコールなどが挙げられ、好ましくは、脂肪族アルコールが挙げられ、具体的には、例えば、メタノール、エタノール、ｎ－プロパノール、イソプロパノール、ｎ－ブタノール、イソブタノール（別名：イソブチルアルコール）、ｓｅｃ－ブタノール、ｔｅｒｔ－ブタノール、ペンタノール、ヘキサノール、２－エチルヘキサノール、オクタノール、デカノールなどの１価脂肪族アルコール、例えば、エチレングリコール、１，２－プロパンジオール、１，３－プロパンジオール、１，３－ブチレングリコール、１，４－ブチレングリコール、１，５－ペンタンジオール、１，６－ヘキサンジオールなどの２価脂肪族アルコール、例えば、グリセリン、トリメチロールプロパンなどの３価脂肪族アルコール、例えば、テトラメチロールメタンなどの４価以上の脂肪族アルコールなどが挙げられる。
【００３５】
また、アルコール類としては、例えば、分子量２５０～３０００のポリエステルポリオール、ポリエーテルポリオール、ポリカーボネートポリオールなども挙げられる。
【００３６】
これらアルコール類は、単独使用または２種類以上併用することができる。アルコール類として、好ましくは、１価脂肪族アルコールが挙げられ、より好ましくは、炭素数１～４の１価脂肪族アルコールが挙げられ、さらに好ましくは、イソブタノール（別名：イソブチルアルコール）が挙げられる。
【００３７】
脂肪族ジイソシアネートのイソシアヌレート誘導体を、アルコール類により変性する方法としては、例えば、まず、脂肪族ジイソシアネートとアルコール類とを反応させ、次いで、イソシアヌレート化触媒の存在下にイソシアヌレート化反応させる方法や、例えば、まず、脂肪族ジイソシアネートのみをイソシアヌレート化した後、得られたポリイソシアヌレートとアルコール類とを反応させる方法などが挙げられる。
【００３８】
好ましくは、まず、脂肪族ジイソシアネートとアルコール類とを反応させ、次いで、イソシアヌレート化触媒の存在下にイソシアヌレート化反応させる。
【００３９】
このような反応において、脂肪族ジイソシアネートとアルコール類との配合割合は、目的および用途に応じて、適宜設定されるが、脂肪族ジイソシアネート１００質量部に対して、アルコール類が、例えば、０．０５質量部以上、好ましくは、０．１質量部以上であり、また、例えば、１０質量部以下、好ましくは、５質量部以下である。
【００４０】
また、脂肪族ジイソシアネートとアルコール類との反応条件は、目的および用途に応じて、適宜設定される。また、イソシアネート基（ウレタン化後の残存イソシアネート基）の転化率（アロファネート基またはトリマー基への転化率）が、所定の割合（例えば、５～２０％）に達した時点で、例えば、リン酸、モノクロル酢酸、塩化ベンゾイル、ドデシルベンゼンスルホン酸、オルトトルエンスルホン酸、パラトルエンスルホン酸などの反応停止剤を反応液に添加して、触媒を失活させて反応を停止させることもできる。
【００４１】
なお、脂肪族ジイソシアネートとアルコール類との反応は、ウレタン化反応およびアロファネート化反応であり、脂肪族ジイソシアネートのアロファネート誘導体が、副生成物として生成する場合がある。すなわち、アルコール類により変性された脂肪族ジイソシアネートのイソシアヌレート誘導体は、イソシアヌレート基と、アロファネート基とを併有する場合がある。
【００４２】
そのような場合、アロファネート基のモル比率は、イソシアヌレート基のモル比率より少なく、具体的には、イソシアヌレート基１モルに対して、アロファネート基が、例えば、０．０５モル以上であり、例えば、１．０モル未満、好ましくは，０．５モル以下であ

る。
【００４３】
アロファネート基のモル比率が上記範囲であれば、耐熱性の向上を図ることができる。
【００４４】
なお、アロファネート基とイソシアヌレート基とのモル比率は、後述する実施例に準拠して求めることができる。
【００４５】
さらに、多官能性脂肪族ポリイソシアネートとしては、上記の他、例えば、３官能性の脂肪族ポリイソシアネートモノマーが挙げられる。３官能性の脂肪族ポリイソシアネートモノマーとしては、例えば、１，６，１１－ウンデカメチレントリイソシアネート、１，３，６－ヘキサメチレントリイソシアネート、１，８－ジイソシアネート－４－イソシアナトメチルオクタン、２，５，７－トリメチル－１，８－ジイソシアネート－５－イソシアナトメチルオクタン、リシントリイソシアネートなどの脂肪族トリイソシアネートなどが挙げられる。
【００４６】
これら多官能性脂肪族ポリイソシアネートは、単独使用または２種類以上併用することができる。
【００４７】
多官能性脂肪族ポリイソシアネートは、耐熱性の向上を図る観点から、好ましくは、脂肪族ジイソシアネートのイソシアヌレート誘導体、より好ましくは、ペンタメチレンジイソシアネートのイソシアヌレート誘導体の単独使用が挙げられる（ただし、イソシアヌレート誘導体の製造時に副生するアロファネート誘導体およびウレトジオン誘導体の含有を許容する。）。
【００４８】
多官能性脂肪族ポリイソシアネートの平均官能基数は、２．０を超過し、好ましくは、２．５以上、より好ましくは、２．８以上、さらに好ましくは、３．０以上であり、また、３．５以下、好ましくは、３．３以下である。
【００４９】
多官能性脂肪族ポリイソシアネートの平均官能基数は、後述する実施例に準拠して算出される。
【００５０】
多官能性脂肪族ポリイソシアネートの平均官能基数を上記の範囲とすることにより、後述するように、ポリオール成分と相まってポリウレタンに適度な３次元ネットワークを形成することができる。
【００５１】
なお、また、多官能性脂肪族ポリイソシアネートは、本発明の優れた効果を阻害しない範囲で、官能基数が２．０以下の脂肪族ポリイソシアネートや、官能基数が３．５を超過する脂肪族ポリイソシアネートを含有することができる。このような場合も、多官能性脂肪族ポリイソシアネートの平均官能基数は、上記の範囲に調整される。
【００５２】
また、ポリイソシアネート成分は、任意成分として、上記した平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネート以外のポリイソシアネート（以下、その他のポリイソシアネートと称する。）を含有することができる。
【００５３】
その他のポリイソシアネートとしては、例えば、芳香族ポリイソシアネート、芳香脂肪族ポリイソシアネート、脂環族ポリイソシアネートなどのポリイソシアネートモノマー（すなわち、脂肪族ポリイソシアネート以外のポリイソシアネートモノマー）が挙げられる。
【００５４】
芳香族ポリイソシアネートとしては、例えば、トリレンジイソシアネート（２，４－ま

たは２，６－トリレンジイソシアネートもしくはその混合物）（ＴＤＩ）、フェニレンジイソシアネート（ｍ－、ｐ－フェニレンジイソシアネートもしくはその混合物）、４，４’－ジフェニルジイソシアネート、１，５－ナフタレンジイソシアネート（ＮＤＩ）、ジフェニルメタンジイソシネート（４，４’－、２，４’－または２，２’－ジフェニルメタンジイソシネートもしくはその混合物）（ＭＤＩ）、４，４’－トルイジンジイソシアネート（ＴＯＤＩ）、４，４’－ジフェニルエーテルジイソシアネートなどの芳香族ジイソシアネートなどが挙げられる。

【００５５】

芳香脂肪族ポリイソシアネートとしては、例えば、キシリレンジイソシアネート（１，３－または１，４－キシリレンジイソシアネートもしくはその混合物）（ＸＤＩ）、テトラメチルキシリレンジイソシアネート（１，３－または１，４－テトラメチルキシリレンジイソシアネートもしくはその混合物）（ＴＭＸＤＩ）、ω，ω’－ジイソシアネート－１，４－ジエチルベンゼンなどの芳香脂肪族ジイソシアネートなどが挙げられる。

【００５６】

脂環族ポリイソシアネートとしては、例えば、１，３－シクロペンタンジイソシアネート、１，３－シクロペンテンジイソシアネート、シクロヘキサンジイソシアネート（１，４－シクロヘキサンジイソシアネート、１，３－シクロヘキサンジイソシアネート）、３－イソシアナトメチル－３，５，５－トリメチルシクロヘキシルイソシアネート（イソホロンジイソシアネート）（ＩＰＤＩ）、メチレンビス（シクロヘキシルイソシアネート）（４，４’－、２，４’－または２，２’－メチレンビス（シクロヘキシルイソシアネート、これらのＴｒａｎｓ，Ｔｒａｎｓ－体、Ｔｒａｎｓ，Ｃｉｓ－体、Ｃｉｓ，Ｃｉｓ－体、もしくはその混合物））（H_{12}ＭＤＩ）、メチルシクロヘキサンジイソシアネート（メチル－２，４－シクロヘキサンジイソシアネート、メチル－２，６－シクロヘキサンジイソシアネート）、ノルボルナンジイソシアネート（各種異性体もしくはその混合物）（ＮＢＤＩ）、ビス（イソシアナトメチル）シクロヘキサン（１，３－または１，４－ビス（イソシアナトメチル）シクロヘキサンもしくはその混合物）（H_6ＸＤＩ）などの脂環族ジイソシアネートなどが挙げられる。

【００５７】

また、その他のポリイソシアネートとしては、上記したポリイソシアネートモノマー（すなわち、脂肪族ポリイソシアネート以外のポリイソシアネートモノマー）の誘導体も挙げられる。そのような誘導体としては、例えば、ポリイソシアネートモノマーの多量体（例えば、２量体、３量体（例えば、イソシアヌレート変性体、イミノオキサジアジンジオン変性体）、５量体、７量体など）、アロファネート誘導体、ビウレット誘導体、オキサジアジントリオン誘導体、ウレトンイミン誘導体などが挙げられる。

【００５８】

これらその他のポリイソシアネートは、単独使用または２種類以上併用することができる。

【００５９】

その他のポリイソシアネートの含有割合は、本発明の優れた効果を損なわない観点から、ポリイソシアネート成分の総量に対して、例えば、５０質量％未満、好ましくは、３０質量％以下、より好ましくは、１０質量％以下、さらに好ましくは、５質量％以下、とりわけ好ましくは、０質量％である。

【００６０】

すなわち、ポリイソシアネート成分は、好ましくは、その他のポリイソシアネートを含有せず、平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを単独で含有する。

【００６１】

ポリイソシアネート成分の平均官能基数は、例えば、２．０を超過し、好ましくは、２．５以上、より好ましくは、２．８以上、さらに好ましくは、３．０以上であり、また、例えば、３．５以下、好ましくは、３．３以下である。

【００６２】
また、ポリイソシアネート成分のイソシアネート基濃度は、例えば、２０．０質量％以上、好ましくは、２３．０質量％以上であり、例えば、３０．０質量％以下、好ましくは、２５．０質量％以下、より好ましくは、２４．６質量％以下である。
【００６３】
ポリオール成分は、必須成分として、２官能性ポリオールを特定割合（後述）で含有する。
【００６４】
本発明では、ポリイソシアネート成分の平均官能基数が上記の範囲である一方、ポリオール成分が２官能性ポリオールを特定割合（後述）で含有するため、得られるポリウレタンが適度なネットワークを形成し、後述するように、溶媒を比較的多く含有することができる。そのため、本発明によれば、優れた触感（柔軟性、弾力）およびデザイン性（透明感、潤い感、ぷるぷる感など）と、優れた保型性を両立することができ、また、溶媒の揮散性に優れ、さらには、溶媒の揮散に伴うポリウレタンゲルの収縮性にも優れる。
【００６５】
２官能性ポリオールとしては、例えば、低分子量ジオール、高分子量ジオールが挙げられる。
【００６６】
低分子量ジオールは、水酸基を２つ有する数平均分子量４００未満、４０以上の化合物であって、具体的には、例えば、エチレングリコール、プロピレングリコール（１，２－プロパンジオール）、１，３－プロパンジオール、１，４－ブチレングリコール、１，３－ブチレングリコール、１，２－ブチレングリコール、１，５－ペンタンジオール、１，６－ヘキサンジオール、ネオペンチルグリコール、３－メチル－１，５－ペンタンジオール、２，２，２－トリメチルペンタンジオール、３，３－ジメチロールヘプタン、アルカン（Ｃ７～２０）ジオール、１，３－または１，４－シクロヘキサンジメタノールおよびそれらの混合物、１，３－または１，４－シクロヘキサンジオールおよびそれらの混合物、水素化ビスフェノールＡ、１，４－ジヒドロキシ－２－ブテン、２，６－ジメチル－１－オクテン－３，８－ジオール、ビスフェノールＡ、ジエチレングリコール、トリエチレングリコール、ジプロピレングリコールなどの２価アルコールなどが挙げられる。
【００６７】
これら低分子量ジオールは、単独使用または２種類以上併用することができる。
【００６８】
高分子量ジオールは、水酸基を２つ有する数平均分子量４００以上、１００００以下の化合物であって、例えば、ポリエーテルジオール、ポリエステルジオール、ポリカーボネートジオールなどが挙げられる。
【００６９】
ポリエーテルジオールとしては、例えば、ポリオキシアルキレンジオール、ポリテトラメチレンエーテルグリコール、ポリトリメチレンエーテルグリコールなどが挙げられる。
【００７０】
ポリオキシアルキレンジオールとしては、上記した２価アルコールを開始剤とする、エチレンオキサイド、プロピレンオキサイドなどのアルキレンオキサイドの付加重合物（２種以上のアルキレンオキサイドのランダムおよび／またはブロック共重合体を含む。）が挙げられる。より具体的には、例えば、ポリエチレングリコール、ポリプロピレングリコール、ポリオキシエチレン・ポリオキシプロピレン（ランダムおよび／またはブロック）共重合体などが挙げられる。
【００７１】
ポリテトラメチレンエーテルグリコールとしては、例えば、テトラヒドロフランのカチオン重合により得られる開環重合物や、テトラヒドロフランの重合単位に上記した２価アルコールを共重合した非晶性ポリテトラメチレンエーテルグリコール（平均官能基数２）などが挙げられる。

【００７２】
非晶性ポリテトラメチレンエーテルグリコールは、例えば、テトラヒドロフランと、アルキル置換テトラヒドロフラン（例えば、３－メチルテトラヒドロフランなど）との共重合体（テトラヒドロフラン／アルキル置換テトラヒドロフラン（モル比）＝１５／８５～８５／１５、数平均分子量５００～４０００、好ましくは、８００～２５００）や、例えば、テトラヒドロフランと、分岐状グリコール（例えば、ネオペンチルグリコールなど）との共重合体（テトラヒドロフラン／分岐状グリコール（モル比）＝１５／８５～８５／１５、数平均分子量５００～４０００、好ましくは、８００～２５００）などとして、得ることができる。
【００７３】
なお、非晶性（非結晶性）とは、常温（２５℃）において液状であることを示す（以下同様）。
【００７４】
また、フルフラールなどの植物由原料をもとに製造されたテトラヒドロフランを出発原料とした植物由来のポリテトラメチレンエーテルグリコールも使用することができる。
【００７５】
ポリトリメチレンエーテルグリコールとしては、例えば、植物由来の１，３－プロパンジオールの縮重合により製造されるポリオールが挙げられる。
【００７６】
ポリエステルジオールは、ジカルボン酸と、上記した２価アルコールとの縮合反応や、ジカルボン酸のアルキルエステルと、上記した２価アルコールとのエステル交換反応により得ることができる。
【００７７】
ジカルボン酸としては、例えば、シュウ酸、マロン酸、コハク酸、メチルコハク酸、グルタール酸、アジピン酸、１，１－ジメチル－１，３－ジカルボキシプロパン、３－メチル－３－エチルグルタール酸、アゼライン酸、セバシン酸、その他の飽和脂肪族ジカルボン酸（炭素数１１～１３）、例えば、マレイン酸、フマル酸、イタコン酸、その他の不飽和脂肪族ジカルボン酸、例えば、オルソフタル酸、イソフタル酸、テレフタル酸、トルエンジカルボン酸、ナフタレンジカルボン酸、その他の芳香族ジカルボン酸、例えば、ヘキサヒドロフタル酸、その他の脂環族ジカルボン酸、例えば、ダイマー酸、水添ダイマー酸、ヘット酸などのその他のカルボン酸などが挙げられる。さらには、ジカルボン酸から誘導される酸無水物、例えば、無水シュウ酸、無水コハク酸、無水メチルコハク酸、無水マレイン酸、無水フタル酸、無水ヘキサヒドロフタル酸、または、これらのジカルボン酸から誘導される酸ハライド、例えば、シュウ酸ジクロライド、アジピン酸ジクロライド、セバシン酸ジクロライドなどが挙げられる。
【００７８】
また、ジカルボン酸のアルキルエステルとしては、例えば、上記したジカルボン酸のＣ１～４アルキルエステルが挙げられる。
【００７９】
ポリカーボネートジオールとしては、例えば、上記した２価アルコールを開始剤とするエチレンカーボネートの開環重合物や、例えば、１，４－ブタンジオール、１，５－ペンタンジオール、３－メチル－１，５－ペンタンジオールや１，６－ヘキサンジオールなどの２価アルコールと、開環重合物とを共重合した非晶性ポリカーボネートジオールなどが挙げられる。
【００８０】
また、ポリカーボネートジオールとして、例えば、植物由来のポリカーボネートジオールが挙げられ、具体的には、植物由来原料であるグルコースなどから誘導されたイソソルビドなどの脂環式ジヒドロキシ化合物や、上記した２価アルコールを、炭酸ジフェニルとエステル交換反応させて得られるポリカーボネートジオールなどが挙げられる。
【００８１】

これら高分子量ジオールは、単独使用または２種類以上併用することができる。

【００８２】

ポリウレタンゲルの製造時における溶媒との相溶性の観点から、好ましくは、非晶性の高分子量ジオールが挙げられ、より好ましくは、ポリオキシアルキレングリコール、非晶性ポリテトラメチレンエーテルグリコール、非晶性ポリカーボネートジオール、ポリエステルポリオールが挙げられる。

【００８３】

また、耐熱性および透明性の向上を図る観点から、好ましくは、ポリエーテルジオールが挙げられ、より好ましくは、ポリテトラメチレンエーテルグリコールが挙げられ、さらに好ましくは、非晶性ポリテトラメチレンエーテルグリコールが挙げられる。

【００８４】

これら２官能性ポリオールは、単独使用または２種類以上併用することができる。

【００８５】

２官能性ポリオールとして、好ましくは、高分子量ジオールが挙げられる。

【００８６】

また、ポリオール成分は、任意成分として、その他のポリオール（３官能性以上のポリオール）や、モノオールを含有することができる。

【００８７】

その他のポリオール（３官能性以上のポリオール）としては、３官能性以上の低分子量ポリオール、３官能性以上の高分子量ポリオールが挙げられる。

【００８８】

３官能性以上の低分子量ポリオールは、水酸基を３つ以上有する数平均分子量４００未満、４０以上の化合物であって、具体的には、例えば、グリセリン、トリメチロールプロパン、トリイソプロパノールアミンなどの３価アルコール、例えば、テトラメチロールメタン（ペンタエリスリトール）、ジグリセリンなどの４価アルコール、例えば、キシリトールなどの５価アルコール、例えば、ソルビトール、マンニトール、アリトール、イジトール、ダルシトール、アルトリトール、イノシトール、ジペンタエリスリトールなどの６価アルコール、例えば、ペルセイトールなどの７価アルコール、例えば、ショ糖などの８価アルコールなどが挙げられる。

【００８９】

これら３官能性以上の低分子量ポリオールは、単独使用または２種類以上併用することができる。

【００９０】

３官能性以上の高分子量ポリオールは、水酸基を３つ以上有する数平均分子量４００以上、１００００以下の化合物であって、例えば、ポリエーテルトリオール（上記３価アルコールを開始剤とした炭素数２～３のアルキレンオキサイドの付加重合体など）、ポリエーテルテトラオール（上記４価アルコールを開始剤とした炭素数２～３のアルキレンオキサイドの付加重合体など）、ポリエステルトリオール（２塩基酸および／またはそのアルキルエステルと、上記３価アルコール（および２価アルコール）との反応生成物など）、ポリエステルテトラオール（２塩基酸および／またはそのアルキルエステルと、上記４価アルコール（および２～３価アルコール）との反応生成物など）、ポリカーボネートトリオール（上記３価アルコールを開始剤とするエチレンカーボネートの開環重合物など）、ポリカーボネートテトラオール（上記４価アルコールを開始剤とするエチレンカーボネートの開環重合物など）などが挙げられる。

【００９１】

これら３官能性以上の高分子量ポリオールは、単独使用または２種類以上併用することができる。

【００９２】

モノオールとしては、例えば、メタノール、エタノール、プロパノール、イソプロパノール、ブタノール、イソブタノール、ｓ－ブタノール、ｔ－ブタノール、ペンタノール、

ヘキサノール、ヘプタノール、オクタノールなどの１価アルコールが挙げられる。
【００９３】
また、モノオールとしては、例えば、上記した高分子量ジオールの片末端の水酸基がアルキルエステル基に置換されたモノアルキルエステルや、例えば、上記した高分子量ジオールの片末端の水酸基がアルキルエーテル基に置換されたモノアルキルエーテル（例えば、ポリオキシエチレンモノアルキルエーテルなど）が挙げられる。
【００９４】
これらモノオールは、単独使用または２種類以上併用することができる。
【００９５】
ポリオール成分において、２官能性ポリオールの含有割合は、透明性、触感、デザイン性、吸収性、保持力、揮散性、保型性、耐熱性および速硬化性の向上を図る観点から、ポリオール成分の総量に対して、８０質量％以上、好ましくは、８５質量％以上、より好ましくは、９０質量％以上、さらに好ましくは、９５質量％以上、とりわけ好ましくは、１００質量％である。
【００９６】
すなわち、ポリオール成分は、好ましくは、３官能性以上のポリオールおよびモノオールを含有せず、２官能性ポリオールを単独で含有する。
【００９７】
ポリオール成分の平均官能基数は、３．０以下、好ましくは、２．５以下であり、通常、２．０以上である。ポリオールの平均官能基数として、とりわけ好ましくは、２．０である。
【００９８】
また、ポリオール成分の水酸基価（ＯＨ価）は、例えば、１０ｍｇＫＯＨ／ｇ以上、好ましくは、１２ｍｇＫＯＨ／ｇ以上、より好ましくは、１５ｍｇＫＯＨ／ｇ以上であり、例えば、１５０ｍｇＫＯＨ／ｇ以下、好ましくは、１２０ｍｇＫＯＨ／ｇ以下、より好ましくは、１００ｍｇＫＯＨ／ｇ以下である。
【００９９】
なお、ポリオール成分の平均官能基数は、仕込みの配合処方から算出され、ポリオールの水酸基価は、ＪＩＳ　Ｋ　１５５７－１（２００７年）の記載に準拠して測定される。
【０１００】
そして、ポリウレタンゲルは、上記のポリイソシアネート成分と上記のポリオール成分とがウレタン化触媒および溶媒の存在下においてウレタン化反応した反応生成物として得られる。
【０１０１】
ポリウレタンゲルの製造方法として、より具体的には、まず、上記したポリイソシアネート成分と、上記したポリオール成分と、ウレタン化触媒と、溶媒とを配合する（配合工程）。
【０１０２】
より具体的には、この工程では、ポリイソシアネート成分と、ポリオール成分と、ウレタン化触媒と、溶媒とを、順次配合するのではなく、一括で配合する。
【０１０３】
ポリイソシアネート成分およびポリオール成分の配合割合は、ポリオール成分の水酸基に対する、ポリイソシアネート成分のイソシアネート基の当量比（ＮＣＯ／ＯＨ）が、例えば、０．６以上、好ましくは、０．７以上、より好ましくは、０．７５以上、さらに好ましくは、０．８以上であり、例えば、１．２以下、好ましくは、１以下、比較的緩いネットワークを形成して、より多くの溶媒をポリウレタン中に内包する観点から、より好ましくは、１未満、より好ましくは、０．９５以下、さらに好ましくは、０．９以下である。
【０１０４】
ウレタン化触媒としては、公知のウレタン化触媒が挙げられ、具体的には、アミン類、

有機金属化合物、カリウム塩が挙げられる。
【０１０５】
アミン類としては、例えば、トリエチルアミン、トリエチレンジアミン、ビス－（２－ジメチルアミノエチル）エーテル、Ｎ－メチルモルホリンなどの３級アミン類、例えば、テトラエチルヒドロキシルアンモニウムなどの４級アンモニウム塩、例えば、イミダゾール、２－エチル－４－メチルイミダゾールなどのイミダゾール類などが挙げられる。
【０１０６】
有機金属化合物としては、例えば、酢酸錫、オクチル酸錫、オレイン酸錫、ラウリル酸錫、ジブチル錫ジアセテート、ジメチル錫ジラウレート、ジブチル錫ジラウレート、ジブチル錫ジメルカプチド、ジブチル錫マレエート、ジブチル錫ジラウレート（ジラウリン酸ジブチル錫（ＩＶ））、ジブチル錫ジネオデカノエート、ジオクチル錫ジメルカプチド、ジオクチル錫ジラウリレート、ジブチル錫ジクロリドなどの有機錫化合物、例えば、オクタン酸鉛、ナフテン酸鉛などの有機鉛化合物、例えば、ナフテン酸ニッケルなどの有機ニッケル化合物、例えば、ナフテン酸コバルトなどの有機コバルト化合物、例えば、オクテン酸銅などの有機銅化合物、例えば、オクチル酸ビスマス、ネオデカン酸ビスマスなどの有機ビスマス化合物などが挙げられる。
【０１０７】
カリウム塩としては、例えば、炭酸カリウム、酢酸カリウム、オクチル酸カリウムなどが挙げられる。
【０１０８】
これらウレタン化触媒は、単独使用または２種類以上併用することができる。
【０１０９】
ウレタン化触媒として、好ましくは、有機金属化合物が挙げられ、より好ましくは、有機錫化合物が挙げられ、とりわけ好ましくは、ジブチル錫ジラウレートが挙げられる。
【０１１０】
ウレタン化触媒の配合割合は、室温での反応性の向上を図る観点から、通常のポリウレタン製造における配合割合よりも相対的に多く、具体的には、ポリイソシアネート成分およびポリオール成分の総量１００質量部に対して、例えば、０．０５質量部以上、好ましくは、０．１質量部を超過し、より好ましくは、０．２質量部以上であり、例えば、１．５質量部以下、好ましくは、１質量部以下、より好ましくは、０．５質量部以下である。
【０１１１】
溶媒としては、例えば、アセトン、メチルエチルケトン、メチルイソブチルケトン、シクロヘキサノンなどのケトン類、例えば、アセトニトリルなどのニトリル類、酢酸メチル、酢酸エチル、酢酸ブチル、酢酸イソブチル、乳酸メチルなどのアルキルエステル類、例えば、ｎ－ヘキサン、ｎ－ヘプタン、オクタンなどの脂肪族炭化水素類、例えば、シクロヘキサン、メチルシクロヘキサンなどの脂環族炭化水素類、例えば、トルエン、キシレン、エチルベンゼンなどの芳香族炭化水素類、例えば、メチルセロソルブアセテート、エチルセロソルブアセテート、メチルカルビトールアセテート、エチルカルビトールアセテート、エチレングリコールメチルエーテルアセテート、エチレングリコールエチルエーテルアセテート、プロピレングリコールメチルエーテルアセテート（ＰＭＡ）、３－メチル－３－メトキシブチルアセテート、ジプロピレングリコールメチルエーテルアセテート、プロピレングリコールジアセテート、エチル－３－エトキシプロピオネートなどのグリコールエーテルエステル類、例えば、ジエチルエーテル、テトラヒドロフラン、ジオキサン、１，２－ジメトキシエタン、ジエチレングリコールジメチルエーテル、ジエチレングリコールジエチルエーテル、ジプロピレングリコールジメチルエーテル、ジプロピレングリコールジエチルエーテル、エチレングリコールジエチルエーテル１，２－ジエトキシエタン、１，８－シネオール、バニリン、エチルバニリンなどのエーテル類、例えば、塩化メチル、塩化メチレン、クロロホルム、四塩化炭素、臭化メチル、ヨウ化メチレン、ジクロロエタンなどのハロゲン化脂肪族炭化水素類、例えば、Ｎ－メチルピロリドン、Ｎ，Ｎ’－ジメチルホルムアミド、Ｎ，Ｎ’－ジメチルアセトアミド、ジメチルスルホキシド、ヘキ

サメチルホスホニルアミドなどの極性非プロトン類、さらには、植物油脂、天然由来油脂などが挙げられる。

【０１１２】

これら溶媒は、単独使用または２種類以上併用することもできる。

【０１１３】

溶媒として、揮散性の観点から、好ましくは、グリコールエーテルエステル類、エーテル類が挙げられ、より好ましくは、グリコールエーテルエステル類が挙げられる。

【０１１４】

溶剤の配合割合は、得られるポリウレタンゲルの総量に対して、透明性、触感、デザイン性および揮散性の向上を図る観点から、ポリウレタンゲルにより多く含まれることが好ましく、具体的には、５０質量％以上、好ましくは、５０質量％を超過し、より好ましくは、７０質量％以上であり、触感、デザイン性、吸収性、保持力、揮散性、保型性、耐熱性および速硬化性の向上を図る観点から、９５質量％以下、好ましくは、９３質量％以下、より好ましくは、９０質量％以下である。

【０１１５】

次いで、この方法では、上記のように配合されたポリイソシアネート成分およびポリオール成分を、ウレタン化触媒および溶媒の存在下、ウレタン化反応させる（反応工程）。

【０１１６】

より具体的には、ウレタン化反応における反応温度は、溶媒の揮発を抑制する観点から、室温（加熱することのない室内環境雰囲気温度）であり、例えば、１５℃以上、好ましくは、１８℃以上であり、例えば、３５℃以下、好ましくは、３０℃以下である。また、反応時間が、例えば、２時間以上、好ましくは、４時間以上であり、例えば、４８時間以下、好ましくは、２４時間以下である。

【０１１７】

これにより、ポリイソシアネート成分およびポリオール成分の反応により得られるポリウレタンのネットワーク中に、溶媒が内包されるポリウレタンゲルが得られる。

【０１１８】

得られるポリウレタンゲルにおいて、溶媒の含有割合は、ポリウレタンゲルの総量に対して、５０質量％以上、好ましくは、５０質量％を超過し、より好ましくは、７０質量％以上であり、９５質量％以下、好ましくは、９３質量％以下、より好ましくは、９０質量％以下である。

【０１１９】

溶媒の含有割合が上記範囲であれば、透明性に優れ、また、触感、デザイン性、吸収性、保持力および揮散性に優れ、さらには、保型性、耐熱性および速硬化性に優れるポリウレタンゲルが得られる。

【０１２０】

また、得られるポリウレタンゲルにおいて、ウレタン化触媒の含有割合は、ポリイソシアネート成分およびポリオール成分の総量１００質量部に対して、例えば、０．０５質量部以上、好ましくは、０．１質量部を超過し、より好ましくは、０．２質量部以上であり、例えば、２質量部以下、好ましくは、１質量部以下、より好ましくは、０．５質量部以下である。

【０１２１】

ウレタン化触媒の含有割合が上記範囲であれば、揮散性、保型性および速硬化性に優れるポリウレタンゲルが得られる。

【０１２２】

また、ポリウレタンゲルは、必要に応じて、公知の添加剤を含有することができる。添加剤としては、例えば、香料、防虫剤、殺虫剤、抗菌剤、殺菌剤、忌避剤、農薬などの揮散性有効成分、さらには、貯蔵安定剤（ｏ－トルエンスルホンアミド、ｐ－トルエンスルホンアミドなど）、ブロッキング防止剤、耐熱安定剤、耐光安定剤、紫外線吸収剤、酸化防止剤、消泡剤、離型剤、顔料、染料、滑剤、フィラー、加水分解防止剤などが挙げられ

る。
【０１２３】
これら添加剤は、単独使用または２種類以上併用することができる。
【０１２４】
また、添加剤の添加量は、特に制限されず、目的および用途に応じて、適宜設定される。
【０１２５】
なお、ポリウレタンゲルに添加剤を含有させる方法は、特に制限されず、例えば、ポリイソシアネート成分、ポリオール成分、ウレタン化触媒および溶媒からなる群から選択される１種以上に対して、予め添加してもよく、また、それらの配合と同時に添加してもよく、さらには、それらを配合した後に、別途添加してもよい。また、添加剤の添加割合は、特に制限されず、目的および用途に応じて、適宜設定される。
【０１２６】
また、ポリウレタンゲルの形状およびサイズは、特に制限されず、目的および用途に応じて、所定の金型を用いることにより、適宜設定される。具体的には、例えば、立方体状、直方体状、多角柱状、球状、塊状など、種々の形状が挙げられる。
【０１２７】
そして、このようなポリウレタンゲルは、平均官能基数が２．０を超過し３．５以下である多官能性脂肪族ポリイソシアネートを含有するポリイソシアネート成分と、２官能性ポリオールを８０質量％以上含有するポリオール成分とが反応してなり、また、特定割合で溶媒を含有するため、透明性に優れ、また、触感（柔軟性、弾力）、デザイン性（透明感、潤い感、ぷるぷる感など）、吸収性、保持力および揮散性に優れ、さらには、保型性、耐熱性および速硬化性に優れる。
【０１２８】
また、上記したように、溶媒が揮散性である場合、溶媒の放出に伴ってポリウレタンゲルが収縮する。すなわち、溶媒の含有量が多い状態では、ポリウレタンゲルの体積が比較的大きく、また、溶媒が揮散するに従って、ポリウレタンゲルの体積が小さくなる。そのため、溶媒の残量が外観で判断可能である。
【０１２９】
そのため、ポリウレタンゲルは、例えば、揮散性の溶媒とともに揮散性有効成分を含有することにより、種々の産業分野において好適に用いられる。具体的には、添加剤として香料を含有するポリウレタンゲルは、芳香ゲルとして好適に用いられ、また、添加剤として防虫剤や忌避剤を含有するポリウレタンゲルは、防虫ゲルとして好適に用いられ、例えば、添加剤として抗菌剤、殺菌剤を含有するポリウレタンゲルは、抗菌ゲル、殺菌ゲルとして好適に用いられる。
【実施例】
【０１３０】
次に、本発明を、製造例、実施例および比較例に基づいて説明するが、本発明は、下記の実施例によって限定されるものではない。なお、「部」および「％」は、特に言及がない限り、質量基準である。また、以下の記載において用いられる配合割合（含有割合）、物性値、パラメータなどの具体的数値は、上記の「発明を実施するための形態」において記載されている、それらに対応する配合割合（含有割合）、物性値、パラメータなど該当記載の上限値（「以下」、「未満」として定義されている数値）または下限値（「以上」、「超過」として定義されている数値）に代替することができる。
【０１３１】
また、各製造例、各実施例および各比較例において採用される測定方法を下記する。
１．測定方法
＜イソシアネート基濃度（単位：質量％）、イソシアネート基の転化率（単位：質量％）＞
電位差滴定装置（京都電子工業社製、型番：ＡＴ－５１０）を用いて、ＪＩＳ　Ｋ－１

６０３－１（２００７年）に準拠したトルエン／ジブチルアミン・塩酸法によりイソシアネート基濃度（イソシアネート基含有率）を測定し、以下の式により、測定試料のイソシアネート基の転化率を算出した。

【０１３２】

イソシアネート基の転化率＝［（反応前の反応液のイソシアネート基濃度－反応終了後の反応液のイソシアネート基濃度）／反応前の反応液のイソシアネート基濃度］×１００

＜^{1}Ｈ－ＮＭＲによるアロファネート基とイソシアヌレート基とのモル比率＞

下記の装置および条件にて^{1}Ｈ－ＮＭＲを測定し、イソシアヌレート基1モルに対するアロファネート基の含有割合（アロファネート基／イソシアヌレート基のモル比率）を以下の式により算出した。なお、化学シフトｐｐｍの基準として、Ｄ^{6}－ＤＭＳＯ溶媒中のテトラメチルシラン（０ｐｐｍ）を用いた。

装置；　ＪＮＭ－ＡＬ４００（ＪＥＯＬ製）

条件；　測定周波数：４００ＭＨｚ、溶媒：Ｄ^{6}－ＤＭＳＯ、溶質濃度：５質量％

イソシアヌレート基（イソシアヌレート基に直接結合するメチレン基（CH_2基））のプロトンの帰属ピーク（６Ｈ）：３．８ｐｐｍ

アロファネート基（アロファネート基内のＮＨ基）のプロトンの帰属ピーク（１Ｈ）：８．３～８．７ｐｐｍ

アロファネート基／イソシアヌレート基（モル比率）＝アロファネート基のプロトンの帰属ピークの積分値／（イソシアヌレート基のプロトンの帰属ピークの積分値／６）

＜平均イソシアネート基数（平均官能基数）＞

ポリイソシアネートの平均イソシアネート基数を、イソシアネート基濃度、固形分濃度（ＮＶ）、および、以下の装置および条件にて測定されるゲルパーミエーションクロマトグラフィーの数平均分子量から、下記式により算出した。

【０１３３】

平均イソシアネート基数＝Ａ／Ｂ×Ｃ／４２．０２

（式中、Ａは、イソシアネート基濃度を示し、Ｂは、固形分濃度を示し、Ｃは、数平均分子量を示す。）

装置：ＨＬＣ－８２２０ＧＰＣ（東ソー製）

カラム：ＴＳＫｇｅｌＧ１０００ＨＸＬ、ＴＳＫｇｅｌＧ２０００ＨＸＬ、およびＴＳＫｇｅｌＧ３０００ＨＸＬ（東ソー製）を直列に連結した。

検出器：　示差屈折率計

測定条件

注入量：１００μＬ

溶離液：テトラヒドロフラン

流量：０．８ｍＬ／ｍｉｎ

温度：４０℃

検量線：１０６～２２４５０の範囲の標準ポリエチレンオキシド（東ソー製、商品名：ＴＳＫ標準ポリエチレンオキシド）

製造例１（ペンタメチレンジイソシアネート（ａ）の製造）

国際公開パンフレットＷＯ２０１２／１２１２９１号の明細書における実施例１と同様の操作にて、９９．９質量％のペンタメチレンジイソシアネート（以後ＰＤＩと略する場合がある。）（ａ）を得た。

【０１３４】

製造例２（ＰＤＩのイソシアヌレート誘導体（Ａ））

温度計、撹拌装置、還流管、および、窒素導入管を備えた４つ口フラスコに、製造例１により得られたペンタメチレンジイソシアネート（ａ）を５００質量部、イソブチルアルコールを０．５２質量部、２，６－ジ（ｔｅｒｔ－ブチル）－４－メチルフェノールを０．３質量部、トリス（トリデシル）ホスファイトを０．３質量部、それぞれ装入し、８０℃で２時間反応させた。

【０１３５】
次いで、イソシアヌレート化触媒としてＮ－（２－ヒドロキシプロピル）－Ｎ，Ｎ，Ｎ－トリメチルアンモニウム－２－エチルヘキサノエートを０．０５質量部配合した。イソシアネート基濃度を測定し、その濃度が４８．９質量％（すなわち、転化率１０質量％）に至るまで反応を継続した。５０分後に所定の転化率（転化率１０質量％）に達したところで、ｏ－トルエンスルホンアミド（貯蔵安定剤）を０．１２質量部添加した。
【０１３６】
その後、得られた反応混合液を薄膜蒸留装置（温度：１５０℃、真空度：０．０９３ｋＰａ）に通液して、未反応の１，５－ペンタメチレンジイソシアネートを除去した。
【０１３７】
さらに、得られたろ物１００質量部に対し、ｏ－トルエンスルホンアミド（貯蔵安定剤）０．０２質量部、および、塩化ベンゾイル（反応停止剤）０．００３質量部を添加し、ＰＤＩのイソシアヌレート誘導体（Ａ）（以下、ＰＤＩ誘導体（Ａ）とする。）を得た。
【０１３８】
このＰＤＩ誘導体（Ａ）におけるＰＤＩモノマー濃度は０．５質量％、イソシアネート基濃度は２４．６質量％、イソシアネート基の平均官能基数は３．１、２５℃における粘度は２０００ｍＰａ・ｓであった。
【０１３９】
また、このＰＤＩ誘導体（Ａ）の^{1}Ｈ－ＮＭＲ測定によるアロファネート基とイソシアヌレート基とのモル比率は、アロファネート基／イソシアヌレート基＝８／１００（すなわち、アロファネート基の含有割合は、イソシアヌレート基１モルに対して、０．０８モル）であった。
【０１４０】
製造例３（ＰＤＩのイソシアヌレート誘導体（Ｂ））
温度計、撹拌装置、還流管、および、窒素導入管を備えた４つ口フラスコに、製造例１により得られた１，５－ペンタメチレンジイソシアネート（ａ）を５００質量部、イソブチルアルコールを９．８質量部、２，６－ジ（ｔｅｒｔ－ブチル）－４－メチルフェノールを０．３質量部、トリス（トリデシル）ホスファイトを０．３質量部、それぞれ、装入し、８０℃で２時間反応させた。
【０１４１】
次いで、イソシアヌレート化触媒としてＮ－（２－ヒドロキシプロピル）－Ｎ，Ｎ，Ｎ－トリメチルアンモニウム－２－エチルヘキサノエートを０．０５質量部配合した。イソシアネート基濃度を測定し、その濃度が、４７．１質量％（すなわち、転化率１０質量％）に至るまで反応を継続した。２０分後に所定の転化率（転化率１０質量％）に達したため、ｏ－トルエンスルホンアミド（貯蔵安定剤）を０．１２質量部添加した。
【０１４２】
その後、得られた反応混合液を薄膜蒸留装置（温度：１５０℃、真空度：０．０９３ｋＰａ）に通液して未反応の１，５－ペンタメチレンジイソシアネートモノマーを除去した。
【０１４３】
さらに、得られたろ物１００質量部に対し、ｏ－トルエンスルホンアミド（貯蔵安定剤）０．０２質量部、および、塩化ベンゾイル（反応停止剤）０．００３質量部を添加し、ＰＤＩのイソシアヌレート誘導体（Ｂ）（以下、ＰＤＩ誘導体（Ｂ）とする。）を得た。
【０１４４】
ＰＤＩ誘導体（Ｂ）におけるＰＤＩモノマー濃度は０．６質量％、イソシアネート基濃度は２３．５質量％、イソシアネート基の平均官能基数は２．８、２５℃における粘度は９００ｍＰａ・ｓであった。
【０１４５】
また、このＰＤＩ誘導体（Ｂ）の^{1}Ｈ－ＮＭＲ測定によるアロファネート基とイソシアヌレート基とのモル比率は、アロファネート基／イソシアヌレート基＝５５／１００（す

なわち、アロファネート基の含有割合は、イソシアヌレート基１モルに対して、０．５５モル）であった。

【０１４６】

製造例４（ＰＤＩのウレトジオン誘導体（Ｃ））

温度計、撹拌装置、還流管、および、窒素導入管を備えた４つ口フラスコに、窒素雰囲気下、製造例１により得られたペンタメチレンジイソシアネートを５００質量部、２，６－ジ（ｔｅｒｔ－ブチル）－４－メチルフェノールを０．３質量部、トリス（トリデシル）ホスファイト（商品名：ＪＰ－３３３Ｅ、城北化学社製）を０．３質量部、それぞれ装入し、１５０℃に昇温した。次いで、同温度で１０時間反応継続した後、反応を終了した。

【０１４７】

そして、得られた反応混合液を、薄膜蒸留装置（温度：１２０℃、真空度：９３．３Ｐａ）に通液して、未反応の１，５－ペンタメチレンジイソシアネートモノマーを除去し、ＰＤＩのウレトジオン誘導体（Ｃ）（以下、ＰＤＩ誘導体（Ｃ）とする。）を得た。

【０１４８】

ＰＤＩ誘導体（Ｃ）におけるＰＤＩモノマー濃度は０．５質量％、イソシアネート基濃度は２６．５質量％、イソシアネート基の官能基数は２．０、２５℃における粘度は８０ｍＰａ・ｓであった。

【０１４９】

また、このＰＤＩ誘導体（Ｃ）の^{1}ＨーＮＭＲ測定ではアロファネート基とイソシアヌレート基は検出されなかった。

【０１５０】

製造例５（ＨＤＩのイソシアヌレート誘導体（Ｄ））

１，５－ペンタメチレンジイソシアネートに代えてヘキサメチレンジイソシアネート（三井化学社製　タケネート７００（以後ＨＤＩと略する場合がある。））を用いた以外は、製造例３と同様の操作にて、ＨＤＩのイソシアヌレート誘導体（Ｄ）（以下、ＨＤＩ誘導体（Ｄ）とする。）を得た。

【０１５１】

ＨＤＩ誘導体（Ｄ）におけるＨＤＩモノマー濃度は０．７質量％、イソシアネート基濃度は２２．３質量％、イソシアネート基の官能基数は２．８、２５℃における粘度は１，２００ｍＰａ・ｓであった。

【０１５２】

また、このＨＤＩ誘導体（Ｄ）の^{1}ＨーＮＭＲ測定によるアロファネート基とイソシアヌレート基とのモル比率は、アロファネート基／イソシアヌレート基＝５５／１００（すなわち、アロファネート基の含有割合は、イソシアヌレート基１モルに対して、０．５５モル）であった。

【０１５３】

実施例１～２０、比較例１～６

ポリイソシアネート成分、ポリオール成分、溶媒およびウレタン化触媒を、表１～表３に記載の配合処方（総量２０ｇ）となるように、６０ｍｌで密栓ができるガラススクリュービンにて一括で配合した。

【０１５４】

次いで、ガラススクリュービンを密栓し、マグネチックスターラーで均一になるように１分撹拌した後、マグネチックスターラーを取り出した。

【０１５５】

その後、２３℃で２４時間の恒温槽内で所定時間反応および硬化させ、ポリウレタンゲルを得た。

【０１５６】

得られたポリウレタンゲルの２５℃における剪断弾性率は、1×10^{3}～1×10^{5}Ｐａの範囲であった。

【０１５７】
＜＜評価＞＞
ポリウレタンゲルを、以下の方法で評価した。その結果を、表1 ～表3 に示す。
【０１５８】
＜透明性＞
２３℃で２４時間硬化後のポリウレタンゲルの外観を、目視で判断し、以下の基準に従って評価した。
３：透明。
２：やや白濁。
１：白濁。
【０１５９】
＜保型性＞
２３℃で２４時間硬化後のポリウレタンゲルを取り出し、形状の変化を目視で確認し、以下の基準に従って評価した。
３：崩れなし。
２：一部崩れ。
１：崩れて広がる。
【０１６０】
＜触感・デザイン性＞
２３℃で２４時間硬化後のポリウレタンゲルを触診し、以下の基準に従って評価した。
３：弾力感・ぷるぷる感あり。
２：弾力感あり、ぷるぷる感なし。
１：弾力感なし。
【０１６１】
＜未含浸溶媒（吸収性および保持力）＞
２３℃で２４時間硬化後のポリウレタンゲルを取り出し、ポリウレタンゲル中に含浸されずに残存した溶媒を目視で確認し、以下の基準に従って評価した。
３：なし。
２：ゲル上にうっすらあり。
１：ゲル周辺にあり。
【０１６２】
＜硬化性＞
ポリウレタンゲルの製造時において２３℃で２４時間放置した後の硬化状態、および、１０℃で４８時間放置した後の硬化状態を確認し、以下の基準に従って評価した。
３：硬化。
２：一部未硬化。
１：未硬化。
＜耐熱性＞
２３℃で２４時間硬化後のポリウレタンゲルを、密閉状態のまま８０℃７２時間静置した。その後、外観を目視で確認し、以下の基準に従って評価した。
３：変化なし。
２：やや変色、または、一部溶解。
１：変色。
＜揮散性＞
２３℃で２４時間硬化後のポリウレタンゲルを取り出し、常温および常圧環境下に開放した状態にて、４０℃で1 週間保管した。その後の外観を目視で確認し、以下の基準に従って評価した。
３：収縮変形　大
２：収縮変形　中
１：収縮変形　小

表１

No.		官能基数	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7	実施例8	実施例9	実施例10
ポリイソシアネート成分（NCO当量比）	PDI誘導体(A)	3.1	0.75	0.8	0.9	0.9	0.95	–	–	–	0.9	0.9
	PDI誘導体(B)	2.8	–	–	–	–	–	0.9	0.75	–	–	–
	PDI誘導体(C)	2.0	–	–	–	–	–	–	–	–	–	–
	HDI誘導体(D)	2.8	–	–	–	–	–	–	–	0.9	–	–
	TDI誘導体(E)	3.2	–	–	–	–	–	–	–	-	–	–
ポリオール成分（OH当量比）	PTXG-1800	2.0	1	1	1	1	1	1	1	1	1	1
	T-5652	2.0	–	–	–	–	–	–	–	–	–	–
	P-2010	2.0	–	–	–	–	–	–	–	–	–	–
	T-3000	3.0	–	–	–	–	–	–	–	–	–	–
	ひまし油	2.7	–	–	–	–	–	–	–	–	–	–
ウレタン化触媒（ポリイソシアネート成分とポリオール成分との総量100質量部に対する質量）	DBTDL		0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.8	1
溶媒（総質量に対する質量割合(%)）	PMA		85	85	85	–	85	85	85	85	85	85
	DMM		–	–	–	85	–	–	–	–	–	–
外観 23℃24時間後	透明性		3	3	3	3	3	3	3	3	3	3
	保型性		2	3	3	3	3	3	2	2	3	3
	触感・デザイン性		3	3	3	3	3	3	3	3	3	3
	未含浸溶媒（吸収性・保持力）		3	3	3	3	3	3	3	3	3	3
硬化性	23℃×24時間 硬化性		3	3	3	3	3	3	3	2	3	3
	10℃×48時間 硬化性		2	3	3	3	3	3	2	2	3	3
耐熱性	80℃×72時間後 外観		3	3	3	3	3	3	3	2	3	2
揮散性	40℃×1週間後 外観		3	3	3	3	3	3	3	3	3	3

【０１６４】
【表２】

表2

No.		官能基数	実施例11	実施例12	実施例13	実施例14	実施例15	実施例16	実施例17	実施例18	実施例19	実施例20
ポリイソシアネート成分（NCO当量比）	PDI誘導体(A)	3.1	0.9	0.9	0.9	0.9	0.8	0.9	0.9	0.9	0.6	1
	PDI誘導体(B)	2.8	–	–	–	–	–	–	–	–	–	–
	PDI誘導体(C)	2.0	–	–	–	–	–	–	–	–	–	–
	HDI誘導体(D)	2.8	–	–	–	–	–	–	–	–	–	–
	TDI誘導体(E)	3.2	–	–	–	–	–	–	–	–	–	–
ポリオール成分（OH当量比）	PTXG-1800	2.0	1	1	1	1	1	–	–	0.9	1	1
	T-5652	2.0	–	–	–	–	–	1	–	–	–	–
	P-2010	2.0	–	–	–	–	–	–	1	–	–	–
	T-3000	3.0	–	–	–	–	–	–	–	0.1	–	–
	ひまし油	2.7	–	–	–	–	–	–	–	–	–	–
ウレタン化触媒（ポリイソシアネート成分とポリオール成分との総量100質量部に対する質量）	DBTDL		0.05	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
溶媒（総質量に対する質量割合(%)）	PMA		85	80	90	93	60	85	85	85	90	90
	DMM		–	–	–	–	–	–	–	–	–	–
外観 23℃24時間後	透明性		3	3	3	3	3	3	3	2	3	2
	保型性		2	3	3	2	3	3	3	2	1	3
	触感･デザイン性		3	3	2	2	2	3	3	2	1	3
	未含浸溶媒（吸収性･保持力）		3	3	3	3	3	3	3	2	1	2
硬化性	23℃×24時間 硬化性		3	3	3	2	3	3	3	3	3	3
	10℃×48時間 硬化性		2	3	2	1	3	3	3	1	1	3
耐熱性	80℃×72時間後 外観		3	3	2	1	3	3	2	3	2	3
揮散性	40℃×1週間後 外観		3	3	3	3	2	2	2	2	3	2

【０１６５】
【表３】

表３

No.		官能基数	比較例1	比較例2	比較例3	比較例4	比較例5	比較例6	比較例7
ポリイソシアネート成分（NCO当量比）	PDI誘導体(A)	3.1	0.9	0.9	–	0.9	0.9	0.9	–
	PDI誘導体(B)	2.8	–	–	–	–	–	–	–
	PDI誘導体(C)	2.0	–	–	–	–	–	–	0.9
	HDI誘導体(D)	2.8	–	–	–	–	–	–	–
	TDI誘導体(E)	3.2	–	–	0.9	–	–	–	–
ポリオール成分（OH当量比）	PTXG-1800	2.0	1	1	1	–	–	0.7	1
	T-5652	2.0	–	–	–	–	–	–	–
	P-2010	2.0	–	–	–	–	–	–	–
	T-3000	3.0	–	–	–	1	–	0.3	–
	ひまし油	2.7	–	–	–	–	1	–	–
ウレタン化触媒（ポリイソシアネート成分とポリオール成分との総量100質量部に対する質量）	DBTDL		0.3	0.3	0.05	0.3	0.3	0.3	0.3
溶媒（総質量に対する質量割合(%)）	PMA		40	97	90	85	85	85	85
	DMM		–	–	–	–	–	–	–
外観 23℃24時間後	透明性		1	3	3	–	1	2	–
	保型性		3	1	2	–	2	3	–
	触感・デザイン性		1	1	1	–	1	2	–
	未含浸溶媒（吸収性・保持力）		3	1	1	–	1	1	–
硬化性	23℃×24時間　硬化性		3	1	3	1	3	3	1
	10℃×48時間　硬化性		3	1	1	1	3	1	1
耐熱性	80℃×72時間後　外観		3	1	1	–	1	3	–
揮散性	40℃×1週間後　外観		1	1	3	–	1	2	–

【０１６６】
表中の略号の詳細を下記する。
・ポリイソシアネート成分
ＴＤＩ誘導体（Ｅ）：トリレンジイソシアネートのトリメチロールプロパン付加体
・ポリオール成分

ＰＴＸＧ１８００：旭化成せんい社製　非晶性ポリエーテルジオール　分子量１８００　平均官能基数２
Ｔ－５６５２：エターナコールＴ－５６５２　旭化成社製　非晶性ポリカーボネートジオール　分子量２０００　平均官能基数２
Ｐ－２０１０：クラレポリオールＰ－２０１０　クラレ社製　非晶性ポリエステルポリオール　分子量２０００　平均官能基数２
Ｔ－３０００：三井化学社製　ポリエーテルポリオール　分子量３０００　官能基数３
ひまし油：伊藤製油社製　精製ひまし油　平均官能基数　２．７
・ウレタン化触媒
ＤＢＴＤＬ：ジブチル錫ジラウレート
・溶媒
ＰＭＡ：ダワノールＰＭＡ　プロピレングリコールメチルエーテルアセテート　ダウ・ケミカル社製
ＤＭＭ：プログライドＤＭＭ　ジプロピレングリコールジメチルエーテルダウ・ケミカル社製

フロントページの続き

(72) 発明者　森田　広一
千葉県袖ケ浦市長浦５８０番地３２　三井化学株式会社内
(72) 発明者　山崎　聡
千葉県袖ケ浦市長浦５８０番地３２　三井化学株式会社内

Ｆターム(参考)　4J034 BA03 BA07 BA08 CA02 CA03 CA04 CA05 CB01 CB02 CB03
CB04 CB05 CB07 CC03 CC12 CC26 CC37 CC45 CC61 CC62
DA01 DB04 DC50 DF02 DF16 DF17 DF20 DF21 DG02 DG03
DG04 DG06 DG10 DG12 HA01 HA07 HA08 HB05 HB06 HB08
HB11 HC03 HC08 HC12 HC22 HC35 HC45 HC46 HC52 HC54
HC61 HC64 HC67 HC71 HC73 JA02 JA12 JA24 JA42 KA01
KA02 KB02 KB03 KC02 KC17 KC18 KC23 KC35 KD02 KD03
KD07 KD08 KD11 KD12 KD21 KD22 KD25 KE02 MA12 QA03
QB04 QB13 QB14 QB15 QB17 QC06 RA01 RA02 RA03

PTO/SB/08a (01-22)
Approved for use through 05/31/2024. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM
Art Unit	1699
Examiner Name	Brian M GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	5908631	A	1999-06-01	ARNAUD, et al.	
	2	7799874	B2	2010-09-21	CARR, et al.	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20120270992	A1	2012-10-25	LAROCK, et al.	
	2	20130149260	A1	2013-06-13	DELVALLE, et al.	

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2]	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	2018090662	JP	A	2018-06-14	MITSUI CHEMICALS INC	English Abstract	☒

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM
Art Unit	1699
Examiner Name	Brian M GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

If you wish to add additional Foreign Patent Document citation information please click the Add button [Add]

NON-PATENT LITERATURE DOCUMENTS [Remove]

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	AGUILAR-CASTRO et al., "Biobased polyester obtained from bifunctional monomers through metathesis of fatty acids as precursor to synthesis of polyurethanes." J. Appl. Polym. Sci., 136: 47095 (2018).	☐
	2	Jones, Charla, 'What Is Coco-Caprylate Doing In My Natural Skin Care Products?" Eu2Be (08 May 2015): pages 1-2 <https://eu2be.com/blogs/discover/19389252-what-is-coco-caprylate-doing-in-my-natural-skin-care-producls>; page 2	☐

If you wish to add additional non-patent literature document citation information please click the Add button [Add]

EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM
Art Unit	1699
Examiner Name	Brian M GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

CERTIFICATION STATEMENT

Please see 37 CFR 1.97(e) to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☒ A certification statement is not submitted herewith.

FEE

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

COPIES

☐ An identification of an earlier application pursuant to 37 CFR 1.98 (d) (1) is attached.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Michael N. Mercanti/	Date (YYYY-MM-DD)	2024-07-09
Name/Print	Michael N. Mercanti	Registration Number	33966

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
18/066,105	**07/09/2024 12:52:48 PM Z ET**	**GRAN-1012-U-D**

Title of Invention

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	1563	FILED BY	Yu Jin In
PATENT CENTER #	66285904	FILING DATE	12/14/2022
CUSTOMER #	20311	FIRST NAMED INVENTOR	Anna K. CROOM
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Michael Mercanti

Documents

TOTAL DOCUMENTS: 4

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
GRAN-1012-U-D_IDS.pdf	4	Information Disclosure Statement (IDS) Form (SB08)	1313 KB
AguilarCastro.pdf	12	Non Patent Literature	1298 KB
Jones_Charla.pdf	2	Non Patent Literature	386 KB
JP2018090662A.pdf	25	Foreign Reference	1282 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)

GRAN-1012-U-D_IDS.pdf	3A2112D21BA54EC6F830F267B8AAC7CB7D04338602C732477 75E900FF2076B517F35917649CCFAF4A0F049CDC2D11462AE B066EF96C46724C14382E4B64C0758
AguilarCastro.pdf	A31B2B2EBFDE0BE0495CFD4547500544B7F038989AD4DEA8 CD51E8967A5C70A7A2F2945D3FAA7D5544B66AD5463BAF894 AFB1671EB37E517372048B6CFB09A97
Jones_Charla.pdf	307C45B3397C3AD0BFAE33E2725AD5B8B5C87A12EA3BCAA8 1FF1CC6E5E489A875B02D57B176B9AD1E5EFE9605789299B4 3585F08F91234C38C17BC09D20A322D
JP2018090662A.pdf	CA71F60DAFD084AAFA71CB6C117BE659B0C87DF61FB60CA8 F515762F2B8D9A7A87876BF195978B38E962917561FDA2DFF6 80886346CAEE0361BCD9CFB5746B44

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
18/066,105	12/14/2022	Anna K. CROOM	GRAN-1012-U-D	1563

20311 7590 12/19/2024

LUCAS & MERCANTI, LLP
30 BROAD STREET
21st FLOOR
NEW YORK, NY 10004

EXAMINER	
GULLEDGE, BRIAN M	

ART UNIT	PAPER NUMBER
1699	

NOTIFICATION DATE	DELIVERY MODE
12/19/2024	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

info@lmiplaw.com

Office Action Summary	Application No. 18/066,105	Applicant(s) CROOM et al.	
	Examiner Brian Gulledge	Art Unit 1699	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 2 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☐ Responsive to communication(s) filed on _____.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL.** 2b) ☑ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5) ☑ Claim(s) 1-23 is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6) ☐ Claim(s) _____ is/are allowed.

7) ☐ Claim(s) _____ is/are rejected.

8) ☐ Claim(s) _____ is/are objected to.

9) ☑ Claim(s) 1-23 are subject to restriction and/or election requirement

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to **PPHfeedback@uspto.gov.**

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☐ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date _____.

4) ☐ Other: _____.

DETAILED ACTION

Election of Species

The following species election is each required:

"the cross-linked polyurethane elastomer rubber" (e.g. a suitable election would be to specify the materials used to prepare the polyurethane, such as the reaction product of 1,5-pentamethylene diisocyanates trimer and a prepolymer which is a copolymer of C18-unsaturated fatty acid dimers and 1,3-propane diol), with claims 1-23 reading upon this species.

The species are independent or distinct because claims to the different species recite the mutually exclusive characteristics of such species. In addition, these species are not obvious variants of each other based on the current record. There is also a search and/or examination burden for the patentably distinct species as set forth above because the inventions require a different field of search (for example, searching different classes/subclasses or electronic resources, or employing different search queries).

Applicant is required under 35 U.S.C. 121 to elect a single disclosed species for each of the above genera for prosecution on the merits to which the claims shall be restricted if no generic claim is finally held to be allowable. Currently, claims 1-8, 11, and 18 are generic.

Applicant is advised that the reply to this requirement to be complete must include (i) an election of a species to be examined even though the requirement may be traversed (37 CFR 1.143) **and (ii) identification of the claims encompassing the elected species or grouping of patentably indistinct species**, including any claims subsequently added. An argument that a claim is allowable or that all claims are generic is considered nonresponsive unless accompanied by an election.

The election may be made with or without traverse. To preserve a right to petition, the election must be made with traverse. If the reply does not distinctly and specifically point out supposed errors in the election of species requirement, the election shall be treated as an election without traverse. Traversal must be presented at the time of election in order to be considered timely. Failure to timely traverse the requirement will result in the loss of right to petition under 37 CFR 1.144. If claims are added after the election, applicant must indicate which of these claims are readable on the elected species or grouping of patentably indistinct species.

Should applicant traverse on the ground that the species, or groupings of patentably indistinct species from which election is required, are not patentably distinct, applicant should submit evidence or identify such evidence now of record showing them to be obvious variants or clearly admit on the record that this is the case. In either instance, if the examiner finds one of the species unpatentable over the prior art, the evidence or admission may be used in a rejection under 35 U.S.C. 103 or pre-AIA 35 U.S.C. 103(a) of the other species.

Upon the allowance of a generic claim, applicant will be entitled to consideration of claims to additional species which depend from or otherwise require all the limitations of an allowable generic claim as provided by 37 CFR 1.141.

Conclusion

A telephone call was not made to request an oral election to the above restriction requirement because the Examiner considers the requirement complex.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Brian Gulledge whose telephone number is (571) 270-5756. The examiner can normally be reached Monday - Friday 7am - 4pm.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Fereydoun Sajjadi can be reached on (571) 272-3311. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of published or unpublished applications may be obtained from Patent Center. Unpublished application information in Patent Center is available to registered users. To file and manage patent submissions in Patent Center, visit: https://patentcenter.uspto.gov. Visit https://www.uspto.gov/patents/apply/patent-center for more information about Patent Center and https://www.uspto.gov/patents/docx for information about filing in DOCX format. For additional questions, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Brian Gulledge/
Primary Examiner, Art Unit 1699

Espacenet

JP2008201698A HORNY LAYER-PEELING ADHESIVE COMPOSITION AND HORNY LAYER-PEELING ADHESIVE SHEET

Applicants: LINTEC CORP

Inventors: TAKANASHI TAKAYA,TATSUNO TOMOKO

Classifications:
IPC ***A61K8/02; A61K8/81; A61Q19/00;***

Priorities: JP2007038273A 2007-02-19

Application: JP2007038273A·2007-02-19

Publication: JP2008201698A·2008-09-04

Published as: JP2008201698A;**JP5036035B2**

HORNY LAYER-PEELING ADHESIVE COMPOSITION AND HORNY LAYER-PEELING ADHESIVE SHEET

Abstract

PROBLEM TO BE SOLVED: To provide a horny layer-peeling adhesive sheet which can safely and simply be used, and to provide a horny layer-peeling adhesive composition used therefor. SOLUTION: This horny layer-peeling adhesive sheet comprising a support and an adhesive layer laminated to one side of the support is characterized in that the adhesive layer is formed from an adhesive composition comprising a (meth)acrylic polymer, a lactam ring-having (meth)acrylic oligomer, a cross-linking agent, and a liquid component having a number-average mol.wt. (Mn) of < 4,000. The lactam ring-having (meth)acrylic oligomer is preferably a copolymer of N-vinyl-2-pyrrolidone with an alkyl (meth)acrylate. The liquid component is especially preferably a polyhydric alcohol. COPYRIGHT: (C)2008,JPO&INPIT

(19)日本国特許庁(JP)　(12)公開特許公報(A)　(11)特許出願公開番号
特開2008-201698
(P2008-201698A)
(43)公開日　平成20年9月4日(2008.9.4)

(51)Int.Cl.		F I		テーマコード（参考）
A61K 8/81	(2006.01)	A61K	8/81	4C083
A61Q 19/00	(2006.01)	A61Q	19/00	
A61K 8/02	(2006.01)	A61K	8/02	

審査請求 未請求　請求項の数 9　ＯＬ　（全 14 頁）

(21)出願番号　特願2007-38273(P2007-38273)
(22)出願日　平成19年2月19日(2007.2.19)

（特許庁注：以下のものは登録商標）
１．セロテープ

(71)出願人　000102980
リンテック株式会社
東京都板橋区本町２３番２３号
(74)代理人　100108833
弁理士　早川　裕司
(74)代理人　100132207
弁理士　太田　昌孝
(72)発明者　高梨　誉也
東京都板橋区本町２３番２３号　リンテック株式会社内
(72)発明者　辰野　智子
東京都板橋区本町２３番２３号　リンテック株式会社内
Ｆターム(参考)　4C083 AD091 AD092 BB32 CC03 CC22 DD12 EE12

(54)【発明の名称】角質剥離用粘着剤組成物および角質剥離用粘着シート

(57)【要約】
【課題】安全で簡便に使用することのできる角質剥離用粘着シート、およびそれに用いられる角質剥離用粘着剤組成物を提供する。
【解決手段】支持体と、支持体の片面に積層された粘着剤層とからなる角質剥離用粘着シートにおいて、粘着剤層を、（メタ）アクリル系ポリマーと、ラクタム環を有する（メタ）アクリル系オリゴマーと、架橋剤と、数平均分子量（Ｍｎ）４，０００未満の液状成分とを含有する粘着剤組成物を使用して形成する。ラクタム環を有する（メタ）アクリル系オリゴマーは、Ｎ－ビニル－２－ピロリドンと（メタ）アクリル酸アルキルエステルとの共重合体であることが好ましく、液状成分は、特に多価アルコールであることが好ましい。
【選択図】なし

【特許請求の範囲】
【請求項1】
架橋可能な官能基を有する（メタ）アクリル系ポリマー（ａ）と、
ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）と、
架橋剤（ｃ）と、
数平均分子量（Ｍｎ）４，０００未満の液状成分（ｄ）と
を含有することを特徴とする角質剥離用粘着剤組成物。
【請求項2】
前記液状成分（ｄ）は、２０℃における蒸気圧が１０Ｐａ未満である成分を主成分とすることを特徴とする請求項１に記載の角質剥離用粘着剤組成物。
【請求項3】
前記液状成分（ｄ）は、多価アルコール、脂肪酸、脂肪油および脂肪酸エステルからなる群から選ばれる少なくとも１種であることを特徴とする請求項１に記載の角質剥離用粘着剤組成物。
【請求項4】
前記ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）は、ラクタム環を有するビニルモノマーと（メタ）アクリル酸アルキルエステルとの共重合体であることを特徴とする請求項１～３のいずれかに記載の角質剥離用粘着剤組成物。
【請求項5】
前記ラクタム環を有するビニルモノマーは、Ｎ－ビニル－２－ピロリドンであることを特徴とする請求項４に記載の角質剥離用粘着剤組成物。
【請求項6】
前記ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）における前記ラクタム環を有するビニルモノマーの配合量は、５～４５モル％であることを特徴とする請求項４または５に記載の角質剥離用粘着剤組成物。
【請求項7】
前記ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）の数平均分子量（Ｍｎ）は、４，０００～１０，０００であることを特徴とする請求項１～６のいずれかに記載の角質剥離用粘着剤組成物。
【請求項8】
ラクタム環を有する（メタ）アクリル系ポリマーをさらに含有することを特徴とする請求項１～７のいずれかに記載の角質剥離用粘着剤組成物。
【請求項9】
支持体と、前記支持体上に積層された、請求項１～８のいずれかに記載の角質剥離用粘着剤組成物を使用して形成された粘着剤層とを備えたことを特徴とする角質剥離用粘着シート。

【発明の詳細な説明】
【技術分野】
【0001】
本発明は、皮膚に対する貼付・剥離により角質層を剥離することのできる角質剥離用粘着シート、およびかかる角質剥離用粘着シートの粘着剤層に用いることのできる角質剥離用粘着剤組成物に関するものである。
【背景技術】
【0002】
近年、その効果の即効性および有効性からケミカルピーリングに対する注目が非常に高まっている。ケミカルピーリングとは、特定の構造を有する有機酸を含有する皮膚外用剤（α－ハイドロキノン、グリコール酸、乳酸、フェノール等）を、皮膚表面の角質層に塗布することにより、化学的な腐食によって角質層を剥離し、皮膚の新陳代謝を亢進する美容方法の一種である。このケミカルピーリングを用いることにより、皮膚のしみ、黒ずみ、くすみ、ニキビ、ニキビ痕、小じわ等の症状の改善が期待できる。

【0003】
そこで、有機酸および非イオン性水溶性高分子を含有し、ｐＨが２．０以下である皮膚外用剤が提案されている（特許文献１）。
【0004】
また、ケミカルピーリング剤を含有する粘着層を有する美容用テープが提案されている（特許文献２）。
【特許文献1】再表２００４／００４６７５号公報
【特許文献2】特許第３５１５３０３号公報
【発明の開示】
【発明が解決しようとする課題】
【0005】
しかしながら、特許文献１に開示されるような有機酸を含有する皮膚外用剤は、皮膚に塗布して作用させた後、洗い流すまでの間に、液状の皮膚外用剤が皮膚を腐食する深さを制御することが極めて困難であり、やけどなどの皮膚障害が発生してしまうおそれがある。また、治療部位だけでなく、その周囲の健全部にも薬剤が広がってしまうといった問題がある。
【0006】
また、特許文献２に開示される美容用テープの場合には、液状薬剤に比べて作用に長時間を要し、それに伴って皮膚障害が発生するおそれがあり、また使用後に完全に洗い流さなければならないため、簡便性および安全性に欠ける。
【0007】
本発明は、このような実状に鑑みてなされたものであり、安全で簡便に使用することのできる角質剥離用粘着シート、およびそれに用いられる角質剥離用粘着剤組成物を提供することを目的とする。
【課題を解決するための手段】
【0008】
上記目的を達成するために、第１に本発明は、架橋可能な官能基を有する（メタ）アクリル系ポリマー（ａ）と、ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）と、架橋剤（ｃ）と、数平均分子量（Ｍｎ）４，０００未満の液状成分（ｄ）とを含有することを特徴とする角質剥離用粘着剤組成物を提供する（請求項１）。
【0009】
上記発明（請求項１）に係る角質剥離用粘着剤組成物では、ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）および液状成分（ｄ）を使用することにより、好適な角質層剥離力を得ることが可能となる。したがって、上記角質剥離用粘着剤組成物を使用して形成した粘着剤層は、皮膚から角質層を剥離するのに優れた粘着力を有し、角質層を均一に剥離することが可能である。
【0010】
また、上記発明（請求項１）に係る角質剥離用粘着剤組成物では、数平均分子量（Ｍｎ）４，０００未満の液状成分（ｄ）を使用しているが、その液状成分が角質に浸透し、角質を膨潤、軟化させるため、皮膚から角質層を剥離する時の痛みを軽減することができる。
【0011】
上記発明（請求項１）において、前記液状成分（ｄ）は、２０℃における蒸気圧が１０Ｐａ未満である成分を主成分とすることが好ましい（請求項２）。
【0012】
また、上記発明（請求項１）において、前記液状成分（ｄ）は、多価アルコール、脂肪酸、脂肪油および脂肪酸エステルからなる群から選ばれる少なくとも１種であることが好ましい（請求項３）。
【0013】
上記発明（請求項１～３）において、前記ラクタム環を有する（メタ）アクリル系オリ

ゴマー（ｂ）は、ラクタム環を有するビニルモノマーと（メタ）アクリル酸アルキルエステルとの共重合体であることが好ましい（請求項４）。

【0014】

上記発明（請求項４）において、前記ラクタム環を有するビニルモノマーは、Ｎ－ビニル－２－ピロリドンであることが好ましい（請求項５）。

【0015】

上記発明（請求項４，５）において、前記ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）における前記ラクタム環を有するビニルモノマーの配合量は、５～４５モル％であることが好ましい（請求項６）。

【0016】

上記発明（請求項１～６）において、前記ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）の数平均分子量（Ｍｎ）は、４，０００～１０，０００であることが好ましい（請求項７）。

【0017】

上記発明（請求項１～７）に係る角質剥離用粘着剤組成物は、ラクタム環を有する（メタ）アクリル系ポリマーをさらに含有してもよい（請求項８）。

【0018】

第２に本発明は、支持体と、前記支持体上に積層された、前記角質剥離用粘着剤組成物（請求項１～８）を使用して形成された粘着剤層とを備えたことを特徴とする角質剥離用粘着シートを提供する（請求項９）。なお、本明細書において「シート」にはテープ状のものも含まれるものとする。

【0019】

上記発明（請求項９）に係る角質剥離用粘着シートによれば、短時間の貼付・剥離を１～３回程度繰り返すことで、簡便に角質層を剥離することができ、しかも貼付した部分の角質層を均一に剥離することができる。また、剥離時の痛みを低減することができ、さらには皮膚に対する安全性も高い。

【発明の効果】

【0020】

本発明の角質剥離用粘着剤組成物を使用して形成した粘着剤層は、皮膚から角質層を剥離するのに優れた粘着力を有し、角質層を均一に剥離することが可能である。また、皮膚から角質層を剥離する時の痛みを軽減することができ、さらには皮膚に対する安全性も高い。

【0021】

また、本発明の角質剥離用粘着シートによれば、短時間の貼付・剥離を１～３回程度繰り返すことで、簡便に角質層を剥離することができ、しかも貼付した部分の角質層を均一に剥離することができる。また、皮膚から角質層を剥離する時の痛みを軽減することができ、さらには皮膚に対する安全性も高い。

【発明を実施するための最良の形態】

【0022】

以下、本発明の実施形態について説明する。

〔角質剥離用粘着剤組成物〕

本実施形態に係る角質剥離用粘着剤組成物は、（メタ）アクリル系ポリマー（ａ）と、ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）と、架橋剤（ｃ）と、液状成分（ｄ）とを含有する。

【0023】

（ａ）（メタ）アクリル系ポリマー

（メタ）アクリル系ポリマー（ａ）は、少なくとも架橋可能な官能基を有する（メタ）アクリル系ポリマー（ａ１）を含み、架橋可能な官能基を有する（メタ）アクリル系ポリマー（ａ１）および架橋可能な官能基を有しない（メタ）アクリル系ポリマー（ａ２）の両者を含んでいてもよい。

【0024】
架橋可能な官能基を有する（メタ）アクリル系ポリマー（ａ１）は、架橋可能な官能基を有するビニルモノマーと（メタ）アクリル酸アルキルエステルとの共重合体であることが好ましい。また、架橋可能な官能基を有しない（メタ）アクリル系ポリマー（ａ２）は、（メタ）アクリル酸アルキルエステルの単独重合体、またはビニルモノマーと（メタ）アクリル酸アルキルエステルとの共重合体であることが好ましく、特にビニルモノマーと（メタ）アクリル酸アルキルエステルとの共重合体であることが好ましく、さらにビニルモノマーはラクタム環を有するものであることが好ましい。
【0025】
（メタ）アクリル酸アルキルエステルとしては、アルキル基の炭素数が１～１４のものが好ましく、例えば、（メタ）アクリル酸メチル、（メタ）アクリル酸エチル、（メタ）アクリル酸プロピル、（メタ）アクリル酸イソプロピル、（メタ）アクリル酸２－メトキシエチル、（メタ）アクリル酸ブチル、（メタ）アクリル酸イソブチル、（メタ）アクリル酸ペンチル、（メタ）アクリル酸ヘキシル、（メタ）アクリル酸オクチル、（メタ）アクリル酸イソオクチル、（メタ）アクリル酸２－エチルヘキシル、（メタ）アクリル酸ノニル、（メタ）アクリル酸イソノニル、（メタ）アクリル酸ラウリル等が挙げられ、１種を単独でまたは２種以上を組み合わせて使用することができる。
【0026】
上記架橋可能な官能基を有するビニルモノマーの架橋可能な官能基としては、カルボキシル基、ヒドロキシル基等が挙げられる。かかる架橋可能な官能基を有するビニルモノマーとしては、例えば、カルボキシル基を有する（メタ）アクリル酸や、ヒドロキシル基を有する（メタ）アクリル酸２－ヒドロキシエチル、（メタ）アクリル酸４－ヒドロキシブチル等が挙げられ、１種を単独でまたは２種以上を組み合わせて使用することができる。
【0027】
架橋可能な官能基を有する（メタ）アクリル系ポリマー（ａ１）における架橋可能な官能基を有するビニルモノマーの配合量は、２～３５モル％とすることが好ましい。架橋可能な官能基を有するビニルモノマーの配合量が２モル％未満では、架橋が不十分になり、３５モル％を超えると、十分な角質剥離効果が得られなくなる場合がある。
【0028】
ラクタム環を有するビニルモノマーとしては、Ｎ－ビニル－２－ピロリドン、Ｎ－ビニル－２－ピペリドン、Ｎ－ビニル－ε－カプロラクタム等が好ましく、中でも特に、皮膚親和性の高いＮ－ビニル－２－ピロリドンが好ましい。
【0029】
架橋可能な官能基を有しない（メタ）アクリル系ポリマー（ａ２）におけるラクタム環を有するビニルモノマーの配合量は、１～４０モル％とすることが好ましい。
【0030】
（メタ）アクリル系ポリマー（ａ）（架橋可能な官能基を有する（メタ）アクリル系ポリマー（ａ１）および架橋可能な官能基を有しない（メタ）アクリル系ポリマー（ａ２）のそれぞれ）の数平均分子量（Ｍｎ）は、３００，０００～１，５００，０００であることが好ましく、特に３５０，０００～１，２００，０００であることが好ましく、さらに４００，０００～１，０００，０００であることが好ましい。なお、本明細書における数平均分子量（Ｍｎ）は、ゲルパーミエーションクロマトグラフィー（ＧＰＣ分析）法によって測定し、標準ポリスチレンで換算した値とする。
【0031】
（メタ）アクリル系ポリマー（ａ）の数平均分子量（Ｍｎ）が３００，０００未満では、得られる粘着剤の凝集力が不十分となり、糊残りが生じる場合があり、（メタ）アクリル系ポリマー（ａ）の数平均分子量（Ｍｎ）が１，５００，０００を超えると、高粘度となるため他の成分との均一な混合が困難となり、安定した物性の粘着剤が得られなくなるおそれがある。
【0032】

なお、（メタ）アクリル系ポリマー（ａ）が架橋可能な官能基を有する（メタ）アクリル系ポリマー（ａ１）および架橋可能な官能基を有しない（メタ）アクリル系ポリマー（ａ２）の両者を含む場合、それらの配合量は、架橋可能な官能基を有する（メタ）アクリル系ポリマー（ａ１）１００質量部に対して架橋可能な官能基を有しない（メタ）アクリル系ポリマー（ａ２）が５０～４００質量部であることが好ましく、特に１００～３００質量部であることが好ましい。

【0033】

（ｂ）ラクタム環を有する（メタ）アクリル系オリゴマー

ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）は、ラクタム環を有するビニルモノマーと（メタ）アクリル酸アルキルエステルとの共重合体であることが好ましい。

【0034】

ラクタム環を有するビニルモノマーとしては、Ｎ－ビニル－２－ピロリドン、Ｎ－ビニル－２－ピペリドン、Ｎ－ビニル－ε－カプロラクタム等が好ましく、中でも特に、皮膚親和性の高いＮ－ビニル－２－ピロリドンが好ましい。

【0035】

ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）におけるラクタム環を有するビニルモノマーの配合量は、５～４５モル％とすることが好ましく、特に１０～４０モル％とすることが好ましい。ラクタム環を有するビニルモノマーの配合量が５モル％未満では、皮膚に対する濡れ性が不十分で皮膚密着性、ひいては角質層剥離力が低くなるおそれがある。一方、ラクタム環を有するビニルモノマーの配合量が４５モル％を超えると、得られる粘着剤がゲル化してしまい、角質剥離用粘着シートの製造または取り扱いが困難になるおそれがある。

【0036】

（メタ）アクリル酸アルキルエステルとしては、アルキル基の炭素数が２～１４のものが好ましく、例えば、（メタ）アクリル酸エチル、（メタ）アクリル酸プロピル、（メタ）アクリル酸イソプロピル、（メタ）アクリル酸２－メトキシエチル、（メタ）アクリル酸ブチル、（メタ）アクリル酸イソブチル、（メタ）アクリル酸ペンチル、（メタ）アクリル酸ヘキシル、（メタ）アクリル酸オクチル、（メタ）アクリル酸イソオクチル、（メタ）アクリル酸２－エチルヘキシル、（メタ）アクリル酸ノニル、（メタ）アクリル酸イソノニル、（メタ）アクリル酸ラウリル等が挙げられ、１種を単独でまたは２種以上を組み合わせて使用することができる。

【0037】

ラクタム環を有するビニルモノマーと（メタ）アクリル酸アルキルエステルとの好ましい組み合わせとしては、Ｎ－ビニル－２－ピロリドンと（メタ）アクリル酸２－エチルヘキシルとの組み合わせが挙げられる。

【0038】

ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）の数平均分子量（Ｍｎ）は、４，０００～１０，０００であることが好ましく、特に５，０００～９，０００であることが好ましい。数平均分子量（Ｍｎ）が４，０００未満では、組成物が過度に可塑化されて、角質剥離性能が低下してしまう場合があり、数平均分子量（Ｍｎ）が１０，０００を超えると、ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）の粘度が過度に上昇して、（メタ）アクリル系ポリマー（ａ）と均一に混合することが困難になったり、皮膚に対する濡れ性が低下したりする場合がある。

【0039】

本実施形態に係る角質剥離用粘着剤組成物においては、上記ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）を使用することにより、皮膚に対する濡れ性を向上させて皮膚密着性を高めることができ、それによって好適な角質層剥離力を得ることが可能となる。また、ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）は、（メタ）アクリル系ポリマー（ａ）との相溶性が高く、さらに粘着剤組成物に添加剤を添加した場合にも、それらの成分を分散させ易い。

【0040】
ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）の配合量は、（メタ）アクリル系ポリマー（ａ）１００質量部に対して、５０～７００質量部であることが好ましく、特に８０～５００質量部であることが好ましい。ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）の配合量が５０質量部未満であると、粘着剤の皮膚に対する濡れ性が著しく低下して、必要な粘着力が得られないおそれがあり、ラクタム環を有する（メタ）アクリル系オリゴマー（ｂ）の配合量が７００質量部を超えると、粘着剤の凝集力が過度に低下して、皮膚に糊残りが生じたり、必要な粘着力が得られないおそれがある。
【0041】
（ｃ）架橋剤
架橋剤（ｃ）としては、架橋可能な官能基を有する（メタ）アクリル系ポリマー（ａ１）の架橋可能な官能基と反応性を有する多官能性化合物を使用することができる。かかる多官能性化合物としては、例えば、イソシアネート化合物、エポキシ化合物、アジリジン化合物、金属キレート化合物等が挙げられ、中でもイソシアネート化合物が好ましい。
【0042】
イソシアネート化合物としては、例えば、ヘキサメチレンジイソシアナート等の脂肪族イソシアネート、トリレンジイソシアネート、ジフェニルメタンジイソシアネート、キシリレンジイソシアネート等の芳香族イソシアネート、イソホロンジイソシアネート、水素添加ジフェニルメタンジイソシアネート等の脂環族イソシアネート、およびそれらイソシアネート化合物に、グリセロール、トリメチロールプロパン等のポリオールを反応せしめたアダクト体などが挙げられ、１種を単独でまたは２種以上を組み合わせて使用することができる。
【0043】
架橋剤（ｃ）の添加量は、架橋可能な官能基を有する（メタ）アクリル系ポリマー（ａ１）１００質量部に対して０．０１～１５質量部であることが好ましく、特に０．１～５質量部であることが好ましい。架橋剤（ｃ）の添加量が０．０１質量部未満では、十分に架橋させることができず、架橋剤（ｃ）の添加量が１５質量部を超えると、粘着剤の架橋密度が過度に高くなり、粘着剤の皮膚に対する濡れ性が著しく低下する場合がある。
【0044】
（ｄ）液状成分
液状成分（ｄ）は、角質に浸透し、角質を膨潤、軟化させるものである。これによって、皮膚から角質層を剥離する時の痛みを軽減することができる。角質への浸透性を確保するために、液状成分（ｄ）の数平均分子量（Ｍｎ）は、４，０００未満であることを必要とし、好ましくは９０～３，０００である。
【0045】
また、液状成分（ｄ）のｐＨは６～８であるのが好ましい。ｐＨがこの範囲を外れると、例えば有機酸のように皮膚を腐食するおそれが生じ、皮膚に対する安全性が低下する。
【0046】
液状成分（ｄ）は、常温常圧下で揮発しないものであることが好ましく、したがって、２０℃における蒸気圧が１０００Ｐａ未満、特に１０Ｐａ未満であることが好ましい。液状成分（ｄ）が揮発性のものであると、角質剥離用粘着シートの保管時等に粘着剤層から液状成分（ｄ）が揮発しないように、角質剥離用粘着シートを密封する等の対処が必要になる。
【0047】
上記のような液状成分（ｄ）としては、例えば、グリセリン、ジグリセリン、トリグリセリン、テトラグリセリン、エチレングリコール、１，３－ブチレングリコール、１，３－プロパンジオール、１，４－ブチレングリコール、プロピレングリコール、ジプロピレングリコール、ポリエチレングリコール、ポリプロピレングリコール等の多価アルコール；カプリン酸、ラウリン酸、ミリスチン酸、ペンタデシル酸、パルミチン酸、ステアリン酸、リノール酸、リノレン酸等の脂肪酸；オリーブ油、ツバキ油、ひまし油、ベニバナ油

、コーン油等の脂肪油；カプリン酸メチル、カプロン酸メチル、ラウリン酸メチル、ミリスチン酸メチル、ステアリン酸メチル、パルミチン酸イソプロピル、ラウリン酸、イソプロピル、パルミチン酸イソオクチル、ステアリン酸イソオクチル、セバシン酸ジエチル等の脂肪酸エステル;流動パラフィン、スクワレン、スクワラン等の炭化水素油;液状界面活性剤等が挙げられ、１種を単独でまたは２種以上を組み合わせて使用することができる。上記の中でも、特に保湿性、安全性等に優れたグリセン、ポリエチレングリコール、ポリプロピレングリコール等の多価アルコールを使用することが好ましい。

【0048】

液状成分（ｄ）の配合量は、角質剥離用粘着剤組成物中、２．５～４０質量％であることが好ましく、特に5～３０質量％であることが好ましい。液状成分（ｄ）の配合量が２．５質量％未満であると、液状成分（ｄ）による効果が低く、角質の剥離時に痛みが発生するおそれがあり、液状成分（ｄ）の配合量が４０質量％を超えると、粘着剤の凝集力が低下して、糊残りが生じるおそれがある。

【0049】

（ｅ）第三成分

本実施形態に係る角質剥離用粘着剤組成物は、上記成分（ａ）～（ｄ）以外の第三成分（ｅ）を含有してもよい。かかる第三成分（ｅ）としては、薬剤、酸化防止剤、粘度調整剤、紫外線吸収剤、隠蔽剤、可塑剤、ワックス、着色剤、無機フィラー、有機フィラー、増量剤、カップリング剤等の各種添加剤等が挙げられ、１種を単独でまたは２種以上を組み合わせて使用することができる。

【0050】

以上説明した成分を含有する本実施形態に係る角質剥離用粘着剤組成物は、常法によって製造することができ、各成分を適宜混合すればよい。

【0051】

本実施形態に係る角質剥離用粘着剤組成物を使用して形成した粘着剤層は、皮膚から角質層を剥離するのに十分な粘着力を有し、角質層を均一に剥離することが可能である。

【0052】

本実施形態に係る角質剥離用粘着剤組成物を使用した粘着剤層を厚さ５０μｍのポリエチレンテレフタレートフィルムに厚さ４０μｍで形成した粘着シートをベークライトに貼付して５分後のＪＩＳ　Ｚ０２３７に準拠した粘着力（モード：１８０°剥離，剥離速度：３００ｍｍ／ｍｉｎ，貼付時間：５分）は、２～２０Ｎ／２５ｍｍであることが好ましく、特に3～１２Ｎ／２５ｍｍであることが好ましい。上記粘着力が２Ｎ／２５ｍｍ未満であると、効果的に角質層を剥離することができない。一方、上記粘着力が２０Ｎ／２５ｍｍを超えると、皮膚からの剥離時に痛みが発生し、また皮膚に糊残りが生じるおそれがある。

【0053】

なお、本発明では、粘着剤組成物を使用した粘着剤層を厚さ５０μｍのポリエチレンテレフタレートフィルムに厚さ４０μｍで形成した粘着シートの粘着力を測定し、その測定値を基準としたが、支持体・粘着剤層の厚さが上記以外の粘着剤組成物および粘着シートであっても、上記の測定方法により測定した結果によって評価を行うことができる。

【0054】

〔角質剥離用粘着シート〕

本実施形態に係る角質剥離用粘着シートは、支持体と、支持体の片面に積層された粘着剤層とから構成される。なお、粘着剤層の露出面には、別途剥離材を積層してもよい。

【0055】

粘着剤層は、前述した角質剥離用粘着剤組成物を支持体に塗布・形成してなる層である。例えば、トルエン、酢酸エチル、メチルエチルケトン、アセトン等の有機溶剤に溶解している角質剥離用粘着剤組成物を、常法により支持体に塗布した後、乾燥させる（架橋可能な組成物は架橋させる）ことにより、粘着剤層を形成することができる。

【0056】

角質剥離用粘着剤組成物を塗布する方法としては、既存の塗布装置を用いることができ、例えば、グラビアコーター、マイヤーバーコーター、コンマコーター、ロールコーター、ナイフコーター、ダイコーター、スクリーンコーター等を挙げることができるが、これらに限定されるものではない。

【0057】

粘着剤層の厚さは、効果的に角質層を剥離するために、５～３００μｍであることが好ましく、特に１０～２００μｍであることが好ましい。

【0058】

支持体の材料としては、角質剥離用粘着シートの使い易さを考慮して適宜選択すればよく、例えば、ポリエチレンテレフタレート等のポリエステル系フィルム、ポリエチレン、ポリプロピレン、エチレン／メタクリル酸共重合体、エチレン／メタクリル酸メチル等のポリオレフィン系フィルム、ポリウレタン系フィルム、ポリスチレン系の熱可塑性エラストマーフィルムなどの樹脂フィルム；各種の合成繊維および／または天然繊維からなる織布、編布、不織布；上質紙、グラシン紙、コート紙等の紙；それらの積層体などを用いることができる。

【0059】

なお、支持体の粘着剤層側の面には、粘着剤層との密着性を高めるために、プライマー処理、コロナ処理、プラズマ処理等の表面処理を施してもよいし、角質剥離用粘着シートを巻取体にする場合には、支持体の表面をシリコーン系剥離剤や長鎖アルキル化合物等によって剥離処理してもよい。

【0060】

支持体の厚さは、通常、フィルムを支持体とする場合には５～２５０μｍ、好ましくは１０～１００μｍ程度とし、織布、不織布、紙等を支持体とする場合には１０～１０００μｍ、好ましくは２０～５００μｍ程度とする。

【0061】

粘着剤層に剥離材を積層する場合、剥離材としては、上質紙、グラシン紙、コート紙、ポリエチレンラミネート紙、ポリプロピレンラミネート紙等の紙；ポリエチレンテレフタレート等のポリエステル系フィルム、ポリエチレン、ポリプロピレン等のポリオレフィン系フィルム等の合成樹脂フィルムなどの材料を使用することができ、必要によりそれら材料の片面または両面に剥離処理を行ってもよい。

【0062】

本実施形態に係る角質剥離用粘着シートによれば、皮膚に対する短時間（例えば３～５分）の貼付・剥離を１～３回程度繰り返すことで、簡便に角質層を剥離することができ、しかも貼付した部分の角質層を均一に剥離することができる。また、皮膚から角質層を剥離する時の痛みはほとんどなく、さらには皮膚に対する安全性も高い。

【実施例】

【0063】

以下、実施例等により本発明をさらに具体的に説明するが、本発明の範囲はこれらの実施例等に限定されるものではない。

【0064】

〔実施例１〕

架橋可能な官能基（カルボキシル基）を有するアクリル系ポリマー（アクリル酸２－エチルヘキシル／アクリル酸共重合体：８２／１８モル％，数平均分子量：約８５０，０００，固形分：５０質量％）２８．６質量部と、架橋可能な官能基を有しないアクリル系ポリマー（アクリル酸２－エチルヘキシル／Ｎ－ビニル－２－ピロリドン共重合体：８８／１２モル％，数平均分子量：約８５０，０００，固形分：４５質量％）４４．４質量部と、ラクタム環を有するアクリル系オリゴマー（アクリル酸２－エチルヘキシル／Ｎ－ビニル－２－ピロリドン共重合体：８０／２０モル％，数平均分子量：約６０００，固形分：９８質量％）３０．６質量部と、液状成分としての濃グリセリン（鹿島ケミカル社製，分子量９２．１，ｐＨ７．４，蒸気圧０．１Ｐａ未満（２０℃））３．２質量部との混合物

に対し、イソシアネート系架橋剤（日本ポリウレタン工業社製，コロネートＨＬ）０．２質量部を添加混合した。

【0065】

得られた粘着剤組成物の溶液を、厚さ５０μｍのポリエチレンテレフタレートフィルム（東レ社製，ルミラーＴ６０）上に、乾燥後の塗布量が５０ｇ／ｍ２（厚さ４０μｍ）となるようにアプリケーターによって塗布し、１００℃で３分間乾燥させて粘着剤層を形成し、これを粘着シートとした。

【0066】

〔実施例２〕

濃グリセリンの配合量を１０．６質量部に変更する以外、実施例１と同様にして粘着剤組成物を調製し、当該粘着剤組成物を使用して実施例１と同様にして粘着シートを作製した。

【0067】

〔実施例３〕

濃グリセリンの配合量を２５．８質量部に変更する以外、実施例１と同様にして粘着剤組成物を調製し、当該粘着剤組成物を使用して実施例１と同様にして粘着シートを作製した。

【0068】

〔実施例４〕

ラクタム環を有するアクリル系オリゴマーとして、アクリル酸２－エチルヘキシルとＮ－ビニル－２－ピロリドン共重合体とのモル比が８８：１２のアクリル系オリゴマー（数平均分子量：約６０００，固形分：９８質量％）を使用する以外、実施例３と同様にして粘着剤組成物を調製し、当該粘着剤組成物を使用して実施例１と同様にして粘着シートを作製した。

【0069】

〔実施例５〕

液状成分を濃グリセリンに代えてポリエチレングリコール（数平均分子量４００，ｐＨ７．１，蒸気圧１０Ｐａ未満（２０℃））６．７質量部に変更する以外、実施例１と同様にして粘着剤組成物を調製し、当該粘着剤組成物を使用して実施例１と同様にして粘着シートを作製した。

【0070】

〔実施例６〕

液状成分を濃グリセリンに代えてポリプロピレングリコール（数平均分子量２０００，ｐＨ７．２，蒸気圧１０Ｐａ未満（２０℃））６．７質量部に変更する以外、実施例１と同様にして粘着剤組成物を調製し、当該粘着剤組成物を使用して実施例１と同様にして粘着シートを作製した。

【0071】

〔比較例１〕

比較例１の粘着シートとして、ニチバン社製セロテープを用意した。なお、セロテープの粘着剤は天然ゴムを主成分とするものである。

【0072】

〔比較例２〕

架橋可能な官能基を有しないアクリル系ポリマー、ラクタム環を有するアクリル系オリゴマーおよび濃グリセリンを用いなかった以外は、実施例１と同様にして粘着剤組成物を調製し、当該粘着剤組成物を使用して実施例１と同様にして粘着シートを作製した。

【0073】

〔比較例３〕

ラクタム環を有するアクリル系オリゴマーおよび濃グリセリンを用いなかった以外は、実施例１と同様にして粘着剤組成物を調製し、当該粘着剤組成物を使用して実施例１と同様にして粘着シートを作製した。

【0074】
　ここで、上記実施例１～６および比較例２～３で調製した粘着剤組成物における各成分の配合比を表１に示す。
【0075】

【0076】

【表1】

	架橋可能な官能基を有するアクリルポリマー（a1）			架橋可能な官能基を有しないアクリルポリマー（a2）			ラクタム環を有するアクリルオリゴマー（b）			イソシアネート架橋剤（c）	液状成分（d）
	2EHA (mol%)	AA (mol%)	組成物中配合量 (質量部)	2EHA (mol%)	NVP (mol%)	組成物中配合量 (質量部)	2EHA (mol%)	NVP (mol%)	組成物中配合量 (質量部)	組成物中配合量 (質量部)	組成物中配合量 (質量部)
実施例1	82	18	28.6 (14.3)	88	12	44.4 (20)	80	20	30.6 (30)	0.2	3.2
実施例2	82	18	28.6 (14.3)	88	12	44.4 (20)	80	20	30.6 (30)	0.2	10.6
実施例3	82	18	28.6 (14.3)	88	12	44.4 (20)	80	20	30.6 (30)	0.2	25.8
実施例4	82	18	28.6 (14.3)	88	12	44.4 (20)	88	12	30.6 (30)	0.2	25.8
実施例5	82	18	28.6 (14.3)	88	12	44.4 (20)	80	20	30.6 (30)	0.2	6.7
実施例6	82	18	28.6 (14.3)	88	12	44.4 (20)	80	20	30.6 (30)	0.2	6.7
比較例2	82	18	28.6 (14.3)	-	-	-	-	-	-	0.2	-
比較例3	82	18	28.6 (14.3)	88	12	44.4 (20)	-	-	-	0.2	-

※組成物中配合量の欄中、括弧内は固形分配合量を示す。

※2EHA:アクリル酸２－エチルヘキシル　AA:アクリル酸　NVP:Ｎ－ビニル－２－ピロリドン

〔試験例１〕（角質膜残存率測定）
　実施例および比較例で得られた粘着シートを幅２５ｍｍ×長さ４０ｍｍに裁断してサンプルとした。
【0077】
　測定部位である人の下腕内側を水で濡らしたタオルで軽く拭き、２０分放置した。そして、高感度角質膜厚・水分計（アサヒバイオメッド社製，高感度角質膜厚・水分計ＡＳＡ－ＭＸ）を使用して、未処理時における測定部位の角質膜の厚さを測定した（５回測定の平均値）。
【0078】
　上記測定部位を水で濡らしたタオルで軽く拭き、２０分放置した。次いで、測定部位にサンプルを５分間貼付した後、人の手によって約２０００ｍｍ／ｍｉｎの速度でサンプルを剥離した。その後、測定部位を水で濡らしたタオルで軽く拭き、２０分放置した。そして、上記高感度角質膜厚・水分計を使用して、第１回処理時における測定部位の角質膜の厚さを測定した（５回測定の平均値）。その測定結果から、未処理時における角質膜の厚さを基準（１００）とする角質膜の残存率（％）を算出した。結果を表２に示す。
【0079】
〔試験例２〕（角質剥離時の官能試験）
　実施例および比較例で得られた粘着シートを幅２５ｍｍ×長さ４０ｍｍに裁断してサンプルとした。
【0080】
　測定部位である人の上腕内側部を水で濡らしたタオルで軽く拭き、２０分放置した。次いで、測定部位にサンプルを５分間貼付した後、人の手によって約２０００ｍｍ／ｍｉｎの速度でサンプルを剥離した。そのときの痛みを下記の基準に従って官能評価した。結果を表２に示す。
◎：痛みがない
○：わずかに痛みを感じた
△：痛みを感じた（我慢できる）
×：非常に痛みを感じた
【0081】
〔試験例３〕（粘着力測定）
　実施例および比較例で得られた粘着シート（厚さ５０μｍのポリエチレンテレフタレートフィルムに粘着剤組成物または接着剤を厚さ４０μｍで形成した粘着シート）について、ＪＩＳ　Ｚ０２３７に準じて粘着力（Ｎ／２５ｍｍ）を測定した。なお、被着体としてはベークライト板（ユーコー商会社製，タイコーライトＦＬ１０６３）を使用し、貼付時間は５分とした。結果を表２に示す。
【0082】

【表2】

	角質膜残存率（%）	官能試験結果	粘着力（N/25mm）
実施例１	４３．８	◎	９．４
実施例２	５５．９	◎	９．５
実施例３	５６．５	◎	１０．４
実施例４	６０．１	◎	３．３
実施例５	５３．２	◎	９．８
実施例６	６１．５	◎	５．２
比較例１	８８．８	○	９．０
比較例２	９８．５	×	５．１
比較例３	７７．１	△	４．２

【0083】
表２より、実施例で得られた粘着シートによれば、角質層を効果的に剥離することができ、また剥離時の痛みもないことが分る。

【産業上の利用可能性】

【0084】
本発明の角質剥離用粘着剤組成物および角質剥離用粘着シートは、ピーリングの他、ピーリングした後の皮膚から薬剤を投与する場合に有用である。

Espacenet

JP2017114773A COSMETIC COMPOSITIONS FOR IMPROVING LASTING EFFECT WHICH CONTAINS FILM-FORMING POLYMER AND COMBINATION OF PARTICULAR FILLER

Applicants: OREAL

Inventors: OKAMOTO MARIKO,YOSHIDA TOMOSHI,JODOI YUKA

Classifications:

IPC ***A61K8/06; A61K8/25; A61K8/37; A61K8/44; A61K8/81; A61K8/87; A61K8/89; A61Q1/00; A61Q19/00;***

CPC **A61K8/06 (EP,KR,US); A61K8/25 (EP,KR,US); A61K8/26 (EP,US); A61K8/37 (EP,US); A61K8/375 (EP,KR,US); A61K8/44 (US); A61K8/8152 (EP,KR,US); A61K8/87 (EP,KR,US); A61K8/89 (US); A61K8/92 (KR); A61Q1/02 (EP,KR,US); A61Q19/00 (EP,KR,US);**

Priorities: JP2015248359A 2015-12-21

Application: JP2015248359A·2015-12-21

Publication: JP2017114773A·2017-06-29

Published as: **BR112018010984A2; BR112018010984B1; CN108366924A; CN108366924B; EP3393428A1; EP3393428B1; ES2764730T3;** JP2017114773A;**JP6732444B2; KR102230447B1; KR20180074791A; US11771631B2; US2018369095A1; US2021007955A1; WO2017111149A1**

COSMETIC COMPOSITIONS FOR IMPROVING LASTING EFFECT WHICH CONTAINS FILM-FORMING POLYMER AND COMBINATION OF PARTICULAR FILLER

Abstract

PROBLEM TO BE SOLVED: To provide cosmetic compositions that can achieve a lasting effect without causing dry feeling, which are cosmetic compositions for skin, preferably cosmetic compositions in liquid emulsion form, particularly makeup bases or liquid foundation.SOLUTION: The object relates to a cosmetic composition for keratin substances for example the skin, for example the facial skin, which comprises (i) at least one moisturizing agent, (ii) at least one film-forming polymer, (iii) a combination of fillers of (a) hydrophobic silica, (b) perlite, (c) urethane polymer powder, and (d) acrylic polymer powder. The "lasting" effect without causing dry feeling of a cosmetic composition for keratin substances which contains at least one moisturizing agent is achieved by using both a film-forming polymer and a combination of fillers of (a) hydrophobic silica, (b) perlite, (c) urethane polymer powders, and (d) acrylic polymer powders.SELECTED DRAWING: None

(19)日本国特許庁(JP)　(12)公開特許公報(A)　(11)特許出願公開番号
特開2017-114773
(P2017-114773A)
(43)公開日　平成29年6月29日(2017.6.29)

(51)Int.Cl.			F I			テーマコード（参考）
A61K	8/25	(2006.01)	A61K	8/25		4C083
A61K	8/87	(2006.01)	A61K	8/87		
A61K	8/81	(2006.01)	A61K	8/81		
A61K	8/37	(2006.01)	A61K	8/37		
A61K	8/44	(2006.01)	A61K	8/44		

審査請求 未請求　請求項の数 15　ＯＬ　外国語出願　（全 32 頁）　最終頁に続く

(21)出願番号　特願2015-248359 (P2015-248359)
(22)出願日　平成27年12月21日 (2015.12.21)

(71)出願人　391023932
ロレアル
フランス国パリ，リュ　ロワイヤル　１４
(74)代理人　100108453
弁理士　村山　靖彦
(74)代理人　100110364
弁理士　実広　信哉
(72)発明者　岡本　まり子
神奈川県川崎市高津区坂戸３－２－１　ケーエスピーアールアンドディー－ビー１１１３　日本ロレアル株式会社内
(72)発明者　吉田　知史
神奈川県川崎市高津区坂戸３－２－１　ケーエスピーアールアンドディー－ビー１１１３　日本ロレアル株式会社内
最終頁に続く

(54)【発明の名称】特定のフィラーの組合せ及び皮膜形成性ポリマーを含む、持続効果を向上させるための化粧用組成物

(57)【要約】
【課題】本発明の目的は、皮膚のための化粧用組成物、好ましくは液体エマルジョンの形態の化粧用組成物、特に化粧下地又は液体ファンデーションであって、乾燥感を生じずに持続効果を達成できる化粧用組成物を提供することである。
【解決手段】前記目的は、(i)少なくとも1種の保湿剤と、(ii)少なくとも1種の皮膜形成性ポリマーと、(iii)(a)疎水性シリカ、(b)パーライト、(c)ウレタンポリマー粉末、及び(d)アクリルポリマー粉末のフィラーの組合せとを含む、ケラチン物質、例えば皮膚、例えば顔の皮膚のための化粧用組成物に関する。少なくとも1種の保湿剤を含む、ケラチン物質のための化粧用組成物の乾燥感を生じない「持続」効果は、皮膜形成性ポリマーと、(a)疎水性シリカ、(b)パーライト、(c)ウレタンポリマー粉末、及び(d)アクリルポリマー粉末のフィラーの組合せとの両方の使用により達成され得る。
【選択図】なし

【特許請求の範囲】
【請求項１】
(i)少なくとも1種の保湿剤と、
(ii)少なくとも1種の皮膜形成性ポリマーと、
(iii)
(a)疎水性シリカ、
(b)パーライト、
(c)ウレタンポリマー粉末、及び
(d)アクリルポリマー粉末
のフィラーの組合せと
を含む、ケラチン物質のための組成物。
【請求項２】
(i)保湿剤が、皮膚軟化剤、湿潤剤、及びこれらの混合物から選択される、請求項1に記載の組成物。
【請求項３】
(i)保湿剤が、皮膚軟化剤から選択され、特に不揮発性油から選択される、請求項1又は2に記載の組成物。
【請求項４】
(i)保湿剤が、エステル油及び親油性アミノ酸誘導体から選択される、請求項1から3のいずれか一項に記載の組成物。
【請求項５】
組成物中の(i)保湿剤の量が、組成物の総質量に対して、0.001質量%から20.0質量%未満、好ましくは0.01質量%から15.0質量%未満、より好ましくは0.05質量%から10.0質量%である、請求項1から4のいずれか一項に記載の組成物。
【請求項６】
(ii)皮膜形成性ポリマーが、シリコーン樹脂から選択され、好ましくはMQ樹脂から選択される、請求項1から5のいずれか一項に記載の組成物。
【請求項７】
組成物中の(ii)皮膜形成性ポリマーの量が、組成物の総質量に対して、0.01質量%から20.0質量%未満、好ましくは0.1質量%から15.0質量%未満、より好ましくは1.0質量%から10.0質量%である、請求項1から6のいずれか一項に記載の組成物。
【請求項８】
(iii)(a)疎水性シリカが、表面がシリル化によって改質されているシリカ粒子である、請求項1から7のいずれか一項に記載の組成物。
【請求項９】
(iii)(c)ウレタンポリマー粉末が、架橋ポリウレタン粉末であり、好ましくはヘキサメチレンジイソシアネート(HDI)/トリメチロールヘキシルラクトンクロスポリマーである、請求項1から8のいずれか一項に記載の組成物。
【請求項１０】
(iii)(d)アクリルポリマー粉末が、クロスポリマー又はコポリマー粉末であり、好ましくはラウリルメタクリレート/グリコールジメタクリレートクロスポリマー又はアクリロニトリル/メタクリレート/塩化ビニリデンコポリマーである、請求項1から9のいずれか一項に記載の組成物。
【請求項１１】
組成物中の(iii)フィラーのうちのそれぞれの量が、組成物の総質量に対して、0.001質量%から10.0質量%未満、好ましくは0.01質量%から8質量%未満、より好ましくは0.05質量%から5.0質量%である、請求項1から10のいずれか一項に記載の組成物。
【請求項１２】
少なくとも1種のUVフィルター、好ましくは少なくとも1種の有機UVフィルターを更に含む、請求項1から11のいずれか一項に記載の組成物。

【請求項１３】
化粧下地又は液体ファンデーションである、請求項1から12のいずれか一項に記載の組成物。
【請求項１４】
O/W W/O又はマルチ型のエマルジョンの形態、特に液体又は半液体の粘稠度のエマルジョンの形態である、請求項1から13のいずれか一項に記載の組成物。
【請求項１５】
ケラチン物質、例えば皮膚、例えば顔の皮膚のための美容方法であって、請求項1から14のいずれか一項に記載の組成物を前記ケラチン物質上に適用する工程を含む、美容方法。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は、ケラチン物質のための化粧用組成物、好ましくは液体エマルジョンの形態の化粧用組成物、特に化粧下地又は液体ファンデーションであって、乾燥感を誘発せずに持続効果を与える化粧用組成物に関する。
【背景技術】
【０００２】
「持続」効果は、特に高温多湿の国において、化粧料の鍵となる基準のうちの1つである。「持続」効果を重視した多くの化粧料が市販されている。しかし、これらの種類の化粧料について、最も重大な欠点のうちの1つは、乾燥した感覚を生じることである。現在は、乾燥した感覚を回避するために、脂肪族化合物が添加され、保湿感を維持している。例えば、WO 2013/190112は、色保持力が改善された流体化粧用皮膚メイクアップ組成物を開示しており、この組成物は、少なくとも1つの連続油相、少なくとも1種の皮脂ポンプフィラー(sebum-pump filler)、少なくとも1種の疎水性皮膜形成性ポリマー、及び少なくとも1種の親油性ゲル化剤を含む。
【０００３】
しかし、脂肪族化合物の添加は、「持続」効果を低下させる。したがって、「持続」効果と保湿感との間のバランスを維持できる化粧品を開発することは難しい。
【０００４】
したがって、皮膚等のケラチン物質のための化粧用組成物であって、「持続」効果を有すると共に、保湿感を維持する化粧用組成物がなお求められている。
【先行技術文献】
【特許文献】
【０００５】
【特許文献１】WO 2013/190112
【特許文献２】特許出願FR 03 02809
【特許文献３】特許出願EP 1 269 986
【特許文献４】特許出願FR 2 796 550
【特許文献５】特許出願EP 1 044 676
【特許文献６】特許出願EP 0 928 608
【特許文献７】特許出願WO 02/051 828
【特許文献８】米国特許第7,470,725号
【特許文献９】米国特許第5,002,698号
【特許文献１０】JP-A-02 243 612
【特許文献１１】USP 5240975
【特許文献１２】EP-669,323
【特許文献１３】米国特許第2,463,264号
【特許文献１４】米国特許第5,237,071号
【特許文献１５】米国特許第5,166,355号

【特許文献16】GB-2,303,549
【特許文献17】DE-197,26,184
【特許文献18】EP-893,119
【特許文献19】WO 93/04665
【特許文献20】DE-19855649
【発明の概要】
【発明が解決しようとする課題】
【0006】
本発明の目的は、皮膚のための化粧用組成物、好ましくは液体エマルジョンの形態の化粧用組成物、特に化粧下地又は液体ファンデーションであって、乾燥感を生じずに持続効果を達成できる化粧用組成物を提供することである。
【課題を解決するための手段】
【0007】
本発明の上記の目的は、
(i)少なくとも1種の保湿剤と、
(ii)少なくとも1種の皮膜形成性ポリマーと、
(iii)
(a)疎水性シリカ、
(b)パーライト、
(c)ウレタンポリマー粉末、及び
(d)アクリルポリマー粉末
のフィラーの組合せと
を含む、ケラチン物質、例えば皮膚、例えば顔の皮膚のための化粧用組成物によって達成され得る。
【0008】
(i)保湿剤は、皮膚軟化剤、湿潤剤、及びこれらの混合物から選択されてもよい。
【0009】
(i)保湿剤は、皮膚軟化剤から選択されてもよく、特に不揮発性油から選択されてもよい。
【0010】
(i)保湿剤は、エステル油及び親油性アミノ酸誘導体から選択されてもよい。
【0011】
組成物中の(i)保湿剤の量は、組成物の総質量に対して、0.001質量%から20.0質量%未満、好ましくは0.01質量%から15.0質量%未満、より好ましくは0.05質量%から10.0質量%であってもよい。
【0012】
(ii)皮膜形成性ポリマーは、シリコーン樹脂であってもよく、好ましくはMQ樹脂から選択されてもよい。
【0013】
組成物中の(ii)皮膜形成性ポリマーの量は、組成物の総質量に対して、0.01質量%から20.0質量%未満、好ましくは0.1質量%から15.0質量%未満、より好ましくは1.0質量%から10.0質量%であってもよい。
【0014】
(iii)(a)疎水性シリカは、表面がシリル化によって改質されているシリカ粒子であってもよい。
【0015】
(iii)(c)ウレタンポリマー粉末は、架橋ポリウレタン粉末であってもよく、好ましくはヘキサメチレンジイソシアネート(HDI)/トリメチロールヘキシルラクトンクロスポリマーであってもよい。
【0016】

(iii)(d)アクリルポリマー粉末は、クロスポリマー又はコポリマー粉末であってもよく、好ましくはラウリルメタクリレート/グリコールジメタクリレートクロスポリマー又はアクリロニトリル/メタクリレート/塩化ビニリデンコポリマーであってもよい。

【００１７】

組成物中の(iii)フィラーのうちのそれぞれの量は、組成物の総質量に対して、0.001質量%から10.0質量%未満、好ましくは0.01質量%から8質量%未満、より好ましくは0.05質量%から5.0質量%であってもよい。

【００１８】

本発明による組成物は、少なくとも1種のUVフィルター、好ましくは少なくとも1種の有機UVフィルターを更に含んでもよい。

【００１９】

本発明による組成物は、化粧下地又は液体ファンデーションであってもよい。

【００２０】

本発明による組成物は、O/W W/O又はマルチ型のエマルジョンの形態、特に液体又は半液体の粘稠度のエマルジョンの形態にあってもよい。

【００２１】

本発明は、ケラチン物質、例えば皮膚、例えば顔の皮膚のための美容方法であって、本発明による組成物をケラチン物質上に適用する工程を含む、美容方法にも関する。

【発明を実施するための形態】

【００２２】

鋭意検討の結果、本発明者らは、少なくとも1種の保湿剤を含む、ケラチン物質のための化粧用組成物の乾燥感を生じない「持続」効果が、皮膜形成性ポリマーと、(a)疎水性シリカ、(b)パーライト、(c)ウレタンポリマー粉末、及び(d)アクリルポリマー粉末のフィラーの組合せとの両方の使用により達成され得ることを見出した。

【００２３】

したがって、本発明の一態様は、

(i)少なくとも1種の保湿剤と、

(ii)少なくとも1種の皮膜形成性ポリマーと、

(iii)

(a)疎水性シリカ、

(b)パーライト、

(c)ウレタンポリマー粉末、及び

(d)アクリルポリマー粉末

のフィラーの組合せと

を含む、ケラチン物質、例えば皮膚、例えば顔の皮膚のための化粧用組成物である。

【００２４】

本発明の別の態様は、ケラチン物質、例えば皮膚、例えば顔の皮膚のための美容方法であって、本発明による組成物をケラチン物質上に適用する工程を含む、美容方法である。

【００２５】

以下では、本発明による組成物及び方法をそれぞれ詳細に説明する。

【００２６】

[組成物]

(保湿剤)

本発明の組成物は、少なくとも1種の保湿剤を含む。2種以上の保湿剤を組み合わせて使用してもよい。したがって、単一の種類の保湿剤、又は異なる種類の保湿剤の組合せを使用することができる。

【００２７】

保湿剤は、外部潤滑剤挙動(external lubricant behavior)を付与する、例えば皮膚を軟化し、鎮静化(soothe)する物質であり、これは、保湿剤が皮膚の保水力を向上させるからである。保湿剤は、皮膚軟化剤から選択されてもよく、皮膚軟化剤は、皮膚表面上又は

角質層内に留まり、潤滑剤として作用することができ、剥離を減少させることができ、皮膚の外観を改善することができる。

【００２８】

また、保湿剤は、皮膚の上層の含水量を増加させるように意図される湿潤剤から選択されてもよい。この成分の群は、主に、この特定の目的のために用いられる吸湿剤を含む。

【００２９】

本発明の好ましい実施形態によると、保湿剤は、皮膚軟化剤、湿潤剤、及びこれらの混合物から選択される。

【００３０】

a) 皮膚軟化剤

一実施形態では、保湿剤は、皮膚軟化剤から選択され、より詳細には、不揮発性油から選択される。「油」という用語は、室温(25℃)及び大気圧で液状形態の任意の脂肪物質を意味するものとして理解される。

【００３１】

本発明の意味の範囲内で、「不揮発性油」という用語は、0.13Pa(0.01mmHg)未満の蒸気圧を有する油を意味するものとして理解される。

【００３２】

不揮発性油は、特に、不揮発性炭化水素油(適切な場合はフッ素化されたもの)及び/又は不揮発性シリコーン油から選択できる。

【００３３】

本発明における使用に適する不揮発性油の例としては、以下を挙げることができる:

- 動物由来の炭化水素油、
- 植物由来の炭化水素油、例えばフィトステリルエステル、例としてオレイン酸フィトステリル、イソステアリン酸フィトステリル及びラウロイル/オクチルドデシル/フィトステリルグルタメート、例えばEldew PS203という名称で味の素株式会社によって販売されているもの、グリセロールの脂肪酸エステルで構成されたトリグリセリドであって、その脂肪酸はC_4～C_{24}の多様な鎖長を有することができ、グリセロールは直鎖状又は分枝状、及び飽和又は不飽和であってもよいトリグリセリド;このような油として、特にヘプタン酸若しくはオクタン酸トリグリセリド、小麦胚芽油、ヒマワリ油、ブドウ種子油、ゴマ油、トウモロコシ油、アンズ油、ヒマシ油、シア油、アボカド油、オリーブ油、大豆油、スイートアーモンド油、パーム油、菜種油、綿実油、ヘーゼルナッツ油、マカダミア油、ホホバ油、アルファルファ油、ケシ油、カボチャ種子油、キュウリ油、ブラックカラント油、マツヨイグサ油、キビ油、大麦油、キノア油、ライ麦油、ペニバナ油、ククイナッツ油、トケイソウ油又はマスクローズ油;シアバター;或いはカプリル/カプリン酸トリグリセリド、例えばStearineries Dubois社によって販売されているもの、若しくはDynamit Nobel社によってMiglyol 810(登録商標)、812(登録商標)及び818(登録商標)という名称で販売されているもの;又は、Cognis社によってFitodermという名称で販売されている精製した植物性ペルヒドロスクアレン、
- 鉱物又は合成由来の炭化水素油、例えば
・10から40個の炭素原子を有する合成エーテル、
・鉱物又は合成由来の直鎖状又は分枝状炭化水素、例えば液体石油、ポリデセン、水添ポリイソブテン、例えばパールリーム(Parleam)、スクアラン及びそれらの混合物、特に水添ポリイソブテン、
・合成エステル油、例えば式R_1COOR_2の油(式中、R_1は、1から40個の炭素原子を含む直鎖状又は分枝状脂肪酸残基を表し、R_2は、炭化水素鎖、特に1から40個の炭素原子を含む分枝状炭化水素鎖を表し、但しR_1+R_2が≧10である)。

【００３４】

エステル油としては、脂肪酸エステル、例えば以下を挙げることができる:

- 炭酸ジカプリリル(Cognis社製Cetiol CC)、オクタン酸セテアリル、イソプロピルアルコールのエステル、例えばミリスチン酸イソプロピル、パルミチン酸イソプロピル、パル

ミチン酸エチル、パルミチン酸2-エチルヘキシル、ステアリン酸イソプロピル、イソステアリン酸イソプロピル、イソステアリン酸イソステアリル、ステアリン酸オクチル、ヒドロキシル化エステル、例えば乳酸イソステアリル、オクチルヒドロキシステアレート、アジピン酸ジイソプロピル、ヘプタン酸エステル、特に、ヘプタン酸イソステアリル、アルコール又はポリアルコールのオクタン酸エステル、デカン酸エステル又はリシノール酸エステル、例えばプロピレングリコールジオクタノエート、オクタン酸セチル、オクタン酸トリデシル、2-エチルヘキシル4-ジヘプタノエート、パルミチン酸2-エチルヘキシル、安息香酸アルキル、ポリエチレングリコールジヘプタノエート、プロピレングリコールジ(2-エチルヘキサノエート)並びにそれらの混合物、C_{12}～C_{15}アルコールの安息香酸エステル、ラウリン酸ヘキシル、ネオペンタン酸エステル、例えばネオペンタン酸イソデシル、ネオペンタン酸イソトリデシル、ネオペンタン酸イソステアリル又はネオペンタン酸オクチルドデシル、イソノナン酸エステル、例えばイソノナン酸イソノニル、イソノナン酸イソトリデシル又はイソノナン酸オクチル、又はヒドロキシル化エステル、例えば乳酸イソステアリル又はリンゴ酸ジイソステアリル、

- ポリオールエステル及びペンタエリトリトールエステル、例えばポリオールとC_8～C_{40}一脂肪酸との間で形成されるモノエステル又はポリエステルであって、ポリオール、例えば、ペンタエリトリトール、エリトリトール、ジ-ペンタエリトリトール、トリメチロールプロパン、ジ-トリメチロールプロパン、グリセロール、ジグリセロール、ポリグリセロール及びスクロースから選択されるポリオールと、C_8～C_{40}、好ましくはC_{12}～C_{22}一脂肪酸、例えば、場合により置換されているベヘン酸及びステアリン酸、例えばヒドロキシステアリン酸及びイソステアリン酸との間で形成され得るもの、例えばジペンタエリトリチルテトラヒドロキシステアレート/テトライソステアレート、例えば、日清オイリオグループ株式会社によってSalacosS 168 EVという名称で販売されるもの、
- ダイマージオール及びダイマー二酸のエステル、例えば、日本精化株式会社によって販売されているLusplan DD-DA5(登録商標)及びLusplan DD-DA7(登録商標)(特許出願FR 03 02809に記載)。

【００３５】

エステル油の例としては、脂肪族又は芳香族ポリカルボン酸とC_1～C_{10}脂肪族又は芳香族アルコールとの間で形成されるエステルも挙げることができる。

【００３６】

脂肪族及び芳香族アルコールは、1から10個の炭素原子、例えば、1から8個、好ましくは1から6個の炭素原子を含んでもよく、アルコール、ROH(式中、Rは、場合により置換されているメチル、エチル、プロピル、イソプロピル、ブチル、ヘキシル、エチルヘキシル、デシル、イソデシル、及びベンジルから選択される)から選択されてもよい。

【００３７】

脂肪族及び芳香族ポリカルボン酸は、例えば、3から12個の炭素原子、好ましくは3から10個の炭素原子、より好ましくは、3から8個の炭素原子、更により好ましくは6個又は8個の炭素原子を含んでもよい。脂肪族及び芳香族ポリカルボン酸は、ジカルボン酸又はトリカルボン酸であってもよい。

【００３８】

ジカルボン酸の例としては、以下の式

$HOOC-(CH_2)_n-COOH$

(式中、nは、1から10、好ましくは2から8、より好ましくは2、4、6又は8の範囲にある)

を有するものを挙げることができる。例えば、ジカルボン酸は、コハク酸、アジピン酸及びセバシン酸から選択されてもよい。

【００３９】

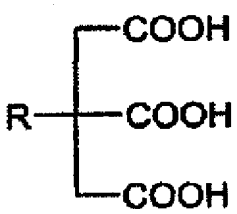
また、ジカルボン酸は、フタル酸及びその誘導体、例えば、フタル酸ブチルベンジル、フタル酸ジブチル、フタル酸ジエチルヘキシル、フタル酸ジエチル及びフタル酸ジメチルから選択されてもよい。

【００４０】

トリカルボン酸の例としては、以下の式

【００４１】

【化１】



【００４２】

[式中、Rは炭化水素基であり、例えば、H、-OH又は-OCOR'(式中、R'はアルキルであり、例えば1から6個の炭素原子を含むアルキルである)である]

を有するものを挙げることができる。例えば、トリカルボン酸は、アセチルクエン酸及びその誘導体から選択されてもよい。

【００４３】

クエン酸エステルの中では、アセチルクエン酸トリブチル、アセチルクエン酸トリエチル、アセチルクエン酸トリエチルヘキシル、アセチルクエン酸トリヘキシル、トリヘキシルブチリルシトレート、クエン酸イソデシル、クエン酸イソプロピル、クエン酸トリブチル及びクエン酸トリエチルヘキシルを挙げることができる。

【００４４】

アジピン酸エステルの中では、アジピン酸ジブチル及びアジピン酸ジ-2-エチルヘキシルを挙げることができる。

【００４５】

セバシン酸エステルの中では、セバシン酸ジブチル、セバシン酸ジエチルヘキシル、セバシン酸ジエチル及びセバシン酸ジイソプロピルを挙げることができる。

【００４６】

コハク酸エステルの中では、コハク酸ジエチルヘキシル及びコハク酸エチルを挙げることができる。

【００４７】

好ましくは、エステルは、コハク酸、アジピン酸及びセバシン酸から選択されるジカルボン酸と、メタノール、エタノール、プロパノール、イソプロパノール、ブタノール、ヘキサノール及びエチルヘキサノールから選択されるアルコールとの間で形成される。特に、エステルは、セバシン酸ジイソプロピル、例えば、Stearinerie Dubois社によってDub Disという名称で販売されるものであってもよい。

【００４８】

また、不揮発性油の例として、以下を挙げることもできる:

- 12から26個の炭素原子を有する、分枝状及び/又は不飽和炭素鎖を含む、室温で液体である脂肪アルコール、例えば2-オクチルドデカノール、イソステアリルアルコール、オレイルアルコール、2-ヘキシルデカノール、2-ブチルオクタノール及び2-ウンデシルペンタデカノール、
- 高級脂肪酸、例えばオレイン酸、リノール酸、リノレン酸、及びそれらの混合物、
- 炭酸ジアルキル(2つのアルキル鎖は同一でもよいし又は異なっていてもよい)、例えば、Cognis社によってCetiol CC(登録商標)という名称で販売されている炭酸ジカプリリル、
- 不揮発性シリコーン油、例えば、不揮発性ポリジメチルシロキサン(PDMS)、ペンダント型及び/又はシリコーン鎖の末端にあるアルキル又はアルコキシ基を含み、各基が2から

24個の炭素原子を有するポリジメチルシロキサン、フェニルシリコーン、例えばフェニルトリメチコン、フェニルジメチコン、フェニル(トリメチルシロキシ)ジフェニルシロキサン、ジフェニルジメチコン、ジフェニル(メチルジフェニル)トリシロキサン及び(2-フェニルエチル)トリメチルシロキシシリケート、粘度が100cSt以下のジメチコン又はフェニルトリメチコン及びそれらの混合物。

【００４９】

また、保湿剤の例として、親油性アミノ酸誘導体を挙げることもできる。親油性アミノ酸誘導体は、特に、C_6～C_{22} N-アシルアミノ酸エステルであり、これは、不揮発性油、特にエステル油としても定義され得る。

【００５０】

これらの誘導体は、特に特許出願EP 1 269 986に記載されるものである。

【００５１】

N-アシルアミノ酸エステルは、一般に、以下の式

$R'_1(CO)N(R'_2)CH(R'_3)(CH_2)n(CO)OR'_4$

(式中、

- nは、0、1又は2に等しい整数であり、
- R'_1は、直鎖状又は分枝状のC_5～C_{21}アルキル又はアルケニル基を表し、
- R'_2は、水素原子又はC_1～C_3アルキル基を表し、
- R'_3は、水素原子、メチル基、エチル基、直鎖状又は分枝状C_3又はC_4アルキル基によって形成される群から選択される基を表し、
- R'_4は、直鎖状若しくは分枝状のC_1～C_{10}アルキル若しくはC_2～C_{10}アルケニル基、又はステロール残基を表す)

のものである。

【００５２】

好ましくは、$R'_1(CO)$-基は、カプリン酸、ラウリン酸、ミリスチン酸、パルミチン酸、ステアリン酸、ベヘン酸、リノール酸、リノレン酸、オレイン酸、イソステアリン酸、2-エチルヘキサン酸、ココナッツ油脂肪酸及びパーム核油脂肪酸によって形成される群から選択される酸のアシル基である。また、これらの脂肪酸は、ヒドロキシル基を含んでもよい。更により好ましくは、この脂肪酸はラウリン酸であろう。

【００５３】

アミノ酸エステルの$-N(R'_2)CH(R'_3)(CH_2)_n(CO)-$部分は、好ましくは、アミノ酸であるグリシン、アラニン、バリン、ロイシン、イソロイシン、セリン、トレオニン、プロリン、ヒドロキシプロリン、β-アラニン、アミノ酪酸、アミノカプロン酸、サルコシン、N-メチル-β-アラニンから選択される。

【００５４】

更により好ましくは、アミノ酸はサルコシンであろう。

【００５５】

OR'_4基に相当するアミノ酸エステルの部分は、メタノール、エタノール、プロパノール、イソプロパノール、ブタノール、tert-ブタノール、イソブタノール、3-メチル-1-ブタノール、2-メチル-1-ブタノール、フーゼル油、ペンタノール、ヘキサノール、シクロヘキサノール、オクタノール、2-エチルヘキサノール、デカノール、ラウリルアルコール、ミリスチルアルコール、セチルアルコール、セトステアリルアルコール、ステアリルアルコール、オレイルアルコール、ベヘニルアルコール、ホホバアルコール、2-ヘキサデシルアルコール、2-オクチルドデカノール及びイソステアリルアルコールによって形成される群から選択されるアルコールから得ることができる。

【００５６】

これらのアミノ酸エステルは、特に、アミノ酸の天然原料から得ることができる。この場合、アミノ酸は、天然の植物性タンパク質(オート麦、小麦、大豆、パーム又はココナッツ)の加水分解に由来しており、必ずアミノ酸の混合物となる。続いて、このアミノ酸の混合物は、エステル化後、N-アシル化される必要がある。かかるアミノ酸の調製は、よ

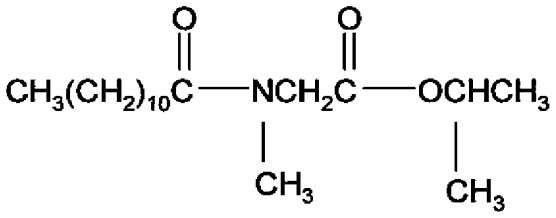
り詳細には、特許出願FR 2 796 550に記載されている。

【００５７】

本発明における使用のために特に好まれるアミノ酸エステルは、以下の式

【００５８】

【化２】



【００５９】

のN-ラウロイルサルコシン酸イソプロピルであり、例えばEldew SL-205という名称で味の素株式会社によって販売されている製品である。

【００６０】

本発明の目的、及びその合成のために好ましく使用されるアミノ酸エステルは、味の素株式会社からの特許出願EP 1 044 676及びEP 0 928 608に記載されている。

【００６１】

b) 湿潤剤

湿潤剤の例として、ソルビトール、多価アルコール、好ましくはC_2～C_8、より好ましくはC_3～C_6の多価アルコール、好ましくは、例えば、グリセロール、プロピレングリコール、1,3-ブチレングリコール、ペンチレングリコール、ヘキシレングリコール、ジプロピレングリコール、ジエチレングリコール、及びジグリセロール、並びにこれらの誘導体及び混合物、グリコールエーテル(とりわけ、3～16個の炭素原子を含有するもの)、例えば、モノ-、ジ-又はトリプロピレングリコール(C_1～C_4)アルキルエーテル、モノ-、ジ-又はトリエチレングリコール(C_1～C_4)アルキルエーテル、尿素及びその誘導体、とりわけ、National Starch社によって販売されるHydrovance(2-ヒドロキシエチル尿素)、乳酸、ヒアルロン酸、AHA、BHA、ピドル酸ナトリウム、キシリトール、セリン、乳酸ナトリウム、エクトイン及びその誘導体、キトサン及びその誘導体、コラーゲン、プランクトン、イムペラタ・シリンドラ(Imperata cylindra)の抽出物(Moist24という名称でSederma社によって販売)、アクリル酸ホモポリマー[例えばNOF Corporation社からのLipidure-HM(登録商標)]、β-グルカン[特にMbelle-AG-Biochemistry社からのカルボキシメチルβ-グルカンナトリウム]、トケイソウ油、アンズ油、トウモロコシ油及び米糠油の混合物[Nestle社によってNutraLipids(登録商標)という名称で販売されているもの]、C-グリコシド誘導体、[例えば特許出願WO 02/051 828に記載されているもの、特に水/プロピレングリコール混合物(60/40質量%)中に有効物質30質量%で含有される溶液形態のC-β-D-キシロピラノシド-2-ヒドロキシプロパン、例えば商品名Mexoryl SBB(登録商標)の商品名でChimex社によって製造されている製品]、Nestle社によって販売されているムスクローズ油、Engelhard Lyon社によってMarine Filling Spheresという名称で販売されているコラーゲンと海洋起源のコンドロイチン硫酸塩(アテロコラーゲン)との球状体、ヒアルロン酸球状体(例えば、Engelhard Lyon社によって販売されているもの)、アルギニン、アルガン油、並びにこれらの混合物を挙げることができる。

【００６２】

組成物中の保湿剤の量は、組成物の総質量に対して、0.001質量%から20.0質量%未満、好ましくは0.01質量%から15.0質量%未満、より好ましくは0.05質量%から10.0質量%であってもよい。

【００６３】
(皮膜形成性ポリマー)
本発明による組成物は、少なくとも1種の皮膜形成性ポリマーを含む。2種以上の皮膜形成性ポリマーを組み合わせて使用してもよい。そのため、単一の種類の皮膜形成性ポリマー、又は異なる種類の皮膜形成性ポリマーの組合せを使用することができる。
【００６４】
本発明の目的では、「ポリマー」という用語は、1つ又は複数の単位(これらの単位はモノマーとして知られる化合物に由来する)の繰り返しに相当する化合物を意味する。この単位は、少なくとも2回繰り返され、好ましくは少なくとも3回繰り返される。
【００６５】
「皮膜形成性ポリマー」という用語は、それ自体によって又は皮膜形成補助剤の存在下で、支持体へ、特にケラチン物質へ付着する巨視的に連続した皮膜を、好ましくは密着性皮膜を、更により良好には、例えば前記皮膜が、非粘着性表面(例えばテフロン(登録商標) で被覆された又はシリコーンで被覆された表面)上へ注がれて調製されるときに、分離可能であり且つ分離された状態で操作可能であるような密着性及び機械的性質を有する皮膜を形成できるポリマーを意味する。
【００６６】
本発明の一実施形態によれば、皮膜形成性ポリマーは、以下を含む群から選択されてもよい:
- 有機溶媒の媒体に溶解性である皮膜形成性ポリマー、特に脂溶性ポリマー(これは、ポリマーが有機媒体に溶解性又は混和性であり、それが媒体中へ組み込まれたときに単一の均一相を形成することになることを意味する)、
- 有機溶媒の媒体に分散性である皮膜形成性ポリマー(これは、ポリマーが、有機媒体中に不溶性相を形成し、ポリマーが、この媒体中に組み込まれても安定で且つ/又は混和性であり続けることを意味する。特に、こうしたポリマーは、ポリマー粒子の非水性分散体、好ましくはシリコーン系油又は炭化水素系油中の分散体の形態にあり;一実施形態では、ポリマーの非水性分散体は、その表面上で少なくとも1種の安定剤で安定化されたポリマー粒子を含み;それらの非水性分散体は、「NAD」と称されることが多い)、及び
- ポリマー粒子の水性分散体の形態の皮膜形成性ポリマー(これは、ポリマーが水中で不溶性相を形成し、ポリマーが、水中に組み込まれても安定で且つ/又は混和性であり続け、ポリマー粒子が表面上で少なくとも1種の安定剤でおそらく安定化されていることを意味する。これらのポリマー粒子はしばしばラテックスと称され;この場合、組成物は水相を含まなければならない)。
【００６７】
組成物中の皮膜形成性ポリマーの量は、組成物の総質量に対して、0.01質量%から20.0質量%未満、好ましくは0.1質量%から15.0質量%未満、より好ましくは1.0質量%から10.0質量%であってもよい。
【００６８】
好ましくは、皮膜形成性ポリマーは、ポリアミド-シリコーンブロックポリマー、エチレン性ブロックポリマー、少なくとも1種のカルボキシルオキサンデンドリマー誘導体を含むビニルポリマー、カルボキシレート基及びポリジメチルシロキサン基を含むコポリマー、シリコーン樹脂、ポリマー粒子の非水性分散体の形態の油分散性ポリマー、非晶質オレフィンコポリマー及び制御された適度な結晶化を伴うオレフィンコポリマーから選択されるオレフィンコポリマー、数平均分子量が10,000g/mol以下である炭化水素系樹脂、並びにそれらの混合物からなる群から選択され、より好ましくはシリコーン樹脂から選択される。
【００６９】
皮膜形成性シリコーン樹脂は、皮膜形成特性を有する任意のシリコーン樹脂であってもよい。
【００７０】

本発明の一実施形態によれば、皮膜形成性シリコーン樹脂は、シルセスキオキサン、シロキシシリケート及びヒドロキシシリル化により得られる樹脂から選択されてもよい。

【００７１】

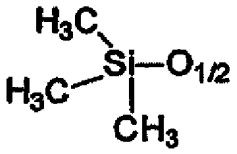
シリコーン樹脂の命名法は、当技術分野において、「MDTQ」命名法の名称で既知であり、「MDTQ」命名法によると、シリコーン樹脂は、ポリマーを構成する様々な繰り返しシロキサンモノマー部分によって記載される。「MDTQ」のうちのそれぞれの文字は、異なる種類の部分に相当する。

【００７２】

記号「M」は、単官能部分$(CH_3)_3SiO_{1/2}$に相当する。この部分は、鎖の形成のために、ケイ素原子がたった1つの酸素を共有するので、単官能であると考えられる。「M」部分は、以下の構造によって表される：

【００７３】

【化３】

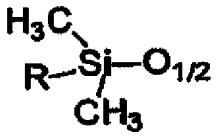


【００７４】

メチル基のうちの少なくとも1つは置換されていてもよく、例えば、$[R(CH_3)_2]SiO_{1/2}$の式を有する部分、例えば、以下の構造

【００７５】

【化４】



【００７６】

(式中、Rはメチル基以外である)

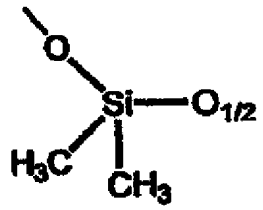
によって表される部分を生じてもよい。

【００７７】

記号「D」は、二官能部分$(CH_3)SiO_{2/2}$に相当し、ケイ素原子の利用可能な結合のうちの2つが、ポリマー鎖の形成のため、酸素と結合するために使用される。「D」部分は、ジメチコン油の必須の構成要素であり、以下の式によって表され得る：

【００７８】

【 化５ 】

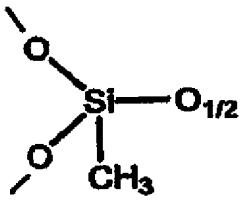


【 ００７９ 】

記号「 T」は、三官能部分(CH_3) $SiO_{3/2}$ に相当し、ケイ素原子の利用可能な結合のうちの3つが、ポリマー鎖の形成のため、酸素と結合するために使用される。「 T」部分は、以下の構造によって表される：

【 ００８０ 】

【 化６ 】



【 ００８１ 】

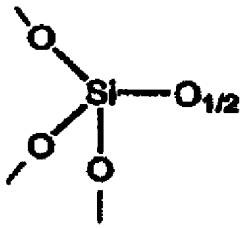
「 M」部分における場合のように、「 D」又は「 T」において、メチル基のうちのいずれか1つは、メチル以外のR基で置換されていてもよい。

【 ００８２ 】

最後に、記号「 Q」は、四官能部分 $SiO_{4/2}$ に相当し、ケイ素原子の4つ全ての利用可能な結合が、ポリマー鎖の形成のため、酸素と結合するために使用される。「 Q」部分は、以下の構造によって表される：

【 ００８３ 】

【 化７ 】



【 ００８４ 】

上記のように、本発明の一実施形態では、皮膜形成性シリコーン樹脂は、シロキシシリケート、シルセスキオキサン及びヒドロキシシリル化により得られる樹脂から選択されてもよい。任意のシロキシシリケート、シルセスキオキサン又はヒドロキシシリル化により得られる樹脂であって、皮膜形成剤として作用するものは、本発明の組成物で使用され得る。皮膜形成性シリコーン樹脂は、好ましくは架橋されている。

【 ００８５ 】

本発明の一実施形態によれば、皮膜形成性シリコーン樹脂は、置換されているシロキシシリケート、シルセスキオキサン及びヒドロキシシリル化により得られる樹脂から選択されてもよい。置換されているシロキシシリケート又は置換されているシルセスキオキサンは、例えば、メチル基が、より長い炭素鎖、例えばエタン、プロパン又はブタン鎖で置換されているシロキシシリケート又はシルセスキオキサンであってもよい。炭素鎖は、飽和であっても不飽和であってもよい。

【００８６】

本発明の一実施形態によれば、皮膜形成性シリコーン樹脂は、シロキシシリケート、例えば以下の式

$[(CH_3)_3SiO_{1/2}]_x(SiO_{4/2})_y$ （MQ部分）

(式中、x及びyは、20から100、好ましくは50から80の範囲の値を有してもよい)

によって表されるMQ樹脂から選択されてもよい。

【００８７】

本発明の別の実施形態によれば、シロキシシリケートは、M部分及びQ部分の全ての組合せ、例えば、$[(R)_3Si]_x(SiO_{4/2})_y$(式中、Rはメチル基及びより長い炭素鎖から選択される)から選択されてもよい。

【００８８】

本発明の別の実施形態によれば、皮膜形成性シリコーン樹脂は、以下の式

$(CH_3SiO_{3/2})_x$ （T部分）

[式中、xは最大数千の範囲であり得る値を有し、CH_3は、R(例えばT部分について上で記載したもの)で置換されていてもよい]

によって表されるシルセスキオキサンから選択されてもよい。

【００８９】

最も好ましくは、皮膜形成性シリコーン樹脂は、トリメチルシロキシシリケートであり、例えばMomentive Performance Materials社によってSR 1000 MQ樹脂という名称で販売されるものである。

【００９０】

(フィラー)

本発明による組成物は、(a)疎水性シリカ、(b)パーライト、(c)ウレタンポリマー粉末、及び(d)アクリルポリマー粉末のフィラーの組合せを含む。

【００９１】

「フィラー」という用語は、組成物が製造される温度にかかわりなく、組成物の媒体に不溶である、任意の形状の無色又は白色の鉱物又は合成粒子を意味する。

【００９２】

組成物中の(a)～(d)フィラーのうちのそれぞれの量は、組成物の総質量に対して、0.001質量%から10.0質量%未満、好ましくは0.01質量%から8質量%未満、より好ましくは0.05質量%から5.0質量%であってもよい。

【００９３】

(a)疎水性シリカ

「疎水性シリカ」という用語は、その表面がシリル化剤、例えばハロゲン化シラン、例えばアルキルクロロシラン、シロキサン、特にジメチルシロキサン、例えばヘキサメチルジシロキサン又はシラザンで処理されて、OH基がシリル基、例えばトリメチルシリル基で官能化されている任意のシリカを意味する。また、シリカは、ジメチルジクロロシラン、又は代わりに、ポリジメチルシロキサンで処理されてもよい。

【００９４】

本発明に適したシリカの商業的参照名の例として、Silica Beads SB 150及びSB 700という参照名で三好化成株式会社から販売されるシリカであって、平均サイズが5ミクロンのシリカ、並びにSunspheres H33、H51及びH53という参照名で旭硝子株式会社から販売されるシリカであって、サイズがそれぞれ約3ミクロン、5ミクロン及び5ミクロンのシリカを挙げることができる。

【００９５】
疎水性シリカとして、疎水性ヒュームドシリカを挙げることもできる。疎水性ヒュームドシリカは、シラノール基の数を減少する化学反応によるシリカの表面の改質によって得ることができ、これらのシラノール基を、特に、疎水基で置換することが可能である。
【００９６】
疎水基は、以下のものであってよい:
- 特にヘキサメチルジシラザンの存在下におけるヒュームドシリカの処理によって得られる、トリメチルシロキシル基(この方法で処理されたシリカは、CTFA(第6版、1995年)に従って、「シリル化シリカ」と称される。これらのシリカは、例えば、参照名「AEROSIL R202(登録商標)」、「AEROSIL R805(登録商標)」及び「AEROSIL R812(登録商標)」でDegussa社によって、並びに「CAB-O-SIL TS-530(登録商標)」でCabot社によって販売されている。)
- 特にポリジメチルシロキサン又はジメチルジクロロシランの存在下におけるヒュームドシリカの処理によって得られるジメチルシリルオキシル又はポリジメチルシロキサン基(この方法で処理されたシリカは、CTFA(第6版、1995年)に従って、「ジメチルシリル化シリカ」と称される。これらのシリカは、例えば、参照名「AEROSIL R972(登録商標)」及び「AEROSIL R974(登録商標)」でDegussa社によって、並びに「CAB-O-SIL TS-610(登録商標)」及び「CAB-O-SIL TS-720(登録商標)」でCabot社によって販売されている)。
【００９７】
疎水性シリカの好ましい例として、以下を挙げることができる。
- VM-2260(INCI名:シリル化シリカ)という名称でDow Corning社によって販売されているエアロゲル(この粒子は、平均サイズがおおよそ1000ミクロンであり、1質量単位当たりの比表面積が600m^2/gから800m^2/gの範囲である)、
- Cabot社によって、参照名Aerogel TLD 201、Aerogel OGD 201、Aerogel TLD 203、Enova(登録商標)Aerogel MT 1100及びEnova Aerogel MT 1200で販売されているエアロゲル、
- VM-2270(INCI名:シリル化シリカ)という名称でDow Corning社によって販売されているエアロゲル(この粒子は、平均サイズが5～15ミクロンの範囲であり、1質量単位当たりの比表面積が600m^2/gから800m^2/gの範囲である)。
【００９８】
疎水性シリカエアロゲル粒子の調製に関しては、文献米国特許第7,470,725号を参照されたい。
【００９９】
最も好ましくは、疎水性シリカは、シリル化シリカであり、例えば、Dow Corning社によってDow Corning VM-2270 Aerogel Fine Particlesという名称で販売されるシリル化シリカである。
【０１００】
(b)パーライト
パーライトは、溶岩の急速冷却から生じる、薄灰色又は輝黒色の、火山起源の天然ガラスから一般に得られ、それは、真珠に似た小粒子の形態である。800℃超で加熱されたとき、パーライトは、それが含有している水を失うという特異な性質、及び多孔質が膨張している形態(初期体積の4～20倍に相当する)を採るという特異な性質を有し、このことが、大量の液体、特に油及び水を吸収できるようにする。そのとき、パーライトは、白色である。
【０１０１】
パーライトは、鉱物起源であって地面から直接取り出され、次いで細かく粉砕されて非常に微細な白色の粉末:パーライト粉末又はパーライト粒子が得られる。
【０１０２】
したがって、パーライト粒子は、非晶質の鉱物材料の粒子であり、これは、有利には、少なくとも1種の火山性岩石から取り出されて膨張される。
【０１０３】

これらの粒子は、ケイ素、アルミニウム及びマグネシウムから選択される少なくとも２種の元素を含み得る。

【０１０４】

より詳細には、これらの鉱物材料は、岩石組成物の総質量に対して、水を1質量%～10質量% 好ましくは1質量%～5質量%含んで、結晶性岩石を、10質量%未満含む、火山性又は「噴出岩性」岩石を熱膨張させ、好ましくは続いて粉砕することによって得ることができる。膨張プロセスの温度は、700℃から1500℃、好ましくは800℃から1100℃の範囲であってよい。米国特許第5,002,698号に記載されている膨張プロセスを、特に使用してよい。

【０１０５】

火山性又は「噴出岩性」岩石は、液体マグマが空気又は水と接触して急速冷却する(ヒアリン岩を生じるクエンチ現象)ことにより一般に生成される。本発明により使用できる火山性岩石は、Streckeisen分類(1974年)に従って定義されているものから選択されてもよい。これらの火山性岩石の中で、粗面岩、ラタイト、安山岩、玄武岩、流紋岩及び石英安山岩を特に挙げることができる。

【０１０６】

例えば、パーライト粒子は火山起源のアルミノシリケートである。それらは、有利には、以下の組成を有する：

70.0～75.0質量%のシリカ(SiO_2)、
12.0～15.0質量%の酸化アルミニウム(Al_2O_3)、
3.0～5.0%の酸化ナトリウム(Na_2O)、
3.0～5.0%の酸化カリウム(K_2O)、
0.5～2%の酸化鉄(Fe_2O_3)、
0.2～0.7%の酸化マグネシウム(MgO)、
0.5～1.5%の酸化カルシウム(CaO)、及び
0.05～0.15%の酸化チタン(TiO_2)。

【０１０７】

好ましくは、本発明による組成物は、三好化成株式会社によってPerlite-M SZ12という名称で販売されるパーライトを含む。

【０１０８】

(c)ウレタンポリマー粉末

「ウレタンポリマー粉末」という用語は、少なくとも部分的にポリウレタン型の材料から構成されるフィラーを意味する。

【０１０９】

本発明の一実施形態によると、ポリウレタン材料は、有利には、架橋された形態にあってもよい。

【０１１０】

本発明の一実施形態によると、ウレタンポリマー粉末は、一般に、実質的に球状であってもよい。「球状」という用語は、本質的に球状の形状を意味し、特にビーズの形態にあり、好ましくは、数平均サイズが1μmから15μmの範囲であり、この範囲は、4、5、6、7、8、9、10、11、12、13、14、15、16、17、18、及び19μm 並びに記述された値の間の全ての部分範囲(subrange)及び値を含む。「数平均サイズ」という用語は、集団の半分のランダム粒径分布によって与えられる寸法を示し、D50として知られている。

【０１１１】

例えば、ウレタンポリマー粉末は、コポリマーを含んでもよい。前記コポリマーは、トリメチロールヘキシルラクトンを含んでもよく、特に、ヘキサメチレンジイソシアネート(HDI)/トリメチロールヘキシルラクトンクロスポリマーを含んでもよい。コポリマーの例として、ウレタンポリマー粉末であって、東色ピグメント株式会社によってPlastic Powder D-400(登録商標)若しくはPlastic Powder D-800(登録商標)という名称で販売されるもの、又はShiki社によってPlastic Powder CS-400(登録商標)という名称で販売されるものを挙げることができる。

【０１１２】
最も好ましくは、ウレタンポリマー粉末として、本発明による組成物は、ヘキサメチレンジイソシアネート(HDI)/トリメチロールヘキシルラクトンクロスポリマー、例えば、東色ピグメント株式会社によってPlastic Powder D 400という名称で販売されるものを含む。
【０１１３】
(d)アクリルポリマー粉末
「アクリルポリマー粉末」という用語は、C_1～C_{20}アルキルで場合により置換されているアクリレート及び/又はメタクリレートモノマーの重合によって得られるフィラーであって、ホモポリマー又はコポリマーの形態のフィラーを意味する。
【０１１４】
アクリルポリマー粉末の例として、ポリメチルメタクリレートの粉末、ポリメチルメタクリレート/エチレングリコールジメタクリレートの粉末、ポリアリルメタクリレート/エチレングリコールジメタクリレートの粉末、ラウリルメタクリレート/エチレングリコールジメタクリレートの粉末、及びアクリロニトリル/メタクリレート/塩化ビニリデンコポリマーの粉末を挙げることができる。
【０１１５】
アクリルポリマー粉末は、一般に、好ましくは、白色で、中空又は中実の球状粒子であって、数平均サイズが一般に、好ましくはマイクロメートルスケールにあり、特に3μmから20μmの範囲、一般に7μmから15μmの範囲の粒子の形態にあり、この範囲は、4、5、6、7、8、9、10、11、12、13、14、15、16、17、18、及び19μm 並びに記述された値の間の全ての部分範囲及び値を含む。
【０１１６】
アクリルポリマー粉末の例として、以下を挙げることができる:
- 架橋されたポリメチルメタクリレートの粉末、例えばLC Wackherr社によって販売される「 Covabead LH85」、又は架橋されていないポリメチルメタクリレートの粉末、例えば日本純薬株式会社によって販売されるSJ Touch 1、
- Sepipress Mという名称でSeppic社によって販売されるメチルメタクリレート/ブチルアクリレートコポリマーの粉末、
- EMAAという名称でKobo Products Inc.社によって販売されるメチルアクリレート/エチレンコポリマーの粉末、
- メチルメタクリレート/エチレングリコールジメタクリレート架橋コポリマーの粉末であって、Ganzpearl GMP 0820という名称でGanz Chemical社によって販売されるもの、Techpolymer MBP-8という名称で積水化成品工業株式会社によって販売されるもの、或いはSUNPMMA-Sという名称でSunjin Chemical社によって販売されるもの、
- ポリメチルメタクリレート/エチレングリコールジメタクリレートの粉末、例えば、Dow Corning社によって販売される「 Dow Corning 5640 Microsponge Skin Oil Adsorber」、
- Ganzpearl PM 030という名称でGanz Chemical社によって販売されるメチルメタクリレート/エチレングリコールジメタクリレート架橋コポリマーの粉末、
- ポリアリルメタクリレート/エチレングリコールジメタクリレートの粉末、例えば、Amcol社によって販売されている「 Poly-Pore L200」、又は「 Poly-Pore E200」、
- ラウリルメタクリレート/エチレングリコールジメタクリレートコポリマーの粉末、例えば、Dow Corning社によって販売されている「 Polytrap 6603」、
- アクリロニトリル/メタクリレート/塩化ビニリデンコポリマーの粉末であって、Expancelという名称でExpancel社によって参照名551 DE 50、551 DE 20、551 DE 12、551 DE 80、及び461 DE 50で販売されるもの。
【０１１７】
好ましくは、アクリルポリマー粉末は、ラウリルメタクリレート/エチレングリコールジメタクリレートクロスポリマー、例えば、Amcol Health & Beauty Solutions社によっ

てPolytrap 6603 Adsorberという名称で販売されるもの、及び/又はアクリロニトリル/メタクリレート/塩化ビニリジンコポリマー、例えば、Akzo Nobel社によってExpancel 551 DE 40 D42という名称で販売されるものである。

【０１１８】

(e)他のフィラー

本発明による組成物は、(a)疎水性シリカ、(b)パーライト、(c)ウレタンポリマー粉末、及び(d)アクリルポリマー粉末以外の少なくとも1種の追加のフィラーを含んでもよい。

【０１１９】

追加のフィラーは、例えば、以下のフィラーから選択することができる:

- エラストマー性架橋オルガノポリシロキサン球状粉末、特に文献JP-A-02 243 612に記載されている粉末、例えば、Trefil Powder E-506Cという名称でDow Corning社によって販売されている粉末、
- カルナウバワックスマイクロビーズであって、Microcare 350(登録商標)という名称でMicro Powders社によって販売されているマイクロビーズ、及びパラフィンワックスマイクロビーズであって、Microease 114S(登録商標)という名称でMicro Powders社によって販売されているマイクロビーズ、
- 粉末形態の金属石鹸、例えば12から22個の炭素原子を含む脂肪酸の金属石鹸、特に、12から18個の炭素原子を含む脂肪酸の金属石鹸(金属石鹸の金属は、特に、亜鉛又はマグネシウムであってもよく、脂肪酸は、ラウリン酸、ミリスチン酸、ステアリン酸及びパルミチン酸から選択されてもよい)、好ましくはラウリン酸亜鉛、ステアリン酸マグネシウム、ミリスチン酸マグネシウム及びステアリン酸亜鉛、及びこれらの混合物、
- タルク又は水和ケイ酸マグネシウム、特に、一般にサイズが40μm未満の粒子の形態のもの、
- 様々な組成のマイカ又はアルミノシリケート、特に、フレーク状で、サイズが2～200μm 好ましくは5～70μmであり、厚さが0.1～5μm 好ましくは0.2～3μmのもの[これらのマイカは、天然由来であってもよく(例えば、硬質雲母、真珠雲母、バナジン雲母、リチア雲母又は黒雲母)、合成由来であってもよい]、
- セリサイト等のクレイ(硬質雲母と同じ化学的及び結晶分類に属する)、
- カオリン又は水和ケイ酸アルミニウム、特に、一般にサイズが30μm未満の等方性粒子の形態のもの、
- 窒化ホウ素、
- テトラフルオロエチレンポリマーの粉末、例えば、Clariant社からのCeridust 9205 F、
- 沈降炭酸カルシウム、特に、サイズが10μmを超える粒子の形態のもの、
- 炭酸マグネシウム及び炭酸水素マグネシウム、
- ヒドロキシアパタイト
- 非膨張合成ポリマーの粉末、例えばポリエチレン、ポリエステル(例えば、ポリエチレンイソフタレート又はテレフタレート)及びポリアミド(例えば、ナイロン)であって、サイズが50μm未満の粒子の形態のもの、
- 球状化した、架橋又は非架橋の合成ポリマーの粉末、例えば、ポリアミド粉末(ポリ-β-アラニン粉末又はナイロン粉末等)、例えばAtochem社からのOrgasol粉末、ポリアクリル酸又はポリメタクリル酸粉末、ジビニルベンゼンで架橋されたポリスチレンの粉末、及びシリコーン樹脂粉末、
- オキシ塩化ビスマス粉末、
- 天然由来の有機物質の粉末、例えば、澱粉、特にトウモロコシ澱粉、小麦澱粉、又は米澱粉、並びに
- これらの混合物。

【０１２０】

本発明の一実施形態によると、本発明による組成物は、ポリアミド粉末、例えば、「ナイロン12」又は「ナイロン6」のCTFA名で列挙されるポリアミド粉末を含んでもよい。ポ

リアミド粉末の混合物、及び例えば、ナイロン6とナイロン12との混合物を使用することができる。

【０１２１】

ポリアミド粉末としては、東レ株式会社によってSP-500という名称で販売されるポリアミド粉末が挙げられる。

【０１２２】

本発明の一実施形態によると、組成物中の追加のフィラーの量は、組成物の総質量に対して、0.01質量%から10.0質量%未満、好ましくは0.1質量%から5.0質量%未満であってもよい。

【０１２３】

(UVフィルター)

本発明による組成物は、少なくとも1種のUVフィルターを含んでもよい。2種以上のUVフィルターを使用する場合、それらは同一であっても異なっていてもよい。

【０１２４】

UVフィルターは、固体又は液体であってもよく、好ましくは液体であってもよい。「固体」及び「液体」という用語は、25℃、1atmでの固体及び液体をそれぞれ意味する。UVフィルターは、少なくとも1種の有機材料又は無機材料、好ましくは少なくとも1種の有機材料で作られていてもよい。したがって、UVフィルターは、好ましくは有機UVフィルターである。

【０１２５】

有機UVフィルターは、アントラニル酸誘導体、ジベンゾイルメタン誘導体、ケイ皮酸誘導体、サリチル酸誘導体、カンファー誘導体、ベンゾフェノン誘導体、β,β-ジフェニルアクリレート誘導体、トリアジン誘導体、ベンゾトリアゾール誘導体、ベンザルマロン酸誘導体、ベンゾイミダゾール誘導体、イミダゾリン誘導体、ビス-ベンゾアゾリル誘導体、p-アミノ安息香酸(PABA)及びその誘導体、ベンゾオキサゾール誘導体、遮断ポリマー及び遮断シリコーン、α-アルキルスチレン由来のダイマー、4,4-ジアリールブタジエン、オクトクリレン及びその誘導体、グアイアズレン及びその誘導体、ルチン及びその誘導体、フラボノイド、ビフラボノイド、オリザノール及びその誘導体、キナ酸及びその誘導体、フェノール、レチノール、システイン、芳香族アミノ酸、芳香族アミノ酸残基含有ペプチド、並びにこれらの混合物からなる群から選択されてもよい。

【０１２６】

有機UVフィルターの例としては、下記にそのINCI名で示すもの、及びそれらの混合物を挙げることができる。

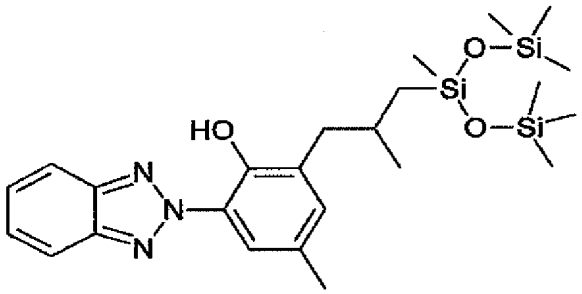
- アントラニル酸誘導体:Haarmann and Reimer社によって「Neo Heliopan MA」の商標で市販されているアントラニル酸メンチル。
- ジベンゾイルメタン誘導体:特に「Parsol 1789」の商標でHoffmann-La Roche社によって販売されているブチルメトキシジベンゾイルメタン、及びイソプロピルジベンゾイルメタン。
- ケイ皮酸誘導体:特に「Parsol MCX」の商標でHoffmann-La Roche社によって販売されているメトキシケイ皮酸エチルヘキシル、メトキシケイ皮酸イソプロピル、イソプロポキシメトキシシンナメート、「Neo Heliopan E 1000」の商標でHaarmann and Reimer社によって販売されているメトキシケイ皮酸イソアミルト、シノキセート(2-エトキシエチル-4-メトキシシンナメート)、メトキシケイ皮酸DEA、メチルケイ皮酸ジイソプロピル、及びエチルヘキサン酸ジメトキシケイヒ酸グリセリル。
- サリチル酸誘導体:Rona/EM Industries社によって「Eusolex HMS」の商標で市販されているホモサレート(サリチル酸ホモメンチル);Haarmann and Reimer社によって「Neo Heliopan OS」の商標で市販されているサリチル酸エチルヘキシル;サリチル酸グリコール;サリチル酸ブチルオクチル;サリチル酸フェニル;Scher社によって「Dipsal」の商標で市販されているサリチル酸ジプロピレングリコール;及びHaarmann and Reimer社によって「Neo Heliopan TS」の商標で市販されているサリチル酸TEA。

- カンファー誘導体、特にベンジリデンカンファー誘導体:Chimex社によって「Mexoryl SD」の商標で製造されている3-ベンジリデンカンファー;Merck社によって「Eusolex 6300」の商標で市販されている4-メチルベンジリデンカンファー;Chimex社によって「Mexoryl SL」の商標で製造されているベンジリデンカンファースルホン酸;Chimex社によって「Mexoryl SO」の商標で製造されているカンファーベンザルコニウムメトスルフェート;Chimex社によって「Mexoryl SX」の商標で製造されているテレフタリリデンジカンファースルホン酸;及びChimex社によって「Mexoryl SW」の商標で製造されているポリアクリルアミドメチルベンジリデンカンファー。
- ベンゾフェノン誘導体:BASF社によって「Uvinul 400」の商標で市販されているベンゾフェノン-1(2,4-ジヒドロキシベンゾフェノン);BASF社によって「Uvinul D50」の商標で市販されているベンゾフェノン-2(テトラヒドロキシベンゾフェノン);BASF社によって「Uvinul M40」の商標で市販されているベンゾフェノン-3(2-ヒドロキシ-4-メトキシベンゾフェノン)又はオキシベンゾン;BASF社によって「Uvinul MS40」の商標で市販されているベンゾフェノン-4(ヒドロキシメトキシベンゾフェノンスルホン酸);ベンゾフェノン-5(ヒドロキシメトキシベンゾフェノンスルホン酸ナトリウム);Norquay社によって「Helisorb 11」の商標で市販されているベンゾフェノン-6(ジヒドロキシジメトキシベンゾフェノン);American Cyanamid社によって「Spectra-Sorb UV-24」の商標で市販されているベンゾフェノン-8;BASF社によって「Uvinul DS-49」の商標で市販されているベンゾフェノン-9(ジヒドロキシジメトキシベンゾフェノンジスルホン酸二ナトリウム);ベンゾフェノン-12、及び2-(4-ジエチルアミノ-2-ヒドロキシベンゾイル)安息香酸n-ヘキシル。
- β,β-ジフェニルアクリレート誘導体:特にBASF社によって「Uvinul N539」の商標で市販されているオクトクリレン;及び特にBASF社によって「Uvinul N35」の商標で市販されているエトクリレン。
- トリアジン誘導体:Sigma 3V社によって「Uvasorb HEB」の商標で市販されているジエチルヘキシルブタミドトリアゾン;2,4,6-トリス(ジネオペンチル4'-アミノベンザルマロネート)-s-トリアジン。
- ベンゾトリアゾール誘導体、特にフェニルベンゾトリアゾール誘導体:分枝状及び直鎖状の2-(2H-ベンゾトリアゾール-2-イル)-6-ドデシル-4-メチルフェノール、及びUSP 5240975に記載のもの。
- ベンザルマロネート誘導体:4'-メトキシベンザルマロン酸ジネオペンチル、及びベンザルマロネート官能基を含むポリオルガノシロキサン、例えば、Hoffmann-LaRoche社によって「Parsol SLX」の商標で市販されているポリシリコーン-15。
- ベンゾイミダゾール誘導体、特にフェニルベンゾイミダゾール誘導体:特にMerck社によって「Eusolex 232」の商標で市販されているフェニルベンゾイミダゾールスルホン酸、及びHaarmann and Reimer社によって「Neo Heliopan AP」の商標で市販されているフェニルジベンゾイミダゾールテトラスルホン酸二ナトリウム。
- イミダゾリン誘導体:エチルヘキシルジメトキシベンジリデンジオキソイミダゾリンプロピオネート。
- ビス-ベンゾアゾリル誘導体:EP-669,323及び米国特許第2,463,264号に記載の誘導体。
- パラ-アミノ安息香酸及びその誘導体:PABA(p-アミノ安息香酸)、エチルPABA、エチルジヒドロキシプロピルPABA、ペンチルジメチルPABA、特にISP社によって「Escalol 507」の商標で市販されているエチルヘキシルジメチルPABA、グリセリルPABA、及びBASF社によって「Uvinul P25」の商標で市販されているPEG-25 PABA。
- メチレンビス-(ヒドロキシフェニルベンゾトリアゾール)化合物:例えば、固体形態で、「Mxxim BB/200」の商標でFairmount Chemical社によって市販されている2,2'-メチレンビス[6-(2H-ベンゾトリアゾール-2-イル)-4-メチル-フェノール]、水性分散体中において微粉化形態で、「Tinosorb M」の商標でBASF社によって、又は「Mxxim BB/100」の商標でFairmount Chemical社によって市販されている2,2'-メチレンビス[6-(2H-ベンゾトリアゾール-2-イル)-4-(1,1,3,3-テトラメチルブチル)フェノール]、並びに米国特許第5,237,071号、米国特許第5,166,355号、GB-2,303,549、DE-197,26,184、及びEP-893,119に記

載の誘導体、並びに「 Silatrizole」の商標でRhodia Chimie社によって、又は「 Mexoryl XL」でL'Oreal社によって市販され、以下で表されるドロメトリゾールトリシロキサン、

【 0127 】

【 化8 】



【 0128 】

- ベンゾオキサゾール誘導体:Sigma 3V社によってUvasorb K2Aの商標で市販されている2,4-ビス[5-1(ジメチルプロピル)ベンゾオキサゾール-2-イル-(4-フェニル)イミノ]-6-(2-エチルヘキシル)イミノ-1,3,5-トリアジン。
- 遮蔽性ポリマー及び遮蔽性シリコーン:WO 93/04665に記載のシリコーン。
- α-アルキルスチレンに由来するダイマー:DE-19855649に記載のダイマー。
- 4,4-ジアリールブタジエン誘導体:1,1-ジカルボキシ(2,2'-ジメチルプロピル)-4,4-ジフェニルブタジエン。
- グアイアズレン及びその誘導体:グアイアズレン及びグアイアズレンスルホン酸ナトリウム。
- ルチン及びその誘導体:ルチン及びグルコシルルチン。
- フラボノイド:ロブスチン(イソフラボノイド)、ゲニステイン(フラボノイド)、テクトクリシン(フラボノイド)及びヒスピドン(フラボノイド)。
- ビフラボノイド:ランセオラチンA、ランセオラチンB及びヒプナンビフラボノイドA。
- オリザノール及びその誘導体:γ-オリザノール。
- キナ酸及びその誘導体:キナ酸。
- フェノール:フェノール。
- レチノール:レチノール。
- システイン:L-システイン。
- 芳香族アミノ酸残基含有ペプチド:トリプトファン、チロシン又はフェニルアラニンを有するペプチド。

【 0129 】

好ましい有機UVフィルターは、以下から選択することができる:
ブチルメトキシジベンゾイルメタン、メトキシケイ皮酸エチルヘキシル、ホモサレート、サリチル酸エチルヘキシル、オクトクリレン、フェニルベンゾイミダゾールスルホン酸、ベンゾフェノン-3、ベンゾフェノン-4、ベンゾフェノン-5、2-(4-ジエチルアミノ-2-ヒドロキシベンゾイル)安息香酸n-ヘキシル、4-メチルベンジリデンカンファー、テレフタリリデンジカンファースルホン酸、フェニルジベンゾイミダゾールテトラスルホン酸二ナトリウム、エチルヘキシルトリアゾン、ビス-エチルヘキシルオキシフェノールメトキシフェニルトリアジン、ジエチルヘキシルブタミドトリアゾン、2,4,6-トリス(ジネオペンチル4'-アミノベンザルマロネート)-s-トリアジン、2,4,6-トリス(ジイソブチル4'-アミノベンザルマロネート)-s-トリアジン、メチレンビス-ベンゾトリアゾリルテトラメチルブチルフェノール、ポリシリコーン-15、4'-メトキシベンザルマロン酸ジネオペンチル、1,1-ジカルボキシ(2,2'-ジメチルプロピル)-4,4-ジフェニルブタジエン、2,4-ビス[5-1(ジ

メチルプロピル)ベンゾオキサゾール-2-イル-(4-フェニル)イミノ]-6-(2-エチルヘキシル)イミノ-1,3,5-トリアジン、及びこれらの混合物。より好ましい有機UVフィルターは、ブチルメトキシジベンゾイルメタン(アボベンゾン)である。

【０１３０】

好ましい実施形態において、UVフィルターは、液体有機UVフィルターである。

【０１３１】

液体有機UVフィルターの材料は、有機である限り、限定されない。2種以上の液体有機UVフィルターを使用する場合、液体有機UVフィルターの材料は、互いに同じものでも、異なってもよい。

【０１３２】

液体有機UVフィルターの中で、本発明者らは、以下を挙げることができる:

- ケイ皮酸誘導体:特に「Parsol MCX」の商標でHoffmann-La Roche社によって市販されているメトキシケイ皮酸エチルヘキシル、メトキシケイ皮酸イソプロピル、イソプロポキシメトキシシンナメート、「Neo Heliopan E 1000」の商標でHaarmann and Reimer社によって市販されているメトキシケイ皮酸イソアミル、シノキセート(2-エトキシエチル-4-メトキシシンナメート)、メトキシケイ皮酸DEA、メチルケイ皮酸ジイソプロピル、及びエチルヘキサン酸ジメトキシケイヒ酸グリセリル。
- サリチル酸誘導体:Rona/EM Industries社によって「Eusolex HMS」の商標で市販されているホモサレート(サリチル酸ホモメンチル);Haarmann and Reimer社によって「Neo Heliopan OS」の商標で市販されているサリチル酸エチルヘキシル;グリコール;サリチル酸ブチルオクチル;サリチル酸フェニル;Scher社によって「Dipsal」の商標で市販されているサリチル酸ジプロピレングリコール;及びHaarmann and Reimer社によって「Neo Heliopan TS」の商標で市販されているサリチル酸TEA。
- β,β-ジフェニルアクリレート誘導体:特にBASF社によって「Uvinul N539」の商標で市販されているオクトクリレン;及び特にBASF社によって「Uvinul N35」の商標で市販されているエトクリレン。
- ベンザルマロネート官能基を含むポリオルガノシロキサン、例えば、Hoffmann-LaRoche社によって「Parsol SLX」の商標で市販されているポリシリコーン-15。

【０１３３】

好ましい液体有機UVフィルターは、メトキシ経皮酸エステル、ホモサレート、サリチル酸エチルヘキシル、エチルヘキシルトリアゾン、オクトクリレン、ドロメトリゾールトリシロキサン2-(4-ジエチルアミノ-2-ヒドロキシベンゾイル)安息香酸、n-ヘキシル、テレフタリリデンジカンファースルホン酸、及びビス-エチルヘキシルオキシフェノールメトキシフェニルトリアジンから選択されてもよい。

【０１３４】

UVフィルターは、本発明のために使用される組成物中に、組成物の総質量に対して、0.1質量%~40質量%の範囲、好ましくは1質量%~20質量%、より好ましくは3質量%~10質量%の範囲の含有量で存在してもよい。

【０１３５】

(添加剤)

本発明の特定の実施形態によると、本発明による組成物は、水、親水性溶媒、親油性溶媒、揮発性油、及びそれらの混合物から選択される少なくとも1種の化合物を更に含む。

【０１３６】

親水性溶媒としては、モノアルコール、例えばエタノール、プロパノール、ブタノール、イソプロパノール又はイソブタノール;ポリエチレングリコール;ポリオール、例えばプロピレングリコール、イソプレングリコール、ブチレングリコール、グリセロール又はソルビトール;イソソルビドのモノ-又はジアルキル誘導体、例えばジメチルイソソルビド;グリコールエーテル、例えばジエチレングリコールモノメチル又はモノエチルエーテル、及びプロピレングリコールエーテル、例えばジプロピレングリコールメチルエーテルを挙げることができる。

【０１３７】
本発明による組成物は、例えば、ガム、アニオン性、カチオン性、両性又は非イオン性界面活性剤、シリコーン界面活性剤、樹脂、増粘剤、構造化剤、例えばワックス、分散剤、酸化防止剤、エッセンシャルオイル、保存剤、香料、中和剤、殺菌剤、化粧活性剤、例えばビタミン、皮膚軟化剤、又は顔料、及びこれらの混合物から選択される、検討中の分野において通常使用される任意の添加剤を含むこともできる。
【０１３８】
増粘剤としては、ポリマー増粘剤又は鉱物増粘剤、好ましくは親水性増粘剤、親油性増粘剤、又はこれらの混合物から選択される増粘剤を挙げることができる。より好ましくは、増粘剤は、多糖類バイオポリマー、親油性クレイ、疎水性シリカ、又はこれらの混合物から選択され、更により好ましくは、増粘剤は、キサンタンガム、ジステアルジモニウムヘクトライト(distearidimonium hectorite)、シリル化シリカ、又はこれらの混合物から選択される。最も好ましくは、増粘剤はジステアルジモニウムヘクトライトである。
【０１３９】
顔料としては、白色又は有色の、鉱物又は有機粒子であって、水性溶液に不溶性の粒子、例えば、酸化チタン、酸化ジルコニウム又は酸化セリウム、更にまた酸化亜鉛、酸化鉄又は酸化クロム、フェリクブルー(ferric blue)、マンガンヴァイオレット、ウルトラマリンブルー及びクロム水和物を挙げることができる。
【０１４０】
本発明による化粧用組成物中に存在する添加剤の性質及び量を、所望の化粧特性及びその安定性特性が添加剤により影響を受けないよう調整することは、当業者にとって常法の範囲内である。
【０１４１】
本発明による化粧用組成物は、皮膚メイクアップ製品、特に化粧下地、ファンデーション、高温注型ファンデーション製品、ボディメイクアップ製品、コンシーラー、アイシャドー、リップスティック、又はボディデオドラントの形態であってもよい。特定の実施形態では、化粧用組成物は、化粧下地又は液体ファンデーションであってもよい。
【０１４２】
本発明による組成物は、従来使用される配合形態のいずれかの形態にあってもよく、好ましくはO/W W/O又はマルチ型のエマルジョンの形態、特に液体又は半液体の粘稠度のエマルジョンの形態にあってもよい。
【０１４３】
本発明の一実施形態によると、本発明は、乾燥感を生じずに「持続」効果を改善するための方法において、少なくとも1種の皮膜形成性ポリマー、並びに(a)疎水性シリカ、(b)パーライト、(c)ウレタンポリマー粉末、及び(d)アクリルポリマー粉末のフィラーの組合せを、ケラチン物質、例えば皮膚、例えば顔の皮膚のための化粧用組成物、特に化粧下地又は液体ファンデーションに添加し、化粧用組成物が少なくとも1種の保湿剤を含むことを特徴とする方法にも関する。
【０１４４】
本発明の特定の実施形態によると、本発明は、少なくとも1種の皮膜形成性ポリマー、並びに(a)疎水性シリカ、(b)パーライト、(c)ウレタンポリマー粉末、及び(d)アクリルポリマー粉末のフィラーの組合せの使用であって、少なくとも1種の保湿剤を含む、ケラチン物質のための化粧用組成物に、乾燥感を生じずに「持続」効果を与えるための使用に関する。
【０１４５】
[美容方法]
本発明は、ケラチン物質、例えば皮膚、例えば顔の皮膚のための美容方法であって、本発明による組成物をケラチン物質上に適用する工程を含む、美容方法にも関する。
【０１４６】
皮膜形成性ポリマー、並びに(a)疎水性シリカ、(b)パーライト、(c)ウレタンポリマー

粉末、及び(d)アクリルポリマー粉末のフィラーの組合せを同時に使用することは、保湿剤を含む、ケラチン物質のための化粧用組成物において、乾燥感を生じずに「持続」効果を改善できる。

【実施例】

【０１４７】

本発明を、実施例によって、より詳細に説明することにする。しかしながら、これら実施例が本発明の範囲を限定するものとは解釈すべきでない。

【０１４８】

化粧下地の例

(実施例1及び比較例1～6)

Table 1(表1)に示す実施例1及び比較例1～6による以下の化粧下地組成物を、Table 1(表1)に示す成分を混合することによって次のように調製した:(1)相A1及び相A2をメインビーカーに入れる;(2)相A3を加え、完全に溶解させる;(3)相A4を加え、均一に分散させる;(4)相Bを加え、均一に分散させる;(5)相Cを加え、均一に分散させる;(6)相Dを加え、生じた混合物を乳化させる;(7)相Eを加え、均一に分散させる。Table 1(表1)に示す成分の量についての数値は全て、活性原料としての「質量%」に基づく。

【０１４９】

[表１Ａ]

[０１５０]

Table 1

相	成分	実施例	比較例					
		1	1	2	3	4	5	6
A1	PEG-10 ジメチコン	3.00	3.00	3.00	3.00	3.00	3.00	3.00
	BIS-PEG/PPG-14/14 ジメチコン(及び)ジメチコン	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	ジメチコン	qs 100	qs 100	qs 100	qs 100	qs 100	qs 100	qs 100
A2	ジペンタエリトリチルテトラヒドロキシステアレート/テトライソステアレート(日清オイリオグループ株式会社の SalacosS 168 EV)	0.10	-	0.10	0.30	0.30	0.30	0.30
	メトキシケイ皮酸エチルヘキシル(BASF 社の Uvinul MC 80)	4.00	-	4.00	4.00	4.00	4.00	4.00
A3	トリメチルシロキシシリケート(Momentive Performance Materials 社の SR 1000 MQ Resin)	5.00	5.00	-	5.00	5.00	5.00	5.00
A4	ジステアルジモニウムヘクトライト	0.50	0.50	0.50	0.50	0.50	0.50	0.50
B	シリル化シリカ(Dow Corning VM-2270 Aerogel Fine Particles)	0.10	0.10	0.10	-	0.10	0.10	0.10
	ラウリルメタクリレート/グリコールジメタクリレートクロスポリマー(Amcol Health & Beauty Solutions 社の Polytrap 6603 Adsorber)	1.00	1.00	1.00	1.00	-	1.00	1.00
	パーライト(三好化成株式会社の Perlite-M SZ12)	1.00	1.00	1.00	1.00	1.00	-	1.00
	HDI/トリメチロールヘキシルラクトンクロスポリマー(東色ピグメント株式会社の Plastic Powder D 400)	1.00	1.00	1.00	1.00	1.00	1.00	-
C	二酸化チタン(及び)水酸化アルミニウム(及び)ジメチコン(及び)ハイドロゲンジメチコン	3.00	3.00	3.00	3.00	3.00	3.00	3.00
	酸化鉄(及び)ステアロイルグルタミン酸二ナトリウム(及び)水酸化アルミニウム(NAI-C33-9001-10/三好化成株式会社)	0.03	0.03	0.03	0.03	0.03	0.03	0.03
	酸化鉄(及び)ステアロイルグルタミン酸二ナトリウム(及び)水酸化アルミニウム(NAI-C33-8001-10/三好化成株式会社)	0.01	0.01	0.01	0.01	0.01	0.01	0.01

【 表１ Ｂ 】

D	水	35.00	35.00	35.00	35.00	35.00	35.00	35.00
E	アルコール	10.00	10.00	10.00	10.00	10.00	10.00	10.00
	合計	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	持続性(n=5)	○	○	X	X	X	X	X
	保湿性(n=5)	○	X	○	X	○	○	○

【 ０１５１ 】

液体ファンデーションの例
(実施例2及び3並びに比較例7及び8)
Table 2(表2)に示す実施例2及び3並びに比較例7及び8による以下の液体ファンデーション組成物を、上記の「化粧下地の例」に記載の方法と同じ方法で、Table 2(表2)に示す成分を混合することによって調製した。Table 2(表2)に示す成分の量についての数値は全て、活性原料としての「質量%」に基づく。
【０１５２】

Table 2

相	成分	実施例		比較例	
		2	3	7	8
A1	PEG-10 ジメチコン	3.00	3.00	3.00	3.00
	BIS-PEG/PPG-14/14 ジメチコン(及び)ジメチコン	1.00	1.00	1.00	1.00
	ジメチコン	qs 100	qs 100	qs 100	qs 100
A2	セバシン酸ジイソプロピル(Stearinerie Dubois 社の Dub Dis)	2.00	-	-	2.00
	ラウロイルサルコシン酸イソプロピル(味の素株式会社の Eldew SL-205)	-	2.00	-	-
	ジペンタエリトリチルテトラヒドロキシステアレート/テトライソステアレート(日清オイリオグループ株式会社の SalacosS 168 EV)	0.30	0.30	-	0.30
	メトキシケイ皮酸エチルヘキシル(BASF 社の Uvinul MC 80)	-	-	-	8.00
A3	トリメチルシロキシシリケート(Momentive Performance Materials 社の SR 1000 MQ Resin)	5.00	5.00	5.00	5.00
A4	ジステアルジモニウムヘクトライト	1.00	1.00	1.00	1.00
B	シリル化シリカ(Dow Corning VM-2270 Aerogel Fine Particles)	0.10	1.00	0.10	0.10
	アクリロニトリル/メチルメタクリレート/塩化ビニリデンコポリマー(Akzo Nobel 社の Expancel 551 DE 40 D42)	0.10	0.50	0.10	-
	パーライト(三好化成株式会社の Perlite-M SZ12)	1.00	3.00	1.00	1.00
	HDI/トリメチロールヘキシルラクトンクロスポリマー(東色ピグメント株式会社の Plastic Powder D 400)	0.50	3.00	0.50	0.50
C	二酸化チタン(及び)水酸化アルミニウム(及び)ジメチコン(及び)ハイドロゲンジメチコン	5.00	5.00	5.00	5.00
	二酸化チタン(及び)ステアロイルグルタミン酸二ナトリウム(及び)水酸化アルミニウム (NAI-TAO-77891/三好化成株式会社)	10.72	10.72	10.72	10.72
	酸化鉄(及び)ステアロイルグルタミン酸二ナトリウム(及び)水酸化アルミニウム (NAI-C33-7001-10/三好化成株式会社)	0.11	0.11	0.11	0.11
	酸化鉄(及び)ステアロイルグルタミン酸二ナトリウム(及び)水酸化アルミニウム (NAI-C33-9001-10/三好化成株式会社)	2.12	2.12	2.12	2.12

【 表２ Ｂ 】

	酸化鉄(及び)ステアロイルグルタミン酸二ナトリウム(及び)水酸化アルミニウム (NAI-C33-8001-10/三好化成株式会社)	0.39	0.39	0.39	0.39
D	水	30.00	30.00	30.00	30.00
E	アルコール	7.00	7.00	7.00	7.00
	合計	100.00	100.00	100.00	100.00
	持続性(n=5)	○	○	○	X
	保湿性(n=5)	○	○	X	○

【 ０１５４ 】

[評価]
実施例1～3による組成物を、使用者の顔の半分に、適切な量で適用すると共に、比較例1～8による組成物を、使用者の顔の残りの半分に、同じ量で適用した。その後、組成物を指で広げ、化粧皮膜を形成した。5人の使用者が、評価テストに参加した。
【０１５５】
適用中及び適用後に、保湿効果を評価した。評価の基準は以下の通りである。
O: 保湿感の知覚
X: 保湿感の欠如
【０１５６】
実施例1並びに比較例1～6について、化粧下地組成物上に粉末ファンデーションを適用し、又は実施例2及び3並びに比較例7及び8について、液体ファンデーション組成物上に何も適用せずに、適用の3時間後に顔のてかりをチェックすることにより、「持続」効果を評価した。評価の基準は以下の通りである。
O: ファンデーションの持続が良好である
X: ファンデーションの持続が不良である
【０１５７】
評価の結果をTable 1(表1)及びTable 2(表2)に示す。
【０１５８】
化粧下地組成物に関して(Table 1(表1))、実施例1による組成物[少なくとも1種の保湿剤(ジペンタエリトリチルテトラヒドロキシステアレート/テトライソステアレート)、皮膜形成性ポリマー(トリメチルシロキシシリケート)、及び本発明のフィラーの組合せ(シリル化シリカ、パーライト、HDI/トリメチロールヘキシルラクトンクロスポリマー、及びラウリルメタクリレート/グリコールジメタクリレートクロスポリマー)を含む]は、保湿感を与えることができ、「持続」効果を有していた。
【０１５９】
一方、比較例1による組成物[皮膜形成性ポリマー及び本発明のフィラーの組合せを含むが、保湿剤を含まない]は、保湿感を与えることができなかった。
【０１６０】
比較例2による組成物[保湿剤及び本発明のフィラーの組合せを含むが、皮膜形成性ポリマーを含まない]は、「持続」効果を有していなかった。
【０１６１】
比較例3～6による組成物は、保湿剤及び皮膜形成性ポリマーを含んでいたが、本発明の必須のフィラーのうちの1つを含んでいなかった。これらの組成物は、「持続」効果を有していなかった。
【０１６２】
このことは、「持続」効果を有すると共に、保湿感を与えるために、皮膜形成性ポリマーだけでなく、本発明の必須のフィラーの全て(すなわち、疎水性シリカ、パーライト、ウレタンポリマー粉末、及びアクリルポリマー粉末)も、保湿剤を含む化粧用組成物に加えることが必要であることを示す。
【０１６３】
また、このことは、液体ファンデーション組成物(Table 2(表2))を使用することにより得られる結果においても支持されている。

フロントページの続き

(51)Int.Cl.			FI		テーマコード(参考)
A61K	*8/89*	*(2006.01)*	A61K	8/89	
A61Q	*19/00*	*(2006.01)*	A61Q	19/00	
A61K	*8/06*	*(2006.01)*	A61K	8/06	
A61Q	*1/00*	*(2006.01)*	A61Q	1/00	

(72)発明者　上土井　優香
神奈川県川崎市高津区坂戸３－２－１　ケイエスピーアールアンドディ－－ビー１１１３　日本ロレアル株式会社内

Fターム(参考) 4C083 AB171 AB172 AB222 AB232 AB242 AB432 AC102 AC331 AC342 AC372
AC442 AC581 AC662 AD071 AD072 AD091 AD092 AD151 AD152 AD161
AD162 BB11 BB46 CC03 CC12 DD23 DD27 DD82 DD83 EE06
EE12

【 外 国 語 明 細 書 】
2017114773000001. pdf

Europäisches Patentamt
European Patent Office
Office européen des brevets

Espacenet

JPH04320457A PIGMENT COMPOSITION, ITS PRODUCTION AND COSMETIC CONTAINING THE SAME

Applicants: KUBO YASUSHI,DAITO KASEI KOGYO CO LTD

Inventors: KUBO YASUSHI

Classifications:
IPC ***A61K8/18; A61K8/19; A61K8/25; A61K8/35; A61K8/37; A61K8/40; A61K8/49; A61K8/73; A61K8/96; A61Q1/00; A61Q1/02; A61Q1/04; C08K3/34; C08L1/00; C08L5/08; C09B67/02; C09C1/42; C09C3/08;***
(IPC1-7): A61K7/00; A61K7/02; C08K3/34; C08L5/08; C09B67/02; C09C1/42; C09C3/08;

Priorities: JP11684291A 1991-04-19

Application: JP11684291A·1991-04-19

Publication: JPH04320457A·1992-11-11

Published as: **JP2951033B2**; JPH04320457A

PIGMENT COMPOSITION, ITS PRODUCTION AND COSMETIC CONTAINING THE SAME

Abstract

PURPOSE:To provide a safe and stable pigment composition, a process for its production and a useful cosmetic containing the same. CONSTITUTION:A pigment composition which can develop various hues and excels in the prevention of release of colorant is obtained by allowing a chitosan/swellable smectite composite material to adsorb a colorant and performing crosslinking by the action of a polyfunctional reagent reactive with chitosan. A process for producing such a pigment composition and a cosmetic containing such a pigment composition can be accomplished by this invention. A safe and stable colorant which can develop a markedly extensive range of hues can be provided by using limited kinds of approved colors.

(19)日本国特許庁（ＪＰ）　(12) **公開特許公報（Ａ）**　(11)特許出願公開番号

特開平4－320457

(43)公開日　平成４年(1992)11月11日

(51)Int.Cl.[5]	識別記号	庁内整理番号	ＦＩ	技術表示箇所
Ｃ０９Ｂ　67/02		Ａ　7306－4H		
Ａ６１Ｋ　7/00		Ｋ　7327－4C		
		Ｂ　7327－4C		
7/02		Ｐ　7327－4C		
Ｃ０８Ｋ　3/34		7167－4Ｊ		

審査請求　未請求　請求項の数７(全　5　頁)　最終頁に続く

(21)出願番号　特願平3－116842

(22)出願日　平成３年(1991)４月19日

(71)出願人　591106691
久保　靖
静岡県浜松市広沢１丁目22番12号
(71)出願人　391015373
大東化成工業株式会社
大阪府大阪市旭区赤川１丁目６番28号
(72)発明者　久保　靖
静岡県浜松市広沢１丁目22番12号
(74)代理人　弁理士　杉浦　俊貴

(54)【発明の名称】　顔料組成物とその製造方法およびその顔料組成物配合化粧料

(57)【要約】
【目的】　安全かつ安定な顔料組物とのその製造方法およびその顔料組成物が配合されることよにより優れた有用性を示す化粧料を提供する。
【構成】　キトサンと膨潤性スメクタイトとの複合体に色素を吸着させるとともに、キトサン反応性を有する多官能試薬を作用させて架橋処理を行うことにより、多様な色相の発現が可能で、しかも色素の耐溶出性に優れた顔料組成物が得られる。さらに、このような顔料組成物の製造方法およびその顔料組成物が添加配合された化粧料が本発明により達成される。
【効果】　限られた種類の許可色素の範囲で、発現される色相の範囲が著しく拡大されるとともに、安全で安定な着色料が提供される。

1

【特許請求の範囲】

【請求項１】　キトサンと膨潤性スメクタイトとの複合体に色素を吸着させるとともに、キトサン反応性を有する多官能性試薬を作用させて架橋処理したことを特徴とする顔料組成物。

【請求項２】　前記多官能性試薬は、グルタルアルデヒド、ジカルボン酸エステル、ジカルボン酸ハライド、有機ジイソシアネート、エピハロヒドリン等から選ばれた少なくとも一種である請求項１に記載の顔料組成物。

【請求項３】　キトサン酸性溶液と膨潤性スメクタイト水分散物とを混合する混合工程、この混合工程で得られる混合液にキトサン染着性色素とキトサン反応性を有し水性溶媒中で作用する架橋剤とを添加する添加工程およびこの添加工程で生成した易濾過性の着色スラリーを濾別・洗浄した後、乾燥・粉砕する仕上げ工程、を含むことを特徴とする顔料組成物の製造方法。

【請求項４】　前記添加工程において、混合液に対するキトサン染着性色素と架橋剤との添加が同時または順次のいずれかにより添加させることを特徴とする請求項３に記載の顔料組成物の製造方法。

【請求項５】　キトサン酸性溶液と膨潤性スメクタイト水分散物とを混合する混合工程、この混合工程で得られる混合液にキトサン染着性色素を添加する第一添加工程、この第一添加工程で生成した易濾過性の着色スラリーを濾別・洗浄し、水分を非水性溶媒で置換する置換工程、この置換工程で得られる非水溶性スラリーにキトサン反応性を有し非水性溶媒中で作用する架橋剤を添加する第二添加工程およびこの第二添加工程を経た溶媒中から着色固形分を分離した後、乾燥・粉砕する仕上げ工程を含むことを特徴とする顔組成物の製造方法。

【請求項６】　前記混合工程で得られる混合液に添加されるキトサン染着性色素は、その溶液、懸濁液または粉末のうちのいずれかの状態のものである請求項３または５に記載の顔料組成物の製造方法。

【請求項７】　キトサンと膨潤性スメクタイトとの複合体に色素を吸着させるとともに、キトサン反応性を有する多官能性試薬を作用させて架橋処理して得られる顔料組成物を含有することを特徴とする化粧料。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、安全性に優れるとともに、色相の範囲を拡大した顔料組成物とその製造方法およびその顔料組成物が配合された化粧料に関するものである。

【０００２】

【従来の技術】顔料の中でも、特に食品添加物や化粧品原料としての用途を有するものには、人体無害性が何にもまして重視される。従来、このような目的の着色料としては、水酸化アルミニウムゲル担体やセルロース質担体に食用色素のような人体に無害な水溶性合成色素や天

2

然色素を吸着・担持させた顔料が用いられてきたが、もととなる色素の種類がごく限られているために十分な種類の色相が得られないという不便があった。

【０００３】これに対し、天然多糖類の一種であるキトサンの色素吸着能に着目して、このキトサンをアルミニウムゲルやセルロース質に代わる色素担体として利用し新しい顔料を得ようとする試みがなされてきた。

【０００４】本発明者は、先に前記キトサンの色素吸着能を効果的に発現させることを意図して、キトサンと粘土鉱物の一種である膨潤性スメクタイトとの複合体を色素担体とすることにより得られる安定性に優れ、且つ色調に富む顔料組成物とその製造方法およびそのような顔料組成物の活用の方策を提案した（特願平１－２７７３９９号）。

【０００５】

【発明が解決しようとする課題】天然多糖類であるキトサンに食用合成色素のような水溶性染料やキトサン染着性をもつ天然色素を担持させると、糊状物を多く含む着色ゲルが得られ、この着色ゲルは濾過・洗浄等の処理が実際上不可能と言えるほど困難である。さらにたとえ着色物を固形化し粉砕しても、得られる粉末は水に対して膨潤性を有し、容易にべとつく状態になる。

【０００６】また、前記の粉末は油分散性を全く持たず、したがって着色キトサンゲルから顔料に求められる基本的な特性である微細で分散性の良い安定な粉末状体を得るためには多くの問題点があった。

【０００７】これらの問題点については、前述したように本発明者が特願平１－２７７３９９号により提案した発明、すなわちキトサンをＮａ－モンモリロナイトに代表される粘土鉱物である膨潤性スメクタイトと水中で反応させて得られる層状複合体を担体とする方法によってほとんど解決された。

【０００８】一方、担体上に吸着された色素は、色素に対し溶解性を持つ溶液や溶媒に接すると遊離する傾向を有し、着色料として使用されたときマイグレーション（色移り）またはブリーディング（色泣き）という好ましくない現象を引き起こすことから、担体に吸着された色素の耐溶出性の改善が要望されていた。

【０００９】本発明は、キトサンと膨潤性スメクタイトの複合体に色素を吸着させると同時にまたは吸着させた後で、キトサン反応性を有する多官能性試薬を用いて架橋処理することにより、吸着色素の溶出を防止してより有用な顔料組成物を提供することを目的としている。さらに、このような顔料組成物の製造方法を提供するとともに、前記顔料組成物が配合されることにより得られる有用な化粧料を提供することを併せて目的とするものである。

【００１０】

【課題を解決するための手段】前述したたような目的を達成するために、本発明の顔料組成物は、キトサンと膨

潤性スメクタイトとの複合体に色素を吸着させるとともに、キトサン反応性を有する多官能性試薬を作用させて架橋処理したことを特徴とする。

【００１１】また、本発明の顔料組成物の製造方法は、キトサン酸性溶液と膨潤性スメクタイト水分散物とを混合する混合工程、この混合工程で得られる混合液にキトサン染着性色素とキトサン反応性を有し水性溶媒中で作用する架橋剤とを添加する添加工程およびこの添加工程で生成した易濾過性の着色スラリーを濾別・洗浄した後、乾燥・粉砕する仕上げ工程、を含むことを特徴とする顔料組成物の製造方法、ならびに、キトサン酸性溶液と膨潤性スメクタイト水分散物とを混合する混合工程、この混合工程で得られる混合液にキトサン染着性色素を添加する第一添加工程、この第一添加工程で生成した易濾過性の着色スラリーを濾別・洗浄し、水分を非水性溶媒で置換する置換工程、この置換工程で得られる非水溶性スラリーにキトサン反応性を有し非水性溶媒中で作用する架橋剤を添加する第二添加工程およびこの第二添加工程を経た溶媒中から着色固形分を分離した後、乾燥・粉砕する仕上げ工程を含むことを特徴とする顔組成物の製造方法を要旨とする。

【００１２】さらに、本発明の新規な顔料組成物が配合される化粧料は、キトサンと膨潤性スメクタイトとの複合体に色素を吸着させるとともに、キトサン反応性を有する多官能性試薬を作用させて架橋処理して得られる顔料組成物を含有することを特徴とする。

【００１３】前述したような顔料組成物の製造方法において、キトサン酸性溶液と膨潤性スメクタイト水分散物との混合液に添加されるキトサン染着性色素は、添加時の状態が溶液，懸濁液または粉末のうちのどの状態のものでもよい。また、キトサン酸性溶液と膨潤性スメクタイト水分散物との混合液に、キトサン染着性色素およびキトサン反応性を有するとともに、水性溶媒中で作用する架橋剤を添加するに際しては、キトサン染着性色素および架橋剤を同時に添加してもよく、あるいは両者を順次に添加してもよい。

【００１４】キトサンは，まず希薄酸溶液に溶解し、キトサン酸性溶液とされる。酸としては種々の無機酸または有機酸が使用できる。顔料組成物の製造工程中に架橋処理が行われない場合は酸溶液として酢酸またはクエン酸等の有機酸の使用が好ましいが、本発明のように顔料組成物の製造工程中に架橋処理が含まれる場合には、架橋剤の種類によっては有機酸の使用が好ましくなく、塩酸のような無機酸が酸溶液として使用されることが好ましい。

【００１５】このキトサン酸性溶液と膨潤性スメクタイトの水分散液とを混合すると、カチオン性高分子であるキトサン塩が粘土構造中にインターカレートされて複合体を形成する。この膨潤性スメクタイトとしては天然または合成のモンモリロナイト、バイデライト、サポナイト、ヘクトライト等が使用できるが、天然品を精製処理したＮａ－モンモリロナイトが最も実際的である。また、キトサンが膨潤性スメクタイトと複合体を形成していることは、生成物のＸ線底面反射において粘土構造層間距離の増大が観察されることによって証明される。

【００１６】この混合懸濁液中に色素の水溶液または懸濁液を添加すると、キトサン－スメクタイト複合体に色素が吸着され担持される。この担持される色素としては、キトサン染着性を有する合成または天然色素がすべて対象となり得るが、本発明の目的からは特に食品、医薬品、化粧品用タール色素および天然色素が用いられて意義がある。

【００１７】このような着色料には食用黄色４号（Ｔａｒｔｒａｚｉｎｅ）、黄色5号（Ｓｕｎｓｅｔ　Ｙｅｌｌｏｗ　ＦＣＦ）、青色1号（Ｂｒｉｌｌｉａｎｔ　Ｂｌｕｅ　ＦＣＦ）、赤色3号（Ｅｒｙｔｈｒｏｓｉｎｅ）、赤色２０１号（Ｌｉｔｈｏｌ　Ｒｕｂｉｎ　Ｂ）、カルミン酸、ラッカイン酸、カルサミン、シコニン等が挙げられる。色素の添加時、色素の溶解度や発色性に合せて懸濁液のｐＨを加減する必要がある。

【００１８】キトサン反応性を有し架橋剤として用いられる多官能性試薬としては、グルタルアルデヒド、ジカルボン酸エステル、ジカルボン酸ハライド、有機ジイソシアネート、エピハロヒドリン等が挙げられる。また、溶媒としてはそれぞれの架橋剤に最も適したものが選ばれるが、グルタルアルデヒド架橋剤に対しては水溶液、アジピン酸ジ－ｐ－ニトロフェニルエステルやジ－Ｎ－ヒドロキシスクシミドエステルのようなジカルボン酸エステル、アジピン酸クロライドのようなジカルボン酸ハライド、およびエピクロロヒドリン架橋剤に対してはジメチルホルムアミド、ジメチルアセトアミド等のアミド類溶媒が、ヘキサメチレンジイソシアネートや４，４’ジフェニルメタンジイソシアネートのような有機ジイソシアネート架橋剤に対しては上記アミド類溶媒の他にエタノール、イソプロピルアルコール等のアルコール類やアセトン、メチルエチルケトン等のケトン類溶媒が適する。これらの架橋剤を用いて行われる架橋形成反応は、常温から70℃程度の温度範囲で１～数時間以内に完了し、処理される。

【００１９】架橋処理は、架橋剤がグルタルアルデヒドのように水性溶媒中で作用する場合、色素の吸着と同時に行うことも、色素の吸着後に行うこともできる。前者の方が製品の耐溶出性はより高まる。架橋剤が非水性溶媒中で作用するものである場合は、着色物を一旦濾別し水洗したのち、非水性溶媒で水分を置換して架橋処理を行う。反応後着色固形分を分離し、同じ溶媒で洗浄して未反応の架橋剤を除去し、更に水で洗浄してから乾燥・粉砕する。

【００２０】

【作用】キトサンは天然キチンの脱アセチル化物であ

5

り、脱アセチル化度および重合度にはさまざまなものがある。キトサンの色素吸着能は活性なアミノ基の存在によるもので、脱アセチル化度が高いものほど色素吸着能が大きい。膨潤性スメクタイトは、粘土構造を形成するアルミノケイ酸塩層間に低分子から高分子にわたる種々のカチオン性有機物質を介在させ抱持（インターカレート）する特性を有する。

【００２１】したがって、キトサンと膨潤性スメクタイトとの混合複合体は、キトサン特有の色素吸着能を保持しつつ糊状物を形成しないという特性を有する。この特性はキトサンの重合度の大小に拘らない。

【００２２】一方、キトサンはグルタルアルデヒド、ジカルボン酸エステル、ジカルボン酸ハライド、有機ジイソシアネート、エピハロヒドリン等の多官能性試薬によって架橋化され、この処理によって膨潤性を抑えることができる。

【００２３】このような架橋処理されたキトサンが発現する膨潤性を抑制する特性は、キトサンと膨潤性スメクタイトとの複合体においても保たれることから、色素吸着と同時または色素吸着後に前記複合体に架橋処理を施すことにより色素の耐溶出性が顕著に改善されるのである。

【００２４】

【実施例】次に、本発明の顔料組成物とその製造方法およびその顔料組成物の化粧料への適用について、多様な具体例を挙げて好ましい実施例につき説明する。

【００２５】（具体例１）脱アセチル化度80％、平均分子量40,000のキトサン５ｇを、0.05Ｎ－ＨＣｌ：400mlに溶解してキトサン溶液とした。別にＮａ－モンモリロナイト１ｇを水100 mlに分散させ、これを前記キトサン溶液に温度50℃で除々に混合して１時間攪拌したのち５℃に冷却し、キトサン－モンモリロナイト混合液を調製した。赤色２０１号（Ｌｉｔｈｏｌ　Ｒｕｂｉｎ　Ｂ）2.4 ｇを水に懸濁し、キトサン反応性を有する架橋剤である多官能性試薬としての25％グルタルアルデヒド水溶液：４ｇとともに前記キトサン－モンモリロナイト混合液中に添加した。アンモニア水を用いてｐＨを6.5 に調整し、５℃で20時間攪拌して、易濾過性の黄味赤色着色物を得た。濾別・水洗したのち乾燥・粉砕して顔料とした。本顔料は１％食塩水中での色素の溶出濃度が架橋処理を施さないものに比べて約20分の１であった。

6

【００２６】（具体例２）具体例１と同様にして調製したキトサン溶液とＮａ－モンモリロナイト懸濁液を温度50℃で除々に混合し、１時間攪拌したのち室温に冷却しキトサン－モンモリロナイト混合液を調製した。別に赤色２０１号色素：2.4 ｇを水に懸濁し、この水に懸濁された赤色２０１号色素を前記混合液に添加し室温で２時間攪拌したのち、アンモニア水を用いてｐＨを6.5 に調整した。さらに１時間攪拌したのち、５℃に冷却し、前記25％グルタルアルデヒド水溶液：４ｇを添加して20時間攪拌し、易濾過性の黄味赤色着色物を得た。そして、濾別・水洗したのち乾燥・粉砕して顔料とした。本顔料は１％食塩水中での色素の溶出濃度が架橋処理を施さないものに比べて約10分の１であった。

【００２７】（具体例３）脱アセチル化度80％、平均分子量40,000のキトサン５ｇを、0.25％酢酸水溶液：400 mlに溶解してキトサン溶液とした。別にＮａ－モンモリロナイト１ｇを水100 mlに分散させ、この水に分散させたＮａ－モンモリロナイトを前記キトサン溶液に温度50℃で除々に混合して１時間攪拌したのち、室温に冷却しキトサン－モンモリロナイト混合液を調製した。別に赤色２０１号色素： 2.4ｇを水に懸濁し、この水に懸濁された赤色２０１号色素を前記混合液に添加して室温で２時間攪拌したのち、アンモニア水を用いてｐＨを6.5 に調整し、さらに１時間攪拌して、易濾過性の黄味赤色着色物を得た。そして、濾別・水洗したのち水分をアセトンで完全に置換した。この中へ、キトサン反応を有する架橋剤である多官能性試薬としてのヘキサメチレンジイソシアネート：２ｇを添加し２時間攪拌したのち、未反応の架橋剤をアセトンで洗浄除去し、さらに水で洗浄し、濾別・乾燥・粉砕して顔料とした。本顔料は１％食塩水中での色素の溶出濃度が架橋処理を施さないものに比べて約２分の１であった。

【００２８】（具体例４）具体例３で得られた顔料を用いて、次の処方により口紅を調製した。

基　剤　：	ヒマシ油	４７．０　％
	イソプロピルパルミテート	５．０　％
	ラノリン	１０．０　％
	オゾケライト	７．０　％
	キャンデリラロウ	７．０　％
	カルナウバロウ	４．０　％
色　材　：	酸化チタン	２．０　％
	本発明顔料（具体例３）	１８．０　％
香　料　：	合成香料	適　量

製　法　：　基剤原料を加熱融解し均一に混ぜる。これに色剤を加え、ロールミルで練り均一に分散させた後、再融解して香料を加え、脱泡してから型に流し込み、急冷して固めた。

7

本化粧料は、マイグレーションまたはブリーディング等が見られず、いわゆる化粧もちが良好であった。

【００２９】

【発明の効果】本発明のキトサン－膨潤性スメクタイト複合体を担体として色素を吸着させるとともに、キトサンに架橋処理した顔料組成物は、ａ　同じ色素を用いても、在来の金属イオンやヒドロキシル基を吸着点とする担体の場合とは異なる色相の顔料を得ることができ、限

8

られた種類の許可色素の範囲で、色相の範囲を著しく広げられること、ｂ　特に化粧品用の着色料として、安定であってしかも適度な保湿性や抗菌、抗かび性などキトサンに由来する好ましい属性を併せもった顔料を提供できること、ｃ　食品包装材、トイレタリー、文具、玩具等の分野に、耐溶出性に優れた人体無害な着色料を提供できること、等の効果を奏する。

フロントページの続き

(51)Int.Cl.[5]		識別記号	庁内整理番号	ＦＩ	技術表示箇所
Ｃ０８Ｌ	5/08	ＬＡＭ	6770－４Ｊ		
// Ｃ０９Ｃ	1/42	ＰＢＡ	6904－４Ｊ		
	3/08	ＰＢＵ	6904－４Ｊ		

Espacenet

JP2008260722A COSMETIC

Applicants: DAINICHISEIKA COLOR CHEM,UKIMA CHEM & COLOUR MFG

Inventors: TAKAHASHI KENICHI,SATO HIROMASA,WATANABE AKIHIRO,HANADA KAZUYUKI

Classifications:
IPC ***A61K8/02; A61K8/898;***

Priorities: JP2007105138A 2007-04-12

Application: JP2007105138A·2007-04-12

Publication: JP2008260722A·2008-10-30

Published as: JP2008260722A;**JP4802136B2**

COSMETIC

Abstract

PROBLEM TO BE SOLVED: To provide polyurethane gel particles solving conventional problems, and to provide a cosmetic containing the particles. SOLUTION: The cosmetic contains specific polyurethane gel particles including a functional component and/or a design component in the inside. The gel particle is a polyurethane gel particle (particle C) obtained by covering the surface of a three-dimensionally crosslinked polyurethane gel particles (particle A) by copolymerizing a polyisocyanate, a compound having an active hydrogen group in the molecule, and a polysiloxane having an active hydrogen group in the molecule and/or a reaction product of the polysiloxane with a lactone, at least one of which is tri- or more-functional, with a polyurea colloid particles (particle B) precipitated from a nonaqueous solvent solution of a polyurea colloid. COPYRIGHT: (C)2009,JPO&INPIT

(19)日本国特許庁(JP)　(12)公開特許公報(A)　(11)特許出願公開番号
特開2008-260722
(P2008-260722A)
(43)公開日　平成20年10月30日(2008.10.30)

(51)Int.Cl.			F I		テーマコード（参考）
A61K	8/898	(2006.01)	A61K	8/898	4C083
A61K	8/02	(2006.01)	A61K	8/02	

審査請求 未請求　請求項の数 7　ＯＬ　（全 27 頁）

(21)出願番号　特願2007-105138 (P2007-105138)
(22)出願日　平成19年4月12日 (2007.4.12)

(71)出願人　000002820
大日精化工業株式会社
東京都中央区日本橋馬喰町１丁目７番６号
(71)出願人　000238256
浮間合成株式会社
東京都中央区日本橋馬喰町１丁目７番６号
(74)代理人　100098707
弁理士　近藤　利英子
(74)代理人　100077698
弁理士　吉田　勝広
(74)代理人　100146042
弁理士　梶原　克哲
(72)発明者　高橋　賢一
東京都中央区日本橋馬喰町１丁目７番６号
大日精化工業株式会社内
最終頁に続く

(54)【発明の名称】化粧料

(57)【要約】
【課題】従来の問題を解決したポリウレタンゲル粒子および該粒子を含む化粧料を提供すること。
【解決手段】機能性成分および／または意匠性成分を内包しているポリウレタンゲル粒子を含有する化粧料において、該ゲル粒子が、少なくともいずれかが３官能以上である、ポリイソシアネートと、分子内に活性水素基を有する化合物と、分子内に活性水素基を有するポリシロキサンおよび／または該ポリシロキサンとラクトンとの反応生成物と、を共重合してなる三次元架橋したポリウレタンゲル粒子（粒子Ａ）の表面が、ポリウレアコロイド非水溶媒溶液から析出したポリウレアコロイド粒子（粒子Ｂ）により被覆されているポリウレタンゲル粒子（粒子Ｃ）であることを特徴とする化粧料。
【選択図】なし

【特許請求の範囲】
【請求項1】
機能性成分および／または意匠性成分を内包しているポリウレタンゲル粒子を含有する化粧料において、該ゲル粒子が、少なくともいずれかが３官能以上である、ポリイソシアネートと、分子内に活性水素基を有する化合物と、分子内に活性水素基を有するポリシロキサンおよび／または該ポリシロキサンとラクトンとの反応生成物と、を共重合してなる三次元架橋したポリウレタンゲル粒子（粒子Ａ）の表面が、ポリウレアコロイド非水溶媒溶液から析出したポリウレアコロイド粒子（粒子Ｂ）により被覆されているポリウレタンゲル粒子（粒子Ｃ）であることを特徴とする化粧料。
【請求項2】
機能性成分および／または意匠性成分が、粒子Ａおよび／または粒子Ｂに含まれている請求項１に記載の化粧料。
【請求項3】
機能性成分が、保湿成分、ビタミン成分、抗酸化成分、血行促進成分、紫外線吸収成分、紫外線カット成分、抗菌成分、美白成分および老化防止効能薬剤から選ばれる少なくとも１種であり、意匠性成分が、顔料、染料、天然色素、有機合成色素、パール顔料、合成マイカ、金属粉および金属ペーストから選ばれる少なくとも１種であり、上記各成分の合計割合が、粒子Ｃを構成している樹脂１００質量部あたり０．１～３００質量部である請求項１に記載の化粧料。
【請求項4】
粒子Ｃ中に占めるポリシロキサンセグメントの割合が、０．０１～８０質量％である請求項１に記載の化粧料。
【請求項5】
粒子Ｂが、溶媒に対して溶媒和されている部分と非溶媒和部分とから構成されており、非溶媒和部分の粒子径が０．０１～１．０μｍである請求項１に記載の化粧料。
【請求項6】
粒子Ｂが、油脂変性ポリオールとポリイソシアネートとポリアミンとの反応で得られるポリウレアコロイド粒子であって、非溶媒和部分がウレア結合の水素結合からなっている請求項１に記載の化粧料。
【請求項7】
粒子Ｃの粒子径が、０．５～１００μｍの範囲である請求項１に記載の化粧料。

【発明の詳細な説明】
【技術分野】
【0001】
本発明は、機能性成分および／または意匠性成分を内包されているポリウレタンゲル粒子を含む化粧料に関し、さらに詳しくは均一な粒子径であり、かつ機械強度、耐屈曲性、耐熱性、低温特性、耐摩耗性、耐薬品性に優れており、特に化粧料成分として必要とされる柔軟性（ソフトタッチ感）、滑り性、しっとり感、弾性、変形回復性、透過性、光拡散性、適度な光沢性、肌への伸展性、耐媒体性（膨潤しない）、耐油性（膨潤しない）、皮脂吸収性、皮膚への安全性などに優れ、さらには機能性成分などを内包してなるポリウレタンゲル粒子を含有するメイクアップ化粧料やスキンケアー化粧料などの化粧料に関する。
【背景技術】
【0002】
従来、化粧料に使用される微粒子としては、タルク、カオリン、マイカ、顔料などの微粒子が多く使用されている。さらに有機微粒子としては、ナイロン、結晶セルロース、ウレタン、アクリル、シリコーン、ポリスチレン、ポリエチレン、エチレン・メチルメタクリラート共重合体などの有機微粒子が挙げられる。
【0003】
上記種々の有機微粒子に関しては、粒形においては真球状や非真球状なもの、多孔質球

状微粒子、種々の粒子径、粒度分布、比重、硬度、表面処理（表面性質）など、様々な材料が検討されている。化粧料に使用される代表的な微粒子について述べる。

【0004】

ナイロン１２微粒子は伸展性に優れ、高硬度のためサラサラ感があり、好評であるとともに、真球状で単一な粒度分布であり、耐溶剤性、耐薬品性、耐圧縮性、非熱流動性などの特性がある。しかしながら、ナイロン１２微粒子は、高コストであり、防腐剤であるパラヒドロキシ安息香酸エステルやパラヒドロキシ安息香酸エチルなどを吸収しやすく、防腐効果をなくすことや、口紅など、高温加工する際に融点の問題から、化粧料成分と融着すると云った問題を引き起こす。

【0005】

アクリル微粒子は、低コストで伸展性がよくスライド感も良好で、メイクアップ化粧料、制汗剤やローションなどに使用されているが、上記アクリル微粒子は、柔軟性、フィット感、肌への密着性（化粧持ち）に乏しいといった課題もある。

【0006】

シリコーン微粒子は、高硬度のため伸展性がよく（動摩擦係数が低い）、撥水性、光拡散性や隠蔽性があるのでメイクアップ化粧料に使用される。しかしながら、上記シリコーン微粒子は柔軟性に乏しいことや皮脂の吸収性が悪いことなどが課題としてある。

【0007】

真球状有機微粒子を含有している化粧料は、皮膚に対する刺激性がなく、人体の安全性に問題がない素材であるとともに、滑らかで柔軟な感触性、皮膚への伸展性（ローリング性）、汗や皮脂の吸収性、通気性を付与させたり、透過性、光拡散性、隠蔽効果、光沢性などの光学特性を活かして、皺やしみを隠した自然な肌を演出したナチュラルカバー効果を発揮させたり、テカリ防止、色むら隠し、化粧持ち、小皺や毛穴を隠す機能などを目的に利用される。

【0008】

さらに上記微粒子は、化粧料としての機能の他に化粧料配合において、例えば、化粧料に使用される揮発性シリコーンオイル、精製水、油剤、防腐剤などとの相溶性が良好で、かつ揮発性シリコーンオイル、油剤、防腐剤の吸収性が少なく長期安定性が求められる。

【0009】

また、パウダーファンデーションなどは各製造方式（乾式法、湿式法）での成型性が重要であり、口紅では高温で加工するため、上記微粒子は耐熱性（加工温度で軟化しないこと）や極性が少なく粘着しないことなどの化粧料の加工適性が求められる。

【0010】

かかる問題を解決する方法として、化粧料に球状ポリウレタン粒子を配合する手法が提案されている（特許文献１）。この化粧料は、伸展性、感触性などには問題ないが、化粧料の特性である光拡散性や隠蔽性が乏しく、光学特性としては満足するものではない。

【0011】

また、化粧料にアクリル共重合体微粒子を配合する手法が提案されている（特許文献２）。該アクリル共重合体微粒子を含有させた化粧料は、伸展性などは良好であるものの、微粒子自体が高硬度（ガラス転移温度が高い）であり、人肌とは遠い感触となる。これらの従来の方法では、現在主流と言われる人肌に近い柔軟性が求められるとともに、自然に近いナチュラルカバー効果が得られないと云う問題が解決されない。

【特許文献1】特開平５－２６２６２２号公報

【特許文献2】特開２００１－１５１６２６公報

【発明の開示】

【発明が解決しようとする課題】

【0012】

上記有機微粒子は化粧料において各素材独自の優れた特徴があるものの、幾つかの問題があり、前記した全ての機能を満足するものでない。そのうえ、従来よりも高機能である有機微粒子素材および化粧料が要望されている。従って本発明の目的は、従来の上記の欠

点を解決した有機微粒子を含む化粧料を提供することである。
【課題を解決するための手段】
【0013】
上記目的は以下の本発明によって達成される。すなわち、本発明は、機能性成分および／または意匠性成分（以下両者を「機能性成分など」と云う場合がある）を内包しているポリウレタンゲル粒子を含有する化粧料において、該ゲル粒子が、少なくともいずれかが３官能以上である、ポリイソシアネートと、分子内に活性水素基を有する化合物（以下単に「ポリオール」と云う場合がある）と、分子内に活性水素基を有するポリシロキサンおよび／または該ポリシロキサンとラクトンとの反応生成物（以下これらを纏めて単に「反応性ポリシロキサン」という場合がある）と、を共重合してなる三次元架橋したポリウレタンゲル粒子（以下単に「粒子Ａ」と云う場合がある）の表面が、ポリウレアコロイド非水溶媒溶液から析出したポリウレアコロイド粒子（以下単に「粒子Ｂ」と云う場合がある）により被覆されているポリウレタンゲル粒子（以下単に「粒子Ｃ」と云う場合がある）であることを特徴とする化粧料を提供する。上記機能性成分などは、粒子Ａおよび／または粒子Ｂに含まれている。
【0014】
上記機能性成分としては、保湿成分、ビタミン成分、抗酸化成分、血行促進成分、紫外線吸収成分、紫外線カット成分、抗菌成分、美白成分および老化防止効能薬剤から選ばれる少なくとも１種であり、意匠性成分としては、顔料、染料、天然色素、有機合成色素、パール顔料、合成マイカ、金属粉および金属ペーストから選ばれる少なくとも１種であり、上記各成分の合計割合が、粒子Ｃを構成している樹脂１００質量部あたり０．１～３００質量部であることが好ましい。
【0015】
また、上記粒子Ｃ中に占めるポリシロキサンセグメントの割合が、０．０１～８０質量％であること；上記粒子Ｂが、溶媒に対して溶媒和されている部分と非溶媒和部分とから構成されており、非溶媒和部分の粒子径が０．０１～１．０μｍであること；粒子Ｂが、油脂変性ポリオールとポリイソシアネートとポリアミンとの反応で得られるポリウレアコロイド粒子であって、非溶媒和部分がウレア結合の水素結合からなっていること；粒子Ｃの粒子径が、０．５～１００μｍの範囲であることが好ましい。
【発明の効果】
【0016】
本発明者らは、前記課題を解決すべく鋭意検討を重ねた結果、上記粒子Ｃが、機械強度、耐屈曲性、耐熱性、低温特性、耐摩耗性、耐薬品性などに優れており、化粧料成分として必要とされるナチュラルカバー効果のある適度な透明性、適度な光拡散性、適度な隠蔽性、適度な光沢性であり、テカリ防止、色むら隠し、小皺、毛穴隠し効果および感触（柔軟性（ソフトタッチ感）、滑り性、しっとり感）に優れており、弾性、変形回復性、肌への伸展性、吸油性、皮脂吸収性、皮膚への安全性などに優れ、特に柔軟性（ソフト性）、変形回復力および皮脂（オレイン酸）の吸収性能が高く、かつ粒度分布が狭いことから、これらの粒子に機能性成分などを含有させることで、前記従来技術の課題が解決されることを見いだした。
【発明を実施するための最良の形態】
【0017】
次に発明を実施するための最良の形態を挙げて本発明をさらに詳しく説明する。本発明で用いる粒子Ｃは、ポリイソシアネートとポリオールと反応性ポリシロキサン（これらの内の少なくとも１種には、機能性成分などを内包させてある、以下同じ）とを、ポリウレアコロイド溶液の存在下に不活性溶媒中で乳化分散後、重合させることによって得られる。このようにして得られる粒子Ｃは、その表面が、ポリウレアコロイド溶液から析出した粒子Ｂによって被覆されている。機能性成分などは粒子Ａに代えて、または加えて粒子Ｂ中に包含させることもできる。
【0018】

本発明で用いる粒子Ｃは上記方法によって得られるが、好ましい方法は、不活性溶媒中で撹拌機や乳化機付きのジャケット式合成釜に、ポリイソシアネートとポリオールと反応性ポリシロキサンとを仕込み、ポリウレアコロイド溶液により乳化分散し、これらの合成原料を反応させて粒子Ａを合成した後、粒子Ａの表面をポリウレアコロイド溶液から析出した粒子Ｂで均一に被覆させる方法である。

【0019】

合成温度は特に限定されないが、好ましい温度は４０℃～１４０℃である。また、合成時に使用するポリウレアコロイド溶液は、その固形分としての使用量で、粒子Ａの原料換算で１００質量部あたり０．０１質量部以上を使用することができ、好ましくは０．１～２０質量部である。使用量が０．０１質量部未満では粒子の乳化が不十分で、合成過程で粒子の大きい凝集塊が発生し、目的とする微細な粒子Ｃの分散体が得難い。一方、使用量が２０質量部を越えると、粒子Ａの乳化性には問題はなく、粒子Ｃは製造することができるが、乳化剤としての作用として過剰な量であり、特に利点はない。

【0020】

ポリイソシアネートとポリオールと反応性ポリシロキサンとの不活性溶媒中における濃度は、低い程小さい粒径の粒子Ａまたは粒子Ｃが得られ易いが、生産性から好ましい濃度は２０～７０質量％である。

【0021】

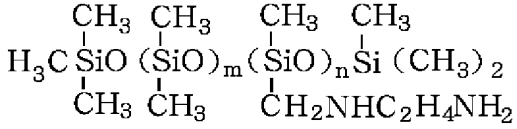
粒子Ａについて以下に説明する。粒子Ａの原料であるポリイソシアネートとポリオールと反応性ポリシロキサンとのいずれかには、機能性成分などが加えられている。ここで機能性成分は、少しずつ徐放されて、目的とする機能を発揮する成分であり、意匠性成分は、意匠性の高い色相や光拡散による特異的な反射光を利用して美しい化粧肌を作り上げる成分である。上記機能性成分などの含有量は、粒子Ｃを構成している樹脂１００質量部あたり０．１～３００質量部であることが好ましい。

【0022】

本発明で使用する反応性ポリシロキサンとしては、例えば、以下のような化合物を用いることが好ましい（この中には活性水素基を利用して変性されたエポキシ変性ポリシロキサンも含んでいるが、イソシアネート基と反応してポリウレタン樹脂中に含有されることとなるので含めている）。反応性ポリシロキサン中の活性水素基とは、例えば、水酸基（－ＯＨ）、カルボキシル基（－ＣＯＯＨ）、アミノ基（－ＮＲＨ、－NH_2など）およびチオール基（－ＳＨ）などであり、これらの中では水酸基およびアミノ基が好ましく使用される。

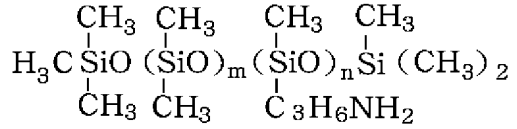
【0023】

（１）アミノ変性ポリシロキサン



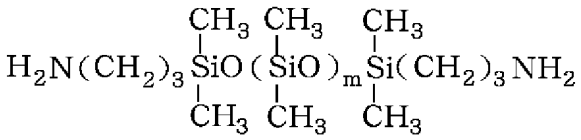
（ｍ＝１～200、ｎ＝２～200）

【0024】



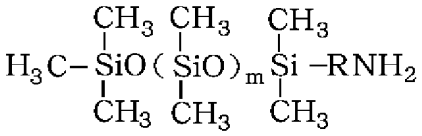
（ｍ＝１～200、ｎ＝２～200）

【0025】



（m＝1～300）

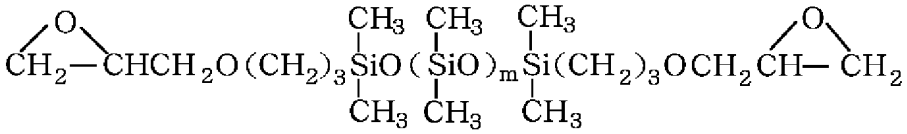
【0026】



（m＝1～300、R＝低級アルキレン基）

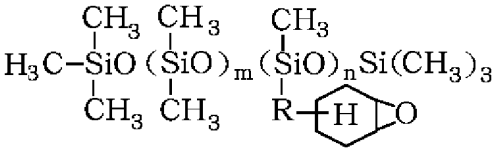
【0027】

（２）エポキシ変性ポリシロキサン



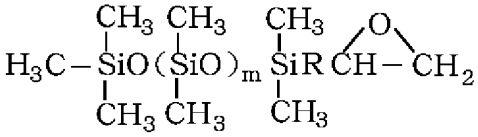
（m＝1～300）

【0028】



（m＝1～200、n＝2～200、R＝低級アルキレン基）

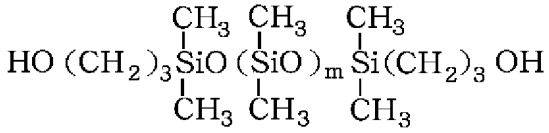
【0029】



（m＝1～300、R＝低級アルキレン基）

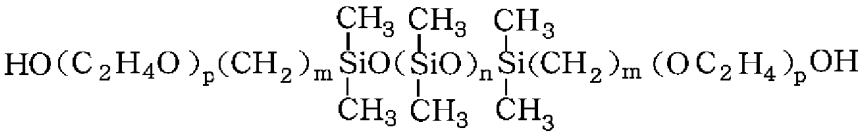
【0030】

（３）アルコール変性ポリシロキサン



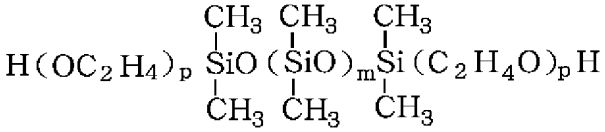
（m＝1～300）

【0031】



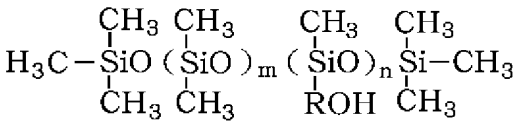
(p＝1～300、m＝2～6、n＝1～300)

【0032】



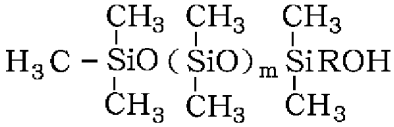
(p＝1～300、m＝1～300)

【0033】



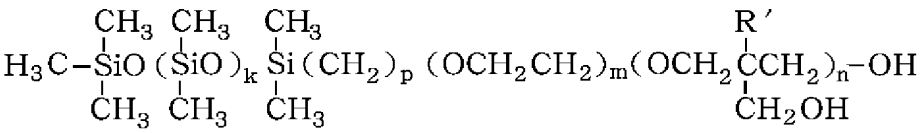
(m＝1～200、n＝2～200、R＝低級アルキレン基)

【0034】



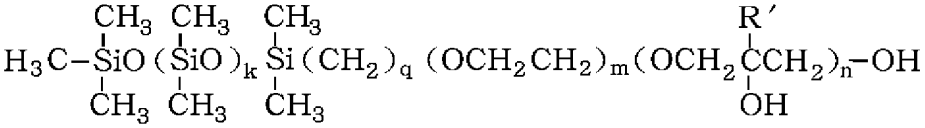
(m＝1～300、R＝低級アルキレン基)

【0035】



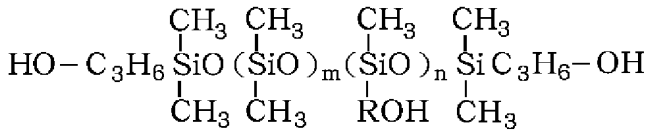
(k＝1～300、p＝0～5、m＝0～50、n＝1～3、
R′＝水素原子またはアルキル基)

【0036】



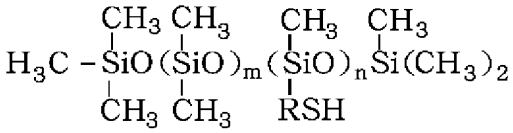
(k＝1～300、q＝0～5、m＝0～50、n＝1～3、
R′＝水素原子またはアルキル基)

【0037】



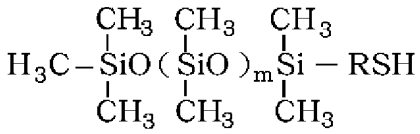
（m＝1～300、n＝1～300、R＝低級アルキレン基）

【0038】
（４）メルカプト変性ポリシロキサン



（m＝1～200、n＝2～200、R＝低級アルキレン基）

【0039】



（m＝1～300、R＝低級アルキレン基）

【0040】
以上列記した反応性ポリシロキサンは本発明において使用する好ましい化合物であるが、本発明はこれらの例示の化合物に限定されるものではない。従って上述の例示の化合物のみならず、その他現在市販されており、市場から容易に入手し得る化合物はいずれも本発明において好ましく使用することができる。本発明において特に好ましい化合物は２個以上の水酸基またはアミノ基を有する反応性ポリシロキサンである。
【0041】
これらの他にも活性水素を有するポリシロキサンをラクトンで変性したポリラクトン（ポリエステル）－ポリシロキサンおよびエチレンオキサイドやプロピレンオキサイドで変性したポリエチレンオキサイド－ポリシロキサンやポリプロピレンオキサイド－ポリシロキサンなども好ましく使用される。特に好ましくはポリシロキサンをラクトンで変性した化合物であり、さらに好ましくは分子内に２個以上の活性水素基を有するポリシロキサンをラクトンで変性したポリラクトン－ポリシロキサンである。
【0042】
ここで使用する好ましいラクトンは、β－プロピオラクトン、γ－ブチロラクトン、δ－バレロラクトン、ε－カプロラクトン、７－ヘプタノリド、８－オクタノリド、γ－バレロラクトン、γ－カプロラクトンおよびδ－カプロラクトンなどである。
【0043】
また、本発明において前記ポリラクトン－ポリシロキサン、すなわち、分子内に少なくとも１個以上の活性水素基を有するポリシロキサンをラクトンで変性したポリラクトン－ポリシロキサンは、分子中に１個または２個以上の活性水素基、例えば、アミノ基、水酸基、カルボキシル基などを有するシロキサンの活性水素原子団がラクトンを開環重合させた後、減圧処理することによって得られる。
【0044】
粒子Ａの合成に使用される活性水素基を有する化合物としてのポリオールとしては、好ましくはポリウレタンの製造に従来から使用されている短鎖ジオール、多価アルコールお

よび高分子ポリオールなどの従来公知のものが、また、活性水素基を有する化合物としてのポリアミンとしてはポリウレタンの製造に従来から使用されている短鎖ジアミン、高分子ポリアミンなどが使用できるが、これらは特に限定されない。以下に使用するそれぞれの化合物について説明する。

【0045】

前記短鎖ジオールとしては、例えば、エチレングリコール、１，２－プロピレングリコール、１，３－プロピレングリコール、１，２－ブチレングリコール、１，３－ブチレングリコール、１，４－ブチレングリコール、１，６－ヘキサメチレングリコールおよびネオペンチルグリコールなどの脂肪族グリコールおよびそのアルキレンオキシド低モル付加物（数平均分子量５００未満）が挙げられる。

【0046】

また、１，４－ビスヒドロキシメチルシクロヘキサンおよび２－メチル－１，１－シクロヘキサンジメタノールなどの脂環式系グリコールおよびそのアルキレンオキシド低モル付加物（数平均分子量５００未満）、キシリレングリコールなどの芳香族グリコールおよびそのアルキレンオキシド低モル付加物（数平均分子量５００未満）、ビスフェノールＡ、チオビスフェノールおよびスルホンビスフェノールなどのビスフェノールおよびそのアルキレンオキシド低モル付加物（数平均分子量５００未満）、およびＣ１～Ｃ１８のアルキルジエタノールアミンなどのアルキルジアルカノールアミンなどの化合物が挙げられる。

【0047】

また、多価アルコールとしては、例えば、グリセリン、トリメチロールエタン、トリメチロールプロパン、ペンタエリトリトール、トリス－（２－ヒドロキシエチル）イソシアヌレート、１，１，１－トリメチロールエタンおよび１，１，１－トリメチロールプロパンなどが挙げられる。これらは単独或いは２種類以上を組み合わせて使用することができる。

【0048】

前記高分子ポリオールとしては、例えば、以下のものが例示される。

（１）ポリエーテルポリオール、例えば、アルキレンオキシド（エチレンオキシド、プロピレンオキシド、ブチレンオキシドなど）および／または複素環式エーテル（テトラヒドロフランなど）を重合または共重合して得られるものが例示され、具体的にはポリエチレングリコール、ポリプロピレングリコール、ポリエチレングリコール－ポリテトラメチレングリコール（ブロックまたはランダム）、ポリテトラメチレンエーテルグリコールおよびポリヘキサメチレングリコールなどのジオールおよび／または３官能以上ポリエーテルポリオールなどが挙げられる。

【0049】

（２）ポリエステルポリオール、例えば、脂肪族系ジカルボン酸（例えば、コハク酸、アジピン酸、セバシン酸、グルタル酸およびアゼライン酸など）および／または芳香族系ジカルボン酸（例えば、イソフタル酸およびテレフタル酸など）と低分子量グリコール（例えば、エチレングリコール、１，２－プロピレングリコール、１，３－プロピレングリコール、１，４－ブチレングリコール、１，６－ヘキサメチレングリコール、ネオペンチルグリコールおよび１，４－ビスヒドロキシメチルシクロヘキサンなど）とを縮重合したものが例示され、具体的にはポリエチレンアジペートジオール、ポリブチレンアジペートジオール、ポリヘキサメチレンアジペートジオール、ポリネオペンチルアジペートジオール、ポリエチレン／ブチレンアジペートジオール、ポリネオペンチル／ヘキシルアジペートジオール、ポリ－３－メチルペンタンアジペートジオールおよびポリブチレンイソフタレートジオールなどのジオールおよび／または３官能以上のポリエステルポリオールなどが挙げられる。

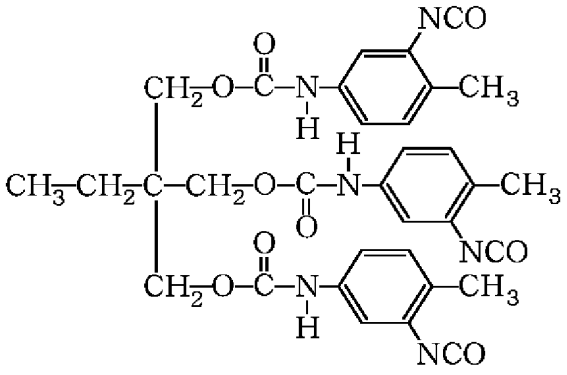
【0050】

（３）ポリラクトンポリオール、例えば、ポリカプロラクトンジオールまたはポリカプロラクトントリオールおよびポリ－３－メチルバレロラクトンジオールなどのジオールおよ

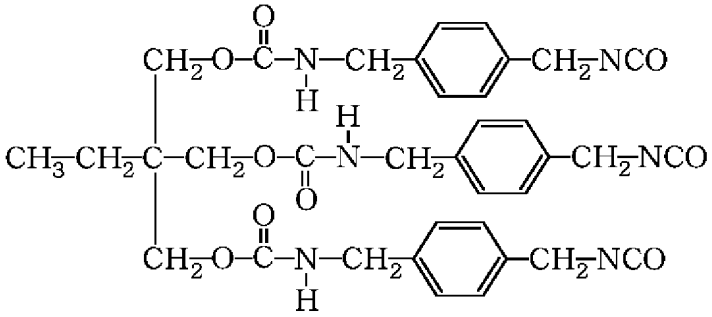
び／または３官能以上のポリラクトンポリオールなどが挙げられる。
（４）ポリカーボネートジオール、例えば、ポリヘキサメチレンカーボネートジオールなどのジオールおよび／または３官能以上のポリカーボネートポリオールなどが挙げられる。
（５）ポリオレフィンポリオール、例えば、ポリブタジエングリコールおよびポリイソプレングリコール、または、その水素化物などのジオールおよび／または３官能以上のポリオレフィンポリオールなどが挙げられる。
【0051】
（６）水素添加ダイマーポリオール、ヒマシポリオールなどのジオールおよび／または３官能以上のダイマーポリオールなどが挙げられる。
（７）ポリメタクリレートジオール、例えば、α，ω－ポリメチルメタクリレートジオールおよびα，ω－ポリブチルメタクリレートジオールなどのジオールおよび３官能以上のポリメタクリレートポリオールなどが挙げられる。
【0052】
これらのポリオールの分子量は特に限定されないが、ポリイソシアネートと反応するものは全て使用可能であり、通常、数平均分子量は５００～２，０００程度が好ましい。また、これらのポリオールは単独或いは２種類以上を組み合わせて使用することができる。ポリオールとしては、活性水素基が２個以上のポリオールが好ましく、特に好ましいのは３個以上の活性水素基を有するポリオールである。
【0053】
前記粒子Ａまたは粒子Ｂの合成に使用するポリイソシアネートとしては、従来公知のポリウレタンの製造に使用されているものがいずれも使用でき特に限定されない。ポリイソシアネートとして好ましいものは、例えば、トルエン－２，４－ジイソシアネート、４－メトキシ－１，３－フェニレンジイソシアネート、４－イソプロピル－１，３－フェニレンジイソシアネート、４－クロル－１，３－フェニレンジイソシアネート、４－ブトキシ－１，３－フェニレンジイソシアネート、２，４－ジイソシアネートジフェニルエーテル、４，４’－メチレンビス（フェニレンイソシアネート）（ＭＤＩ）、ジュリレンジイソシアネート、トリレンジイソシアネート、キシリレンジイソシアネート（ＸＤＩ）、１，５－ナフタレンジイソシアネート、ベンジジンジイソシアネート、ｏ－ニトロベンジジンジイソシアネートおよび４，４’－ジイソシアネートジベンジルなどの芳香族ジイソシアネートが挙げられる。
【0054】
また、メチレンジイソシアネート、１，４－テトラメチレンジイソシアネート、１，６－ヘキサメチレンジイソシアネートおよび１，１０－デカメチレンジイソシアネートなどの脂肪族ジイソシアネート、１，４－シクロヘキシレンジイソシアネート、４，４’－メチレンビス（シクロヘキシルイソシアネート）、１，５－テトラヒドロナフタレンジイソシアネート、イソホロンジイソシアネート、水添ＭＤＩおよび水添ＸＤＩなどの脂環式ジイソシアネートなど、或いはこれらのジイソシアネートと低分子量のポリオールやポリアミンを末端がイソシアネートとなるように反応させて得られるポリウレタンプレポリマーなども当然使用することができる。
【0055】
また、これらの化合物をイソシアヌレート体、ビューレット体、アダクト体、ポリメリック体とした多官能のイソシアネート基を有するもので従来から使用されている公知のものが使用でき特に限定されない。例えば、２，４－トルイレンジイソシアネートの二量体、トリフェニルメタントリイソシアネート、トリス－（ｐ－イソシアネートフェニル）チオフォスファイト、多官能芳香族イソシアネート、多官能芳香族脂肪族イソシアネート、多官能脂肪族イソシアネート、脂肪酸変性多官能脂肪族イソシアネート、ブロック化多官能脂肪族イソシアネートなどのブロック型ポリイソシアネート、ポリイソシアネートプレポリマーなどが挙げられる。
【0056】

これらのうち、芳香族系或いは脂肪族系のどちらでも使用可能であり、好ましくは芳香族系ではジフェニルメタンジイソシアネートおよびトリレンジイソシアネート、脂肪族系ではヘキサメチレンジイソシアネートおよびイソホロンジイソシアネートなどの変性体であり、分子中にイソシアネート基を３個以上含むものが好ましく、前記ポリイソシアネートの多量体や他の化合物との付加体、さらには低分子量のポリオールやポリアミンとを末端イソシアネートになるように反応させたウレタンプレポリマーなども好ましく使用される。それらを下記に構造式を挙げて例示するが、これらに限定されるものではない。

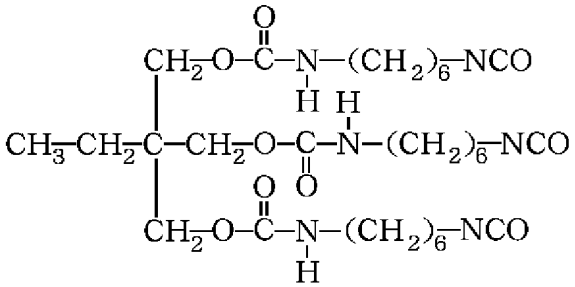
【0057】



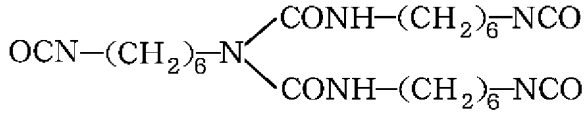
【0058】



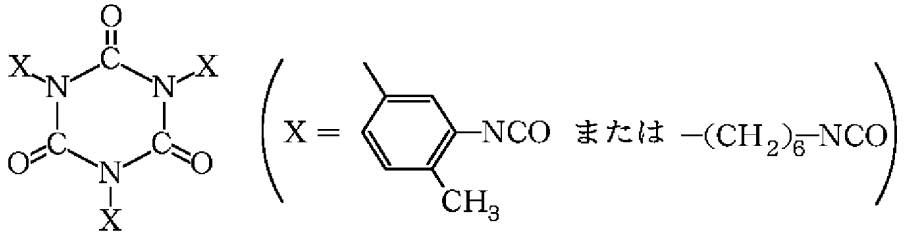
【0059】



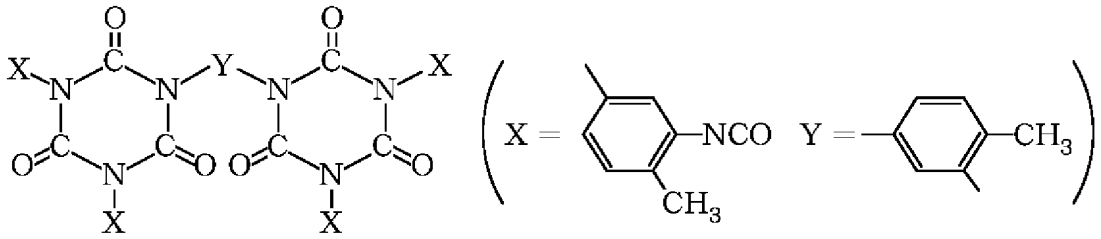
【0060】



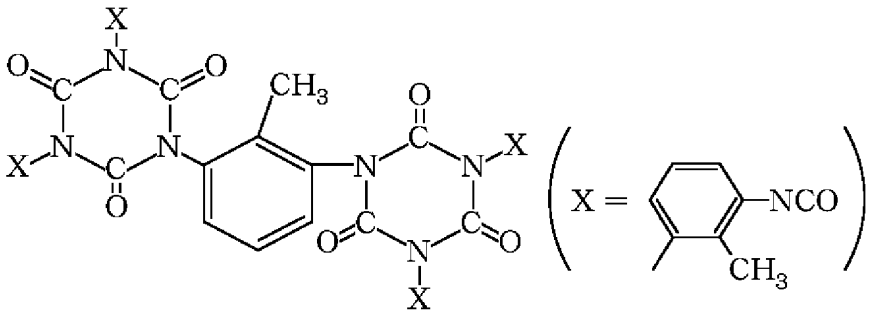
【0061】



【0062】



【0063】



【0064】

本発明で用いる機能性成分としては、保湿成分、ビタミン成分、抗酸化成分、血行促進成分、紫外線吸収成分、紫外線カット成分、抗菌成分、美白成分、芳香成分、消臭成分、老化防止などに効能がある薬剤が挙げられる。例えば、保湿成分としては、グリセリン、スクワラン、１，３－ブタンジオール（トウモロコシ由来も含む）、ソルビトール、コラーゲン、アミノ酸、尿素、セリン、ゼラチン、植物エキス、マリンミネラル、ヒアロン酸、ヒアルロン酸、キトサン、アルロン酸、単糖類、多糖類（トレハロース）、ロイヤルゼリー、天然セラミドなどが挙げられる。

【0065】

ビタミン成分としては、抗酸化作用、美白効果および老化を防ぐ機能がある、例えば、ビタミンＡ、Ｂ、Ｃ、Ｄ、Ｅ、Ｋおよびその誘導体、ポリフェノールなどが挙げられる。血行促進成分としては、ビタミンＥ、植物抽出エキス、酵母エキス、ロイヤルゼリーなどが挙げられる。抗酸化成分としては、ビタミンＣやビタミンＥおよびその誘導体、アルブチン、甘草エキス、植物抽出エキス、カロチン、白金ナノコロイドなどが挙げられる。

【0066】

美白成分としては、メラニン生成を抑える美白成分であり、ビタミンＣやその誘導体、アルブチン、エラグ酸、コウジ酸、甘草エキス、植物抽出エキスなどが挙げられる。紫外線吸収成分または紫外線カット成分としては、メトキシケイヒ酸オクチル、オキシベンゾン、サリチル酸オクチルおよびホモサレートなどの紫外線吸収剤や、酸化亜鉛、酸化チタン、アルミナ、酸化ジルコニウムなどの紫外線カット成分などが挙げられる。

【0067】

抗菌成分としては、パラベンなどを使用するが、肌の弱い人やアレルギー体質の人には

向いていない。天然エキスやカテキンなどが良いとされる。老化防止効能薬剤としては、大豆由来のサポニンとイソフラボン、天然ビタミンＥ、コエンザイムＱ１０などが挙げられる。芳香成分や消臭成分は、肌のトラブルの原因となり得るので、無臭タイプが推奨されるが、必要に応じて、例えばレモン油、ラベンダー油、ローズ油などの公知の芳香剤や、カテキンなどの公知の消臭剤も極微量添加可能である。

【0068】

本発明に使用される意匠性成分としては、顔料、蛍光顔料、染料、天然色素、有機合成色素、パール顔料、合成マイカ、金属素材などが挙げられる。体質顔料としては、マイカ、タルク、カオリン、セリライト、炭酸マグネシウム、炭酸カルシウム、無水珪酸、酸化アルミニウム、硫酸バリウムなど、天然色素としては、カロチノイド系、フラボノイド系、フラビン系など、有機合成色素としては、法定色素Ｉ、II、IIIグループおよびＦＤＡ承認色素など、無機顔料としては、酸化鉄、カーボンブラック、群青、紺青、酸化クロム、水酸化クロムなど、白色顔料としては、酸化チタン、酸化亜鉛などが挙げられる。

【0069】

また、有機染料、顔料としては、アゾ系色素、ニトロ系色素、ニトロソ色素、キサンテン系色素、キノリン系色素、アントラキノン系色素、インジゴ系色素、トリフェニル系色素などのタール色素が挙げられる。

【0070】

パール顔料は、光を反射する微細な板状の物質からなり、化粧料の外観および塗布した際の皮膚表面にパールのような光沢感を出す顔料である。該パール顔料は、小さな板状の雲母を光反射する酸化チタン膜で覆った合成マイカと、ニシンや太刀魚の鱗から板状結晶を採取するものがある。特に、ホワイトパールを主剤とし、色材と混合して使用したり、シルバー調や様々な干渉色として使用している。金属素材としては、各種金属粉、金属ペーストのように光沢のある擬似加工品などが使用される。

【0071】

本発明に使用されるポリイソシアネート、ポリオールおよび反応性ポリシロキサンなどの種類、使用量および使用比率は、得られる粒子Ｃの使用目的によって決定されるが、ポリイソシアネート、ポリオールおよび反応性ポリシロキサンのうちの少なくとも１種が３官能以上であることが必要である。例えば、ポリイソシアネートが２官能である場合には、ポリオールおよび／または反応性ポリシロキサンが３官能以上であり、また、ポリオールおよび／または反応性ポリシロキサンが２官能である場合には、３官能以上のポリイソシアネートが必要である。勿論、全ての成分が３官能以上であってもよい。また、ＮＣＯ／ＯＨ比は、使用する化合物と生成物に要求される性能によって決定されるが、好ましくは０．５～１．２の範囲である。

【0072】

上記全化合物の反応に使用し、生成する粒子の分散体の連続相を形成する不活性溶媒は、生成する粒子に対して実質的に非溶媒であり、かつ活性水素基を有さないものである。その例として、ペンタン、ヘキサン、ヘプタン、オクタン、デカン、石油エーテル、石油ベンジン、リグロイン、石油スピリット、シクロヘキサン、メチルシクロヘキサン、トルエン、キシレン、脂環族炭化水素の構造を有するエチルシクロヘキサン、ジメチルシクロヘキサンなどの炭化水素、ジメチルポリシロキサンなどの単独または混合物が挙げられ、これらの不活性溶媒は、該不活性溶媒と合成された粒子Ｃの分離工程や生産性の点からは１５０℃以下の沸点を有するものが好ましい。粒子Ｃの合成に際しては公知の触媒を使用すれば、反応温度は低温でもよいが、作業面から４０℃以上の反応温度が好ましい。

【0073】

上記粒子Ａの合成時に乳化剤として使用するポリウレアコロイド溶液中の粒子Ｂは、溶媒に対して溶媒和されている部分と非溶媒和部分とから構成されており、非溶媒和部分の粒子径が好ましくは０．０１～１．０μｍの粒子であり、かかるポリウレアコロイド溶液は、例えば、非水溶媒中で、油脂変性ポリオールとポリイソシアネート（またはこれらの化合物からなる末端ＮＣＯプレポリマー）とポリアミンとの反応で得られる。

【0074】
この反応では、反応が進むにつれて、ウレア結合同士の水素結合により、溶媒中に不溶解のウレアドメインが形成され、同時に油脂変性ポリオール鎖が溶媒中で溶媒和されることにより、非溶解性のウレアドメインの凝集などによる粒子Ｂの巨大化が防止され、安定なポリウレアコロイド溶液が容易に得られる。
【0075】
さらに、使用する油脂変性ポリオールが、非水溶媒中での結晶性が少なく、反応が進むにつれて生じる高分子化の過程でも、溶媒中で油脂変性ポリオールを主体とするポリマー鎖がある程度自由に動き得るために、非溶解性結晶部分と溶解性非結晶部分の分離が容易に行われ、ウレア結合同士の水素結合による非溶解性結晶部分を粒子の中心とするウレアドメインを形成し、その周囲に溶媒和されたポリマー鎖が規則正しく外向きに配向される。これは従来のミセル下に重合することにより得られる公知のコロイド溶液の製造方法における界面活性剤とは根本的に異なる作用である。
【0076】
上記ポリウレアコロイド溶液の製造方法をさらに具体的に説明する。先ず、最初に油脂変性ポリオールとポリイソシアネートとを非水溶媒中または無溶媒で反応させ、ＮＣＯ基を有するプレポリマーを合成する。次にこのプレポリマーを撹拌機付きのジャケット式合成釜に仕込み、濃度が５～７０質量％になるように非水系溶媒を添加して濃度を調整する。この溶液を撹拌しながら、予め１～２０質量％の濃度に調整したポリアミンの溶液を徐々に添加し反応を行い、ポリウレア化反応においてポリウレアコロイド溶液を製造する。
【0077】
ポリアミンの添加方法は、上記の方法の他にポリアミン溶液に前記プレポリマーまたはその溶液を添加する方法でもよい。ポリマー合成のための温度は特に限定されないが、好ましい温度は２０～１４０℃である。ポリマー合成のための反応濃度、温度、撹拌機の形態、撹拌力、ポリアミン溶液およびプレポリマーまたはその溶液の添加速度などは特に限定されないが、ポリアミンとプレポリマーのイソシアネート基との反応は速いので、急激な反応が行われないように、反応を制御することが好ましい。
【0078】
ポリウレアコロイド溶液の製造に使用する油脂変性ポリオールは、官能基が２個以下のポリオールであって、好ましい分子量は７００～３，０００であるが、これに限定されない。油脂変性ポリオールの具体例としては、例えば、各種の油脂を低級アルコールやグリコールを用いてアルコリシス化する方法、油脂を部分鹸化する方法、水酸基含有脂肪酸をグリコールによりエステル化する方法などによって、油脂に約２個以下の水酸基を含有させたものが好ましく、上記の水酸基含有脂肪酸としては、例えば、リシノレイン酸、１２－ヒドロキシステアリン酸、ヒマシ油脂肪酸、水添ヒマシ油脂肪酸などが挙げられる。
【0079】
油脂変性ポリオールとポリイソシアネートとの反応は、１＜ＮＣＯ／ＯＨ≦２の条件で行い、溶媒和されるプレポリマー鎖の分子量をコントロールする。このように合成されるプレポリマーの分子量は、特に限定されないが、好ましい範囲は約５００～１５，０００である。粒子Ｂの合成に使用されるポリイソシアネートとしては、公知のポリイソシアネートの全てが挙げられる。特に好ましいものはヘキサメチレンジイソシアネート、水添加ＴＤＩ、水添加ＭＤＩ、イソホロンジイソシアネート、水添ＸＤＩなどの脂肪族または脂環族系ジイソシアネートである。
【0080】
ポリウレアコロイド溶液の製造に使用する非水系溶媒としては、使用原料である油脂変性ポリオール、ジイソシアネートおよびポリアミンを溶解するもので、活性水素基を有さない全ての非水系溶媒を使用することができる。特に好ましいものはペンタン、ヘキサン、ヘプタン、オクタン、デカン、石油エーテル、石油ベンジン、リグロイン、石油スピリット、シクロヘキサン、メチルシクロヘキサン、トルエン、キシレン、脂環族炭化水素の構造を有するエチルシクロヘキサン、ジメチルシクロヘキサンなどの炭化水素、ジメチル

ポリシロキサンなどの単独または混合物が挙げられる。なお、本発明において「溶解」とは常温および高温下での溶解の両方を包含する。

【0081】

ポリウレアコロイド溶液の製造に使用するポリアミンとして、例えば、短鎖ジアミン、脂肪族系ポリアミン、脂環式ポリアミン、芳香族系ポリアミンおよびヒドラジンなどが挙げられる。短鎖ジアミンおよび脂肪族系ポリアミンとしては、例えば、エチレンジアミン、ジアミノプロパン、ジアミノブタン、トリメチレンジアミン、トリメチルヘキサメチレンジアミン、ヘキサメチレンジアミン、オクタメチレンジアミン、ポリオキシプロピレンジアミンおよびポリオキシプロピレントリアミンなどの脂肪族ポリアミン、フェニレンジアミン、３，３’－ジクロロ－４，４’－ジアミノジフェニルメタン、４，４’－メチレンビス（フェニルアミン）、４，４’－ジアミノジフェニルエーテルおよび４，４’－ジアミノジフェニルスルホンなどの芳香族ポリアミンが挙げられる。

【0082】

また、シクロペンタンジアミン、シクロヘキシルジアミン、４，４－ジアミノジシクロヘキシルメタン、１，４－ジアミノシクロヘキサン、ビス－アミノプロピルピペラジン、チオ尿素、メチルイミノビスプロピルアミン、ノルボルナンジアミンおよびイソホロンジアミンなどの脂環式ジアミン化合物などが挙げられる。また、ヒドラジンとしては、ヒドラジン、カルボヒドラジド、アジピン酸ジヒドラジド、セバシン酸ジヒドラジドおよびフタル酸ジヒドラジドなどが挙げられる。これらは単独で或いは２種類以上を組み合わせて使用することができる。

【0083】

ポリウレアコロイド溶液の製造に使用する油脂変性ポリオール、ポリイソシアネート、ポリアミン、得られるプレポリマーの種類、使用量および使用比率は、使用する溶媒中での粒子Ｂの大きさおよび安定性などを制御する目的で決定される。すなわち、本発明で用いるポリウレアコロイド溶液中の粒子Ｂは、溶媒中で溶媒和されない結晶部分のウレアドメインと、そのウレアドメインから伸びて溶媒中で溶媒和されたポリマー鎖により形成されている。

【0084】

ポリウレアコロイド溶液中の粒子Ｂのウレアドメインの大きさおよび溶媒和されたポリマー鎖の大きさと形態がポリウレアコロイド溶液の性質を左右する。このように、ウレアドメインと溶媒和されたポリマー鎖とで形成された粒子Ｂは、溶媒中で安定なポリウレアコロイド溶液であり、その溶液中の粒子Ｂのウレアドメインの粒径は、通常０．０１～１．０μｍであり、溶媒和されているポリマー鎖の１個の分子量は約５００～１５，０００であり、両者の質量比はウレアドメイン（ウレア結合またはポリアミン）／ポリマー鎖が０．５～３０の範囲が好ましい。

【0085】

ウレア結合の割合が上記範囲未満であると、得られる粒子Ｂ中の非溶媒和性ウレアドメインが形成されにくく、粒子Ｂが非水溶媒に溶解し易くなり、良好なポリウレアコロイド溶液が生成されない。一方、ウレア結合の割合が上記範囲を越えると、非溶媒和性ウレアドメインが大きくなり、得られるポリウレアコロイド溶液の安定性が低下し、粒子Ｂの凝集が生じ易くなる。

【0086】

本発明で使用する粒子Ｂの溶媒中における形態は、図１に示すようなものと想像される。この粒子Ｂの粒径の制御については、溶媒和したポリマー部分とウレアドメインを含んだ粒子全体の大きさと、溶媒和したポリマー部分とウレアドメインのそれぞれの大きさについて、両者ともに制御が可能である。なお、先に記載の粒子Ｂの粒径は、ウレアドメイン部分を表現している。

【0087】

安定に制御されたポリウレアコロイド溶液を製造するためには、図１のように、溶媒和したポリマー部分とウレアドメイン部分が明瞭に相分離しているのが望ましく、そのため

には溶媒和されるポリマー鎖と結晶部分のウレアドメインとが混在しないように製造することが必要である。このためには、合成過程で溶媒和したポリマー部分とウレアドメイン部分が分離しやすい合成条件が要求される。

【0088】

ポリウレアコロイド溶液の合成は、ＮＣＯ基を有するプレポリマーの溶液およびポリアミンの溶液の両方の濃度が低く、一方の溶液に他方の溶液を添加する添加速度が遅いほど良好な結果が得られ、撹拌はプロペラミキサー撹拌で充分である。また、原料溶液の濃度が高い場合や溶液の添加速度が速い場合には、ホモジナイザーなどの使用による高剪断力の混合を行いながら合成することが好ましい。反応温度は使用する溶媒の種類と、その溶媒に対するウレアドメインの溶解度により決まるが、好ましい温度は合成を制御し易い２０～１２０℃であるが、この温度範囲に特に限定されない。ウレアドメインの形成は合成過程で形成する方法、或いは高温で合成したものを冷却過程で形成する方法でもよい。

【0089】

ポリウレアコロイド溶液中の粒子Ｂの重要な因子は、その表面基の種類および濃度であり、さらには不活性溶媒中における分散性と分散粒径である。すなわち、ポリウレアコロイド溶液の乳化剤としての作用は、Ｗ／Ｏ、Ｏ／Ｏ型の乳化剤であり、ポリイソシアネート、ポリオールおよび反応性ポリシロキサンの親水性、疎水性の強さと不活性溶媒との相関性で作用する。これらの条件を加味して検討を加えた結果として、ポリイソシアネート、ポリオールおよび反応性ポリシロキサンに対するポリウレアコロイド溶液の添加量の調整で、粒子Ｃの粒径をコントロールすることが可能であり、前記の範囲で添加量が多い程粒径は小さくなり、少ない程粒径が大きくなる。

【0090】

以上の如き原材料から得られた粒子Ｃの分散溶液から、常圧または減圧下で不活性溶媒を分離することによって、本発明で使用する粒子Ｃが得られる。粒子化に用いる装置としてスプレイドライヤー、沪過装置付き真空乾燥機、撹拌装置付真空乾燥機、棚式乾燥機など公知のものがいずれも使用でき、好ましい乾燥温度は不活性溶媒の蒸気圧、ゲル粒子の軟化温度、粒径などに影響されるが、好ましくは減圧下４０～１３０℃である。

【0091】

このようにして製造された粒子Ｃの粒径は、０．５～１００μｍで真球状である。粒径のコントロールは、粒子Ｃの組成が同一の場合、合成釜の乳化型式（プロペラ式、錨型式、ホモジナイザー、螺旋帯式など）および撹拌力の大小に左右されるが、特に不活性溶媒中のポリイソシアネート、ポリオールおよび反応性ポリシロキサンの濃度および機能性成分などの濃度、ポリウレアコロイド溶液の種類および添加量に影響される。ポリイソシアネート、ポリオール、反応性ポリシロキサン、機能性成分などを乳化するための機械的撹拌や剪断力は乳化の初期段階で決定され、これが強力な程分散体の粒径が小さくなる。その後の撹拌および剪断力は大きくは影響しない。かえってその力が強すぎると分散体同士の凝集を促進することになり好ましくない。

【0092】

また、本発明では、上記の粒子Ｃの製造にあたり、原料の少なくとも一部または全部に機能性成分など以外の各種添加剤を混合して、粒子Ｃの合成を行い種々の用途に適した粒子Ｃを得ることも可能である。

【0093】

さらに、本発明においては、粒子Ｃを分散媒（重合媒体）から分離した状態において（乾燥粒子Ｃ）、通常の粒子の場合、粘着性が強く二次凝集してしまうが、該粒子Ｃは、凝集物がなくサラサラした粒子の状態として取り出されるのが特徴である。この作用は従来公知の有機系乳化剤や分散安定剤とは根本的に異なる作用である。

【0094】

これらの粒子Ｃは、図２の電子顕微鏡写真（倍率５００倍）に示すように、ほぼ完全に真球状の粒子であり、図３の想像図に示す如く個々の粒子Ｃの表面にはポリウレアコロイド溶液から析出した粒子Ｂが付着或は被覆されておりかつ粒子Ｂが非粘着性と耐熱性に優

れているため、該粒子Ｃを分散溶媒から単に除去するのみで極めて流動性に富んだ粒子となり、粒子化に当たっては従来技術における如き煩雑かつコスト高な粉砕工程や分級操作を何ら要しないなどの種々の利点を有している。

【実施例】

【0095】

以下に合成例、実施例および比較例を挙げて本発明をさらに具体的に説明するが、本発明はこれに限定されるものではない。また、以下の文中の「部」は質量部、「％」は質量％を示す。

【0096】

（ポリウレアコロイド溶液の作成）

［合成例１］

水酸基価１１９．５の２官能の油脂変性ポリオール（伊藤製油（株）製　ＵＲＩＣ　Ｙ－２０２）１００部中にグルコシルトレハロース２部とホワイトパール０．２部および黄酸化鉄０．１部を均一に分散させたものと、ｎ－オクタン１００部とを撹拌機付き合成釜に仕込み上記ポリオールを溶解した。撹拌しながら温度を５０℃に制御し、ＮＣＯ／ＯＨ＝２になるように予め用意したイソホロンジイソシアネート４７．３部を１時間かけて徐々に添加し、この条件で３時間反応を続け、さらに８０℃、３時間の反応を行い合成した。次にｎ－オクタンで濃度５０％に調整し、ＮＣＯ基を３．０％含有するプレポリマー溶液（ＰＰ－１）を得た。この物の分子量は１，３８３である。

【0097】

上記のＰＰ－１の４０部を、ｎ－オクタン６０部を撹拌機付き合成釜に仕込み溶解した。撹拌しながら温度を７０℃に制御しながら、予め用意したイソホロンジアミンのｎ－オクタンの１０％溶液２４．３部を５時間掛けて徐々に添加し反応を完結して、（ポリアミン（ウレア結合部）／プレポリマー鎖）×１００＝１２．１５％のポリウレアコロイド溶液（固形分１８．０％）（Ｃ－１）を得た。この溶液は青い乳光色の安定な溶液であった。

【0098】

［合成例２］

水酸基価１１９．５の２官能の油脂変性ポリオール（伊藤製油（株）製　ＵＲＩＣ　Ｙ－２０２）１００部中にビタミンＥ（トコフェロール）１部中とホワイトパール０．５部を均一に分散させたものと、ｎ－オクタン１００部とを撹拌機付き合成釜に仕込み上記ポリオールを溶解した。撹拌しながら温度を５０℃に制御し、ＮＣＯ／ＯＨ＝１．１になるように予め用意したイソホロンジイソシアネート２６．０部を１時間掛けて徐々に添加し、この条件で３時間反応を続け、さらに８０℃、４時間の反応を行い合成した。次にｎ－オクタンで濃度５０％に調整し、ＮＣＯ基を０．３６％含有するプレポリマー溶液（ＰＰ－２）を得た。この物の分子量は１１，８３４である。

【0099】

上記のＰＰ－２の２０部とｎ－オクタン８０部とを撹拌機付き合成釜に仕込み上記プレポリマー溶解した。撹拌しながら温度を７０℃に制御しながら、予め用意したイソホロンジアミンのｎ－オクタンの１％溶液１４．４部を８時間掛けて徐々に添加し反応を完結して、（ポリアミン／プレポリマー鎖）×１００＝１．４４％のポリウレアコロイド溶液（固形分８．９％）（Ｃ－２）を得た。この溶液は青い乳光色の安定な溶液であった。

【0100】

［合成例３］

水酸基価１５７．８の１官能の油脂変性ポリオール（伊藤製油（株）製　ＵＲＩＣ　Ｈ－３１）１００部中にヒアロン酸０．３部とシルバー調パール１．０部を均一に分散させたものを、撹拌機付き合成釜に仕込み、撹拌しながら温度を６０℃に制御し、予め用意したトリレンジイソシアネート４９．０部を１時間掛けて徐々に添加し、この条件で５時間の反応を行い合成した。次にｎ－ヘプタンで濃度６０％に調整し、ＮＣＯ基を４．７６％含有するプレポリマー溶液（ＰＰ－３）を得た。この物の分子量は５３０である。

【0101】
上記のＰＰ－３の１００部を撹拌機付き合成釜に仕込み、撹拌しながら温度を５０℃に制御し、予め用意したトリメチルヘキサメチレンジアミンのｎ－ヘプタンの１０％溶液８９．７部を５時間掛けて徐々に添加し反応を完結して、（ポリアミン／プレポリマー鎖）×１００＝１４．９５％のポリウレアコロイド溶液（固形分３６．４％）（Ｃ－３）を得た。この溶液は黄味の乳光色の安定な溶液であった。

【0102】
（ラクトン変性ポリシロキサンの製造）
［合成例４～６］
撹拌機、温度計、窒素ガス導入管および還流冷却器を具備した反応器に、窒素ガスで置換した後、表１に記載したラクトンおよびシロキサンを所定の濃度まで投入し窒素気流下、１００℃にて均一になるまで撹拌した。続いて所定のテトラ－ｎ－ブチルチタネートを投入し、窒素気流下１８０℃の温度下で１０時間反応させた。反応の進行とともに反応物の粘度が上昇してくる。その後、１８０℃で５ｍｍＨｇの減圧下で１時間反応を続け、反応を完了させるとともに、原料のシロキサンに含まれていた非反応性シロキサンおよび未反応物を完全に除去した。得られたポリカプロラクトン変性ポリシロキサンの組成および性状を表１に示す。

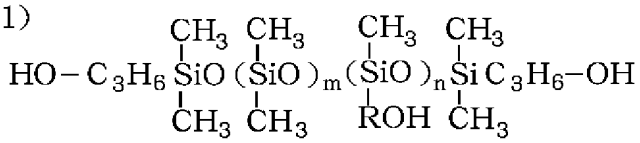
【0103】

表１

		合成例４	合成例５	合成例６
組成	シロキサン（a）	ａ－１	ａ－２	ａ－３
	ラクトン化（b）	ε－カプロラクトン	ε－カプロラクトン	ε－カプロラクトン
	配合比(質量比)a／b	3／7	4／5	5／12
	触媒	テトラ－ｎ－ブチルチタネート 0.05部	テトラ－ｎ－ブチルチタネート 0.05部	テトラ－ｎ－ブチルチタネート 0.05部
性状	外観	白色固体	白色固体	白色固体
	融点（℃）	56	67	74
	水酸基価（OHv）	27	25	8
	シロキサン濃度（%）	30	44	29

【0104】
表１中のポリシロキサン（ａ）は下記の構造を有する。

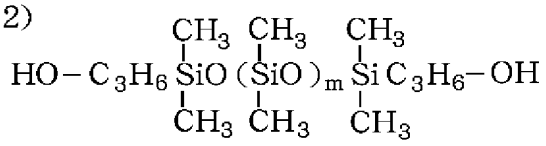
ａ－１）



（ｎ＝１、ｍは平均分子量が1,900となる整数比、Ｒ＝低級アルキレン基を表す。）

【0105】

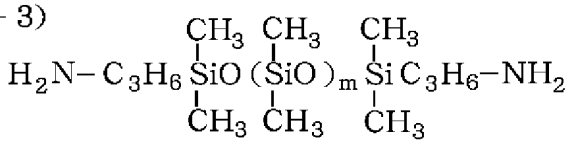
ａ－2)



（ｍは、水酸基当量が56になる値である。）

【0106】

ａ－3)



（ｍは、アミノ基当量が2,000になる値である。）

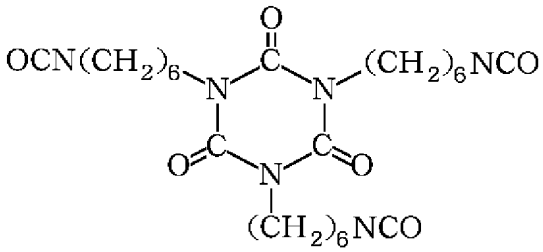
【0107】

（ポリウレタンゲル粒子の製造）

［実施例１］

平均分子量１，０００のポリブチレンアジペートジオール１６部中にビタミンＥ０．１部とビタミンＣ０．２部を均一に分散した分散液およびラクトン変性ポリシロキサン（合成例４）４部を６０℃で溶解し、さらに下記の構造式で示されるヘキサメチレンジイソシアネートのイソシアヌレートポリイソシアネート（旭化成工業（株）製　デュラネートＴＰＡ－１００、ＮＣＯ％＝２３．１）６．１６部を添加し均一に混合した。この物を予め１リットルのステンレス容器に準備した合成例１のポリウレアコロイド溶液（Ｃ－１）３．０部とｎ－オクタン２５部の混合液の中に徐々に加え、ホモジナイザーで１５分間乳化した。この乳化液は分散質の平均分散粒子径が５μｍで分離もなく安定な乳化液であった。

【0108】



【0109】

次にこれを錨型撹拌機付き反応釜に仕込み、４００ｒｐｍの回転をさせながら温度を８０℃まで上げ、６時間の反応を終了しシロキサン変性ポリウレタンゲル粒子の溶液を得た。この溶液を１００Ｔｏｒｒで真空乾燥を行ってｎ－オクタンを分離しシロキサン変性ポリウレタンゲル粒子（１）を得た。このものは平均粒子径が５μｍの真球状の白色粉末状であった。

【0110】

［実施例２］

錨型撹拌機付反応釜に平均分子量２，０００のポリテトラメチレンアジペートジオール７０部中にコエンザイムＱ１０を０．３部を均一に分散した分散液および合成例５のラクトン変性ポリシロキサンを３０部仕込み、７０℃に加熱溶解して撹拌しながらジフェニルメタンジイソシアネート（ＭＤＩ）２０．９部を徐々に添加し、５時間の反応を行いＮＣＯ／ＯＨ＝２のプレポリマーを得た。このものにトリメチロールプロパン３．７部を添加混合した。

【0111】

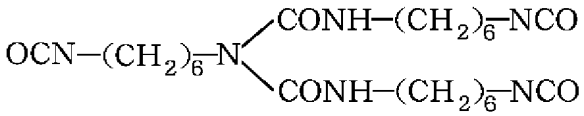
この物の２５部を予め１リットルのステンレス容器に準備した合成例２のポリウレアコロイド溶液（Ｃ－２）１２部とｎ－ヘプタン５０部の混合液の中に徐々に加え、ホモジナイザーで２５分間乳化した。この乳化液は分散質の平均分散粒子径が８μｍで分離もなく安定な乳化液であった。次にこれを錨型撹拌機付き反応釜に仕込み、５００ｒｐｍの回転をさせながら温度を１００℃まで上げ、５時間の反応を終了しシロキサン変性ポリウレタンゲル粒子の溶液を得た。この溶液から実施例１と同様にしてシロキサン変性ポリウレタンゲル粒子（２）を得た。このものは平均粒子径が８μｍの真球状の白色粉末状であった。

【0112】

［実施例３］

５００ミリリットルのセパラブルフラスコに、合成例３のポリウレアコロイド溶液（Ｃ－３）１２部とイソオクタン１５０部とを仕込み混合した。次にこの液をホモミキサーで混合しながら予め５０℃に加温した平均分子量７８５の３官能のポリラクトンポリオール７０部中に白金ナノコロイド５部を均一に分散した分散液および合成例６のラクトン変性ポリシロキサンを３０部仕込み、徐々に添加して乳化させた。さらに下記の構造式で示されるヘキサメチレンジイソシアネートアダクトポリイソシアネート（旭化成工業（株）製デュラネート２４Ａ－１００、ＮＣＯ％＝２３．５）４８．６部を徐々に添加した。

【0113】



【0114】

次にホモミキサーを回転しながら、温度を８０℃に上げ、３時間の反応後に反応触媒としてジブチル錫ジラウレート０．００５部を加え、さらに４時間の反応を行ない、シロキサン変性ポリウレタンゲル粒子の分散液を得た。この分散液から実施例１と同様にしてシロキサン変性ポリウレタンゲル粒子（３）を得た。このものは平均粒子径が３μｍの真球状の白色粉末状であった。

【0115】

［比較例１］

撹拌機および還流冷却器を具備した１，０００ミリリットルのセパラブルフラスコに、メチルメタクリレート５０部、エチルアクリレート３５部、プロピレングリコールジアクリレート５部、エチレングリコールジメタクリレート１０部およびベンゾイルパーオキサイド０．３部を仕込み、さらに、ポリビニルアルコール（ＧＨ－１７、日本合成化学工業社製）の５％水溶液３０部およびイオン交換水２５０部を添加し、ホモミキサーにて４，０００～６，０００ｒｐｍで１０分間分散処理し分散液（１）を調製した。さらに分散液（１）を、窒素雰囲気下で撹拌しながら８０℃、５時間ラジカル重合した。得られたアクリレート系粒子分散液を脱水、洗浄、乾燥後、解砕、篩いを掛けアクリル粒子を得た。このものは平均粒子径が１０μｍの真球状の白色粉末状であった。

【0116】

［比較例２］

シリカ粒子としてサイリシア３５０（富士シリシア化学社製）平均粒子径３．９μｍのものを用いた。

【0117】

表２：実施例１～３及び比較例１、２の各粒子の評価

		実施例１	実施例２	実施例３	比較例１	比較例２
外観色調		○	○	○	×	×
分散性		○	○	○	△	×
吸油量（ml/100g）	亜麻仁油	75	72	80	50	310
	オレイン酸	125	115	135	45	280
分散安定性	1,3－BG	○	○	△	△	△
	揮発性シリコーン	○	○	○	○	×
	IPA	○	○	○	○	△
膨潤性（IPA）		2％	1％	3％	15％	0％
光学特性（％）	全光線透過率	90	88	90	90	87
	拡散透過率	35	33	38	40	65
耐熱性		250℃以上	250℃以上	250℃以上	220℃	250℃以上

1,3－BG；1,3－ブタングリコール
IPA；イソプロピルアルコール

【0118】
＜外観色調＞
各粒子を外観で確認した際の意匠性
○：意匠性が高い。
×：意匠性が低い。
【0119】
＜分散性＞
ディゾルバー撹拌機（１，０００ｒｐｍ）中のＩＰＡ（イソプロピルアルコール）１００ｇに各粒子を５ｇ添加し、２０秒後の分散性を確認した。
評価基準；
○：均一に分散していた。
△：一部凝集物があった。
×：分散しない。
【0120】
＜吸油量＞
ＪＩＳ－Ｋ５１０１に準じて測定した。
各粒子が化粧料に使用する油剤、防腐剤などを吸収すると、それらの効果を発揮できなくなるので、油剤などの例として亜麻仁油を使用してその吸収量を測定した。亜麻仁油の吸収性が低い方がよいとされる。オレイン酸は、人の皮脂成分の代替材料として測定した。オレイン酸の吸収性が高いほど人の皮脂を吸収するので良好とされる。化粧料に使用する油剤、防腐剤の吸収性が低く、かつ皮脂（オレイン酸）の吸収は必要とされる。
【0121】
＜分散安定性＞
１，３－ブタングリコール、揮発性シリコーン、ＩＰＡ１００ｇに対して、各粒子１０ｇを入れ、手撹拌で混合した際の分散安定性を確認した。
評価基準；

○：簡単に分散し３日間後、凝集・沈降もなく安定な溶液が保持できる。
△：簡単に分散するものの３日間後、一部に凝集・沈降が見られる。
×：分散しない。

【0122】

＜膨潤性＞

ＩＰＡ中に、各粒子を２４時間浸漬させた後、粒子径の増加率（％）を比較した。

【0123】

＜光学特性＞

試験片は、ニトロセルロース溶液に各粒子を濃度１０ｐｈｒに加えて塗料とし、塗布膜厚２０μｍでコーティングしたものの光学特性を測定した。全光線透過率は、数値が高いと透明感のある自然な肌を演出してよいとされる。また、拡散透過率は、適度な値（３０～５０）が求められ、光の拡散効果で小じわ、しみなどを隠す作用がある。

【0124】

＜耐熱性＞

熱機械分析（ＴＭＡ、リガク（株））を用い、粒各子と同じ樹脂組成のシートを作製して荷重１０ｇ、昇温速度１０℃／ｍｉｎ．の条件にて針進入法で測定を行った。

【0125】

（実施例１～３および比較例１、２の各粒子の化粧料応用）

＜クリーム処方＞

・各粒子	１２．０部
・シリコーン系界面活性剤	１．０部
・スクワラン	１２．０部
・揮発性シリコーンオイル	１２．０部
・１，３－ＢＧ	５．０部
・精製水	５８．０部

上記化粧処方にて化粧料評価を行った。評価方法および結果を下記表３に示す。

【0126】

表３

	実施例１	実施例２	実施例３	比較例１	比較例２
柔軟性（ソフト性）	○	○	○	△	×
伸展性	○	○	○	△	×
毛穴隠し効果	○	○	○	△	△
機能性	保湿機能効果あり	抗酸化効果あり	美白効果あり	－	－

【0127】

＜柔軟性＞

適正量を手の甲に塗り、乾燥した状態で評価を行った。

○：ソフト性がある。
△：ソフト性が劣る。
×：ハード性が強い。

ソフト性が高いと人肌と近似した感覚であり評価される。

【0128】

＜伸展性（ローリング性）＞

適正量を手の甲に塗り、伸展性が良好であるか確認した。

○：伸展性がある。
△：伸展性が劣る。

×：伸展性が強い。

【0129】

＜毛穴隠し効果＞

適正量を手の甲に塗り、毛穴が隠れるか目視にて観察評価した。

○：毛穴隠し効果がある。

△：毛穴隠し効果が劣る。

×：毛穴隠し効果がない。

【0130】

＜機能性＞

１０人の女性にクリーム処方、リキッドファンデーション処方にて調製したサンプルを腕に塗布してもらい、５名以上が効果を確認した場合を効果ありとした。

【0131】

＜リキッドファンデーション処方＞

・各粒子	１０．０部
・シリコーン系界面活性剤	１．５部
・揮発性シリコーンオイル	２３．０部
・ジメチルシリコーン	５．０部
・酸化チタン	９．０部
・弁柄	０．６部
・黄色酸化鉄	０．２部
・タルク	２．０部
・プロピルパラベン（防腐剤）	０．５部
・１，３－ブタングリコール	１０．０部
・ビタミンＥ	０．２部
・精製水	３８．０部

上記化粧処方にて化粧料評価を行った。前記評価方法による結果を下記表４に示す。

【0132】

表４

	実施例１	実施例２	実施例３	比較例１	比較例２
柔軟性（ソフト性）	○	○	○	×	×
伸展性	○	○	○	△	×
毛穴隠し効果	○	○	○	△	△
機能性	保湿機能効果あり	抗酸化効果あり	美白効果あり	－	－

【0133】

＜パウダーファンデーション処方＞

・各粒子	３．０部
・タルク	３５．０部
・セリサイト	２０．０部
・酸化チタン	９．０部
・弁柄	２．０部
・黄色酸化鉄	３．５部
・黒色酸化鉄	０．５部
・マイカ	１５．０部
・スクワラン	６．０部
・ステアリルアルコール	３．０部

・ミツロウ　　３．０部

上記化粧処方にて化粧料評価を行った。前記評価方法による結果を下記表５に示す。

【0134】

表５

	実施例１	実施例２	実施例３	比較例１	比較例２
柔軟性（ソフト性）	○	○	○	×	×
伸展性	○	○	○	△	×
毛穴隠し効果	○	○	○	△	×
機能性	保湿機能効果あり	抗酸化効果あり	美白効果あり	－	－

【産業上の利用可能性】

【0135】

本発明は下記の効果を奏する。

１．粒径がコントロールされ、機能性成分などを含む粒子Ｃを含む化粧料の提供が可能である。

２．得られた粒子Ｃは真球状であり、該粒子Ｃの表面にはポリウレアコロイド溶液から析出した粒子Ｂが均一に付着または被覆されているため、該微粒子は極めて流動性に優れ、取り扱いが容易であり、化粧料として種々の応用が可能である。

３．以上の効果から、本発明の粒子Ｃは、化粧料成分として有益である。

【図面の簡単な説明】

【0136】

【図1】本発明で使用するポリウレアコロイド溶液中の粒子Ｂの断面の想像図。

【図2】本発明で使用する粒子Ｃの写真。

【図3】本発明で使用する粒子Ｃの断面の想像図。

【符号の説明】

【0137】

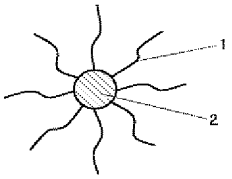
１：溶媒和されているポリマー鎖（油脂セグメント）

２：非溶媒和部分のウレアドメイン

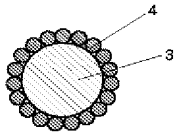
３：粒子Ａ

４：粒子Ｂ

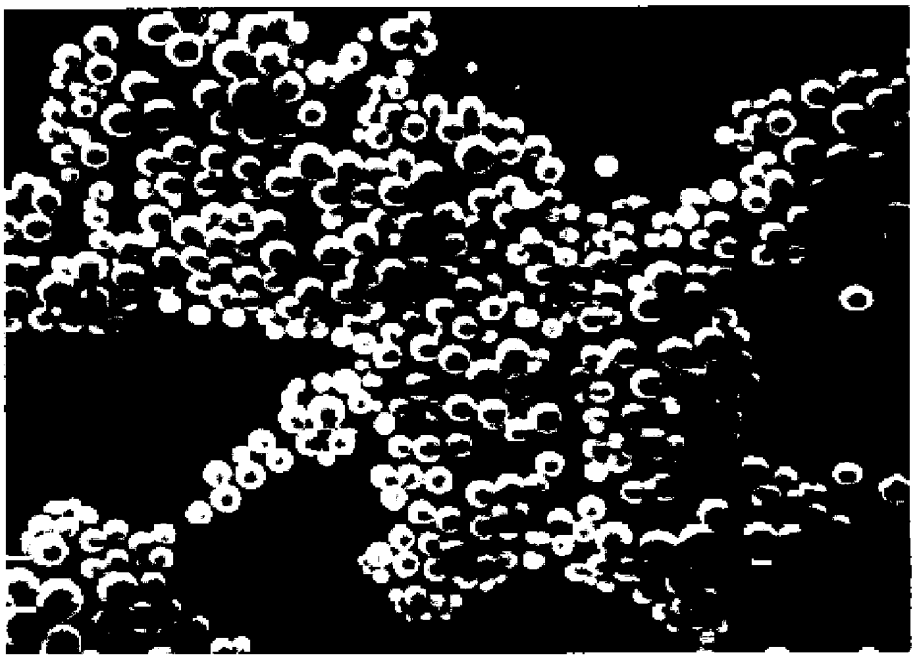
【図1】



【図3】



【図2】



(72)発明者　佐藤　浩正
東京都中央区日本橋馬喰町１丁目７番６号　大日精化工業株式会社内
(72)発明者　渡辺　明弘
東京都中央区日本橋馬喰町１丁目７番６号　大日精化工業株式会社内
(72)発明者　花田　和行
東京都中央区日本橋馬喰町１丁目７番６号　大日精化工業株式会社内

Ｆターム(参考) 4C083 AA082 AB232 AB242 AB432 AC022 AC072 AC112 AC122 AC482 AD152
AD161 AD162 AD662 BB21 BB46 BB47 BB48 CC02 CC05 CC11
CC12 DD16 DD17 DD23 DD27 DD41 EE07 EE09 FF01

Espacenet

WO2018122532A1 MASCARA COMPOSITION AND PACKAGING

Applicants: LVMH RECH [FR]

Inventors: BICHON YOHANN [FR],KOUSSOROS CAROLINE [FR]

Classifications:
IPC ***A61K8/87; A61K8/891; A61Q1/10;***

CPC **A61K8/0241 (KR); A61K8/025 (US); A61K8/87 (EP,KR,US); A61K8/891 (EP,KR,US); A61K8/92 (KR); A61Q1/10 (EP,KR,US);** A61K2800/412 (KR); A61K2800/87 (KR);

Priorities: FR1663569A 2016-12-30

Application: FR2017053851W·2017-12-27

Publication: WO2018122532A1·2018-07-05

Published as: **CN110290836A; EP3562556A1; FR3061432A1; FR3061432B1; JP2020503328A; KR20190102001A; US2019350834A1;** WO2018122532A1

MASCARA COMPOSITION AND PACKAGING

Abstract

The invention relates to a mascara with a high wax content containing an association of elastic polyurethane microspheres and non-compressible and non-porous polymethylsilsesquioxane microspheres. The mascara is packaged in a container provided with flexible parts that can be deformed by manual pressure so as to mix the formula. The invention also relates to a method for applying make-up to eyelashes, using said composition and packaging.

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)

(19) Organisation Mondiale de la Propriété Intellectuelle
Bureau international

(43) Date de la publication internationale
05 juillet 2018 (05.07.2018)

WIPO | PCT

(10) Numéro de publication internationale
WO 2018/122532 A1

(51) Classification internationale des brevets :
A61Q 1/10 (2006.01) *A61K 8/891* (2006.01)
A61K 8/87 (2006.01)

(21) Numéro de la demande internationale :
PCT/FR2017/053851

(22) Date de dépôt international :
27 décembre 2017 (27.12.2017)

(25) Langue de dépôt : français

(26) Langue de publication : français

(30) Données relatives à la priorité :
1663569 30 décembre 2016 (30.12.2016) FR

(71) Déposant : **LVMH RECHERCHE** [FR/FR] ; 185 avenue de Verdun, 45800 Saint Jean de Braye (FR).

(72) Inventeurs : **BICHON, Yohann** ; 12, rue de Reims, 94700 Maisons-Alfort (FR). **KOUSSOROS, Caroline** ; 1, rue Thiers, 45000 Orléans (FR).

(74) Mandataire : **CHANTRAINE, Sylvie** et al. ; Cabinet Beau de Loménie, 158 Rue de l'Université, 75340 Paris Cedex 07 (FR).

(81) États désignés *(sauf indication contraire, pour tout titre de protection nationale disponible)* : AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) États désignés *(sauf indication contraire, pour tout titre de protection régionale disponible)* : ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), eurasien (AM, AZ, BY, KG, KZ, RU, TJ, TM), européen (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Publiée:
— *avec rapport de recherche internationale (Art. 21(3))*

WO 2018/122532 A1

(54) Title: MASCARA COMPOSITION AND PACKAGING

(54) Titre : COMPOSITION DE MASCARA ET CONDITIONNEMENT

(57) Abstract: The invention relates to a mascara with a high wax content containing an association of elastic polyurethane microspheres and non-compressible and non-porous polymethylsilsesquioxane microspheres. The mascara is packaged in a container provided with flexible parts that can be deformed by manual pressure so as to mix the formula. The invention also relates to a method for applying make-up to eyelashes, using said composition and packaging.

(57) Abrégé : La présente invention concerne un mascara à fort taux de cire contenant l'association de microsphères de polyuréthane élastiques et de microsphères de polyméthylsilsesquioxane non compressibles et non poreuses. Ce mascara est conditionné dans un récipient doté de parties souples qui peuvent être déformées par pression de la main, de manière à malaxer la formule. L'invention concerne également une méthode de maquillage des cils mettant en œuvre cette composition et ce conditionnement.

COMPOSITION DE MASCARA ET CONDITIONNEMENT

La présente demande se rapporte au domaine du maquillage ou du soin des cils, et concerne plus spécifiquement une composition de mascara contenant une forte proportion de cires. Cette composition comprend au moins une phase liquide dans laquelle sont dispersées des cires, des particules solides d'au moins un premier polymère, des particules solides d'au moins un deuxième polymère, et des pigments.

L'invention concerne également un ensemble comprenant une composition de mascara et un conditionnement.

ETAT DE LA TECHNIQUE

Bon nombre de mascaras crèmes et de mascaras waterproof sont recherchés pour donner du volume aux cils en les épaississant. C'est en ajustant la quantité de composés solides, notamment de cires, que le formulateur peut améliorer le résultat du maquillage en déposant plus de matière sur les cils.

Il est cependant difficile d'obtenir un effet épaississant ou volumateur sans provoquer l'agglomération des cils entre eux. En effet, un fort extrait sec conduit à une texture visqueuse qui génère des amas de produit lors de l'application, et qui nécessite plusieurs brossages des cils ou plusieurs applications successives, pour mieux répartir le produit.

Il est donc souhaitable de proposer un mascara volumateur dont l'application est lisse, régulière et sans amas de produit.

Il est également souhaitable de proposer un mascara dont les propriétés volumatrices sont améliorées dès la première application et dont la tenue sur les cils est prolongée au cours de la journée. L'absence de coulées ou de débordement du mascara sur le contour des yeux, ainsi qu'un effritement limité du produit enrobant les cils sont recherchés.

Dans un mascara crème, comme dans un mascara waterproof, les cires forment un réseau structurant qui apporte de la consistance au liquide dans lequel elles sont dispersées. Ce réseau des cristaux de cire a tendance à se fragiliser de façon irréversible au cours du temps ce qui diminue la qualité du maquillage au fur et à mesure des utilisations. Le besoin subsiste par conséquent de fournir un mascara dont la structure est stable dans le conditionnement au cours du temps, de façon à conserver un maquillage optimal tout au long de l'utilisation du produit.

Le besoin subsiste également de proposer un mascara dans lequel les cires sont dispersées de façon homogène dans le conditionnement, restent

régulièrement dispersées au cours de la durée d'utilisation du produit, et sont en quantité importante pour obtenir un dépôt chargeant sur les cils.

Il a été découvert à présent que l'association de deux polymères particuliers dans une composition comprenant des forts taux de cires permet d'obtenir un mascara dont l'effet volumateur est amélioré et dont la texture est fluide et crémeuse au moment de l'application. Cette association permet de ralentir la dégradation du réseau de cristaux de cire au cours du temps. Enfin, chacun de ces polymères participe au chargement plus important de la brosse à mascara, quand la composition est placée dans un tube que l'on peut déformer par pression de la main par exemple.

DESCRIPTION DE L'INVENTION

Ainsi, la présente invention décrit une composition destinée au maquillage ou au soin des cils comprenant un liquide, comme l'eau ou une huile, dans lequel sont dispersées des cires, des particules solides d'au moins un premier polymère, des particules solides d'au moins un deuxième polymère, et des pigments, le premier polymère étant choisi parmi les polyuréthanes réticulés, et le deuxième polymère étant choisi parmi les polyméthylsilsesquioxanes et les polyméthylméthacrylates réticulés.

L'invention décrit également un produit de maquillage comprenant une composition de maquillage placée dans un ensemble de conditionnement et d'application présentant une paroi flexible qui peut être déformée en exerçant une pression de la main, ladite composition comprenant un liquide dans lequel sont dispersées des cires et des particules solides d'au moins un polymère, le polymère étant choisi parmi les polyuréthanes réticulés, les polyméthylsilsesquioxanes, les polyméthylméthacrylates réticulés, et leurs mélanges.

L'invention décrit également un procédé de maquillage des cils, qui comprend au moins les étapes suivantes :

- la fourniture à un utilisateur d'une composition de mascara à haut taux de cire contenant un polymère choisi parmi les polyuréthanes réticulés, les polyméthylsilsesquioxanes, les polyméthylméthacrylates réticulés et leurs mélanges, ladite composition étant conditionnée dans un ensemble de conditionnement et d'application comprenant i) un récipient doté d'un moyen d'essorage et d'une partie flexible sur au moins une de ses surfaces internes ou externes et ii) un bouchon duquel est solidaire une brosse d'application qui est plongée dans la composition,
- la pression par l'utilisateur de ladite partie flexible de manière à

malaxer la composition contenue dans le récipient,

- l'ouverture du tube et l'essorage de la brosse recouverte de composition par retrait du bouchon, et

- le brossage des cils.

La combinaison particulière des deux polymères, ou la combinaison particulière d'un polymère et d'un ensemble de conditionnement, permet avantageusement d'assouplir une formule juste avant son application sur les cils. Cet assouplissement peut être obtenu en exerçant une pression sur une partie déformable du conditionnement. Le mascara, qui présente une viscosité élevée du fait d'une forte concentration en cires, peut être appliqué de façon plus régulière, conduire à un recouvrement des cils plus lisse, et permettre un épaississement des cils plus important dès la première application.

La combinaison des deux polymères, ou la combinaison d'un polymère et d'un ensemble de conditionnement, proposée dans le cadre de l'invention, permet encore de restructurer le réseau de cire, de manière à augmenter l'effet volumateur à chaque application et tout au long de la vie d'utilisation du produit. L'effet volumateur peut en outre se prolonger au cours de la journée sur une durée plus longue que les mascaras de l'art antérieur.

La présente invention décrit encore une composition destinée au maquillage ou au soin des cils comprenant un liquide, des cires, des particules solides d'au moins un premier polymère, des particules solides d'au moins un deuxième polymère différent du premier, et des pigments, les particules du premier polymère étant élastiques, et les particules du deuxième polymère ayant des propriétés d'absorption d'huile et d'absorption d'eau très faibles.

Cette composition peut plus précisément comprendre l'association de premières particules solides se déformant sous une contrainte mécanique et retrouvant au moins partiellement leur forme après annulation de la contrainte, et de deuxièmes particules solides, différentes des premières, non poreuses et n'ayant aucune affinité avec le milieu de dispersion liquide, qui conservent leur forme quelle que soit la contrainte mécanique exercée.

Ces deux catégories de matières premières participent au malaxage de la composition à chaque utilisation du produit par un utilisateur, soit par une pression exercée sur le conditionnement dans lequel est contenue la composition, soit par cisaillement de la brosse chargée en produit au moment de son essorage ou de son application.

Ce malaxage a plusieurs conséquences, telles que le maintien de la structure du réseau de cire au cours de la durée de conservation et d'utilisation du produit, une application plus facile du produit sur les cils, et l'obtention d'un

résultat maquillage volumateur immédiat et important.

En outre, le produit présente une texture crémeuse sans nuire aux qualités d'application. Il est épais sans être lourd et apporte beaucoup de matières.

DESCRIPTION DETAILLEE DE L'INVENTION

Ainsi, dans un premier aspect, l'invention porte sur une composition de mascara comprenant au moins une phase liquide, des cires, des particules solides d'au moins un premier polymère, des particules solides d'au moins un deuxième polymère, et des pigments,

la phase liquide représentant de 30% à 60% en poids, de préférence de 40 à 55% en poids,

les cires représentant de 15 à 40% en poids, de préférence de 25 à 40% en poids,

les pigments représentant de 5 à 15% en poids,

la somme de la quantité du premier polymère et de la quantité du deuxième polymère étant comprise entre 0,01 et 5% en poids,

caractérisée en ce que le premier polymère est choisi parmi les polyuréthanes réticulés, et en ce que le deuxième polymère est choisi parmi les polyméthylsilsesquioxanes.

les pourcentages étant exprimés par rapport au poids de la composition.

La texture du produit de l'invention procure un effet volumateur amélioré, de surcroît immédiat, qui se maintient davantage au cours de la journée. Les cils sont beaucoup plus épais, plus allongés, bien courbés, souples, doux et confortables. Le mascara de l'invention recouvre uniformément les cils de la racine à la pointe. Les dépôts successifs de produit se recouvrent bien de passage en passage, et la charge est satisfaisante dès le premier brossage.

La présente demande décrit également une composition de mascara comprenant au moins une phase liquide, des cires, des particules solides d'au moins un premier polymère, des particules solides d'au moins un deuxième polymère, et des pigments, les particules du premier polymère étant élastiques, et les particules du deuxième polymère ayant des propriétés d'absorption d'huile et d'absorption d'eau très faibles.

Le premier polymère est avantageusement sous forme de microsphères qui présentent une dureté (encore appelée compressibilité) assez faible pouvant être mesurée par différentes méthodes. Par exemple, la dureté des particules du premier polymère peut être inférieure à 10 N/mm^2, en

mesurant la force nécessaire pour obtenir une déformation de 10% de l'indice K (notée K(10%)), avec un appareil de compression de référence Shimadzu Microcompression Testing Machine MCTM-500. La dureté des particules, évaluée en mesurant la force nécessaire pour obtenir une déformation de 10% de l'indice K (notée K(10%)), est avantageusement comprise entre 0,01 et 1 N/mm^2, de préférence encore entre 0,1 et 0,5 N/mm^2. Cette méthode permet également d'évaluer le pourcentage de déformation élastique desdites particules : ce dernier est de préférence supérieur à 10%.

La dureté des particules du premier polymère, mesurée par la méthode ASTM D2240 (dureté Shore), peut être inférieure à 10°D, de préférence inférieure à 1°D.

Les particules du premier polymère sont avantageusement élastiques, la valeur de leur élasticité, pouvant être déterminée par différentes méthodes connues de l'homme du métier.

Exprimée comme étant le taux de déformation élastique, l'élasticité des particules peut être mesurée avec un appareil de compression de référence Shimadzu Microcompression Testing Machine MCTM-500. Le taux de déformation élastique est de préférence supérieur à 5%, de préférence encore supérieur à 10%, 15%, 20%, 25%, 30%, voire même 35%, notamment lorsque la force de compression exercée correspond au K(10%) mentionné précédemment.

L'élasticité des particules du premier polymère peut encore être caractérisée par un module d'élasticité, mesuré selon la norme ISO 178 (2010), inférieur à 1000 MPa, de préférence inférieur à 500 MPa, de préférence encore inférieur à 100 MPa.

Le deuxième polymère est de préférence sous forme de microsphères dont la surface spécifique est inférieure à 30 m^2/g, la surface spécifique étant mesurée par une méthode connue de l'homme du métier, notamment la norme ISO 9277 (2010).

Les particules du deuxième polymère présentent de préférence des capacités d'absorption d'eau et d'absorption d'huile très faibles. L'absorption d'huile des particules du deuxième polymère peut être mesurée à 25°C selon une méthode connue de l'homme du métier : elle va, par exemple, de 0 à 0,9 g/1g huile dans les conditions de la norme ASTM D281-8. Selon un mode de mise en œuvre particulier de l'invention, l'absorption d'huile des particules du deuxième polymère, mesurée à 25°C selon cette méthode va de 0 à 0,6 g/1g huile.

L'absorption d'eau des particules du deuxième polymère, évaluée à 20°C grâce à la norme DIN 53 472, peut être inférieure à 1%. Enfin, évaluée à 20°C par la norme ISO 62 (2008), la valeur d'absorption d'eau des particules peut être

inférieure à 1% également.

Les particules du premier polymère peuvent avoir des propriétés d'absorption d'huile et d'eau supérieures ou inférieures à celles des particules du deuxième polymère.

Par contre, on préfère que les particules du deuxième polymère aient une dureté bien supérieure et une élasticité bien inférieure à celles des particules du premier polymère. On préfère également que les particules du deuxième polymère soient pleines et non poreuses

Le produit selon l'invention présente une texture crémeuse plus ou moins fluide : sa viscosité est de préférence supérieure à 150 000 mPa.s, et avantageusement comprise entre 200 000 et 600 000 mPa.s. La viscosité de la composition peut être mesurée à 25 °C à l'aide d'un Rhéomat 180 (Société LAMY) équipé d'un mobile MS-R1, MS-R2, MS-R3, MS-R4 ou MS-R5 choisi en fonction de la consistance de la composition, tournant à une vitesse de rotation de 200 $t.min^{-1}$. La mesure est prise après 10 min de rotation.

La composition peut contenir une ou plusieurs phases liquides, qui peuvent être grasses ou aqueuses.

Par exemple, la composition contient une seule phase liquide comprenant de l'eau ou une seule phase liquide comprenant au moins une huile. La composition peut être anhydre en ce sens que de l'eau n'est pas ajoutée au cours de son procédé de fabrication.

La composition peut également être une émulsion de deux phases liquides, dont de l'eau et une phase grasse liquide comprenant des huiles. Dans ce cas, la composition peut être une émulsion eau-dans-huile ou une émulsion huile-dans-eau.

Outre une ou plusieurs phases liquides, la composition peut également contenir au moins une autre phase qui est solide et dispersée dans une au moins des phases liquides. La composition est par exemple une dispersion de particules solides dans une phase liquide aqueuse, ou dans une phase liquide huileuse.

Les huiles peuvent être choisies parmi les diméthicones volatiles ou non volatiles, les cyclométhicones, l'isododécane, l'isohexadécane ou l'isodécane, l'huile de paraffine, le polydécène hydrogéné, le propylène glycol, l'isononanoate d'isotridécyle, le néopentanoate d'isostéaryle, le néopentanoate de tridécyle, l'octanoate de cétyle), les huiles siliconées non volatiles, notamment les phényltriméthicones. On préfère que la phase grasse liquide comprenne majoritairement voire exclusivement des huiles volatiles sous la forme d'un gel, tel que les diméthicones volatiles, les cyclométhicones, l'isododécane, l'isohexadécane ou l'isodécane, gélifiées avec une argile organomodifiée.

La phase liquide ou le mélange de phases liquides représente par exemple de 30% à 60% en masse, de préférence de 40% à 55% en masse par rapport à la masse de la composition de mascara. La phase liquide est de préférence l'eau ou l'isododécane. Par exemple, l'eau ou l'isododécane représente de 30% à 60% en masse, de préférence de 40% à 55% en masse, par rapport à la masse de la composition de mascara.

Selon un mode de mise en œuvre de l'invention, le liquide représente de 40% à 55% en poids, les cires représentent de 20% à 25% en poids, et les pigments représentent de 8 à 12% en poids.

Le premier polymère peut se présenter sous la forme de particules constituées de un ou plusieurs polymères polyuréthanes, ou sous la forme de particules composites comprenant un cœur non polyuréthane organique ou minéral et une écorce de polyuréthane. Le polyuréthane peut être un polymère polyuréthane ou un copolymère comprenant en partie des motifs uréthanes.

On préfère que les polyuréthanes entrant dans la composition des particules du premier polymère soient réticulés.

Les particules du premier polymère sont par exemple constituées d'un cœur de polyméthylméthacrylate de méthyle enrobé de polyuréthane, ou d'un cœur de silice enrobé de polyuréthane. Les particules du premier polymère peuvent être également constituées de polyuréthane.

On préfère que les particules du premier polymère soient dotées de propriétés d'élasticités. Ainsi, on préfère que le premier polymère ne soit pas un copolymère uréthane-acrylate dont l'élasticité est nulle.

Dans les poudres composites à cœur dur et enrobage polyuréthane, on ajustera la quantité relative du cœur et de l'enrobage de manière à obtenir une élasticité et une dureté satisfaisantes.

Le polyuréthane au sens de l'invention n'est pas introduit dans la composition sous la forme d'une dispersion aqueuse de polyuréthane anionique, tels que les latex de polyuréthane utilisés couramment comme polymère filmogène dans la formulation de mascaras.

Le premier polymère pourra être sous la forme de microsphères d'un polyuréthane réticulé obtenu par copolymérisation d'un diisocyanate aliphatique (typiquement de poids moléculaire entre 100 et 300 $g.mol^{-1}$), de préférence linéaire, d'un triol aliphatique, de préférence de faible poids moléculaire (typiquement entre 100 et 150 $g.mol^{-1}$) et éventuellement d'une lactone. On peut utiliser par exemple un polymère de non INCI HDI/TRIMETHYLOL HEXYLLACTONE CROSSPOLYMER à titre de premier polymère. Un tel polymère est commercialisé sous la marque Plastic Powder® D-400.

On utilisera un pourcentage un ratio molaire entre le monomère diisosocyanate et le monomère triol de manière à obtenir les propriétés de compressibilité souhaitées. Les particules de polyuréthane sont de préférence fabriquées par polycondensation des monomères mentionnés précédemment dans un solvant lipophile.

Le pourcentage des particules du premier polymère, de préférence de polyuréthane réticulé, est par exemple compris entre 0,01 et 5% en poids, de préférence entre 0,05 et 2% en poids, entre 0,08 et 1,5% en poids, entre 0,1 et 1,5% en poids, voire entre 0,2 et 1,0% ou entre 0,2 et 0,5% en poids.

Les particules du premier polymère ont une taille moyenne allant de 1 à 40 microns, de préférence de 1 à 25 microns. Elles sont de préférence sous la forme de microsphères.

Les particules du deuxième polymère ont une taille moyenne allant de 1 à 40 microns, de préférence de 1 à 25 microns. Elles sont de préférence sous la forme de microsphères.

Les particules du premier polymère et les particules du deuxième polymère ont de préférence une taille moyenne allant de 1 à 25 microns.

Le polyuréthane est de préférence de nature lipophile et dispersé dans les cires de la composition.

Le deuxième polymère peut se présenter sous la forme de particules constituées de un ou plusieurs polymères polyméthylsilsesquioxane, ou sous la forme de particules composites comprenant un cœur non polyméthylsilsesquioxane (comme un polymère acrylique) et une écorce de polyiméthylsilsesquioxane.

Selon un mode de réalisation, le deuxième polymère est un polyméthylsilsesquioxane réticulé, de préférence hautement réticulé.

Le polyméthylsilsesquioxane est de préférence lipophile, et ne présentent pas de propriétés amphiphiles ou émulsionnantes. Des exemples de résines siliconées amphiphiles polyméthylsilsesquioxane de marque Silderm Emulsifying® BG ou Silderm Emulsifying® CS ne font donc pas partie de la présente invention. On entend par « lipophile » au sens de l'invention, un polymère qui est compatible avec les ingrédients gras ou lipophiles de la composition, tels que les cires. Un polymère lipophile au sens de l'invention n

Le polyméthylsilsesquioxane de nature lipophile est ainsi avantageusement dispersé dans les cires. Il en va de même du premier polymère.

Les particules du deuxième polymère ont avantageusement une capacité d'absorption des liquides tels que les huiles et l'eau très faible de

manière à maintenir leur dureté intrinsèque une fois introduites dans la composition, et à malaxer les autres ingrédients de la composition, notamment les cires, sous l'effet d'une contrainte mécanique. Les valeurs des capacités d'absorption d'huile et d'absorption d'eau des particules du deuxième polymère, ainsi que leur méthode de mesure, peuvent être conformes à la description qui en a été faire précédemment.

Par exemple, les particules du deuxième polymère ont une absorption d'huile mesurée selon la norme ASTM D281-84 inférieure à 1 g/1g, de préférence encore inférieure à 0,60 g/1g.

Le deuxième polymère peut correspondre aux produits commerciaux Tospearl®, qui sont sous la forme de microsphères hydrophobes de taille moyenne allant de 2.0 à 6.0 microns.

Le pourcentage des particules du deuxième polymère, de préférence de polyméthylsilsequioxane, est par exemple compris entre 0,01 et 5% en poids, de préférence entre 0,05 et 2% en poids, entre 0,08 et 1,5%, entre 0,1 et 1,5% en poids, voire entre 0,2 et 1,0% ou entre 0,2 et 0,5% en poids.

La somme de la quantité du premier polymère et de la quantité du deuxième polymère est par exemple comprise entre 0,01 et 5% en poids, de préférence entre 0,05 et 2% en poids, entre 0,08 et 1,5%, entre 0,1 et 1,5% en poids, voire entre 0,2 et 1,0% ou entre 0,2 et 0,5% en poids.

Le ratio massique entre les particules du premier polymère et les particules du deuxième polymère peut être compris entre 1/5 et 5/1, entre 1/2 et 4/1, de préférence va de 1/2 à 3/1.

Les cires sont connues de l'homme du métier et peuvent être choisies parmi la cire d'abeilles, la cire de carnauba, la cire de Carnauba, la cire de candelilla, la cire de Jojoba hydrogénée, l'huile de palme hydrogénée, la cire de son de riz, les cires de cérésine, la cire de Montan, les cires d'ozokérite, les cires microcristallines, les cires de polyéthylène, les cires d'alcool-polyéthylène, les alcools gras solides tels que l'alcool stéarique et l'alcool béhénique, les dérivés de polyalkylene glycol des cires précédemment citées telles que les dérivés polyoxyéthylénés (PEG 6-20) de la cire d'abeille ou de la cire de carnauba, les triglycérides d'acides gras solides et leurs mélanges.

Une cire où l'entend un homme du métier est un composé d'aspect solide à 25°C qui comprend des phases cristallines. Sa température de fusion peut être définie comme le point de fusion correspondant au début de la fusion de ce composé ou la température correspondant au pic endothermique du composé, ces grandeurs pouvant être mesurées par D.S.C. (Differential Scanning Calorimetry) selon la norme ISO 11357-3. La température de fusion d'une cire

est de préférence supérieure ou égale à 30°C.

On pourra utiliser toute cire connue par l'homme du métier de la formulation de mascara.

La cire utilisée pour fabriquer le mascara peut être mélangée aux autres ingrédients de la composition sous la forme d'une microdispersion dans de l'eau, sous forme de poudre ou de pastilles.

Les cires représentent de 18 à 40% en masse, de préférence de 25% à 35% en masse, de préférence encore de 28% à 32% en masse, par rapport à la masse de la composition.

La composition de mascara comprend des pigments représentant de 5 à 15% en poids, par exemple de 8 à 12% en masse de la composition.

Les pigments sont de préférence choisis parmi le dioxyde de titane, les oxydes de zinc, les oxydes de fer (noir, jaune ou rouge), le violet de manganèse, le bleu outremer, l'hydrate de chrome et le bleu ferrique, les poudres métalliques comme la poudre d'aluminium, la poudre de cuivre. Parmi les pigments organiques, on peut citer le noir de carbone, les pigments de type D & C, et les laques. On peut également citer les pigments réfléchissants et les pigments nacrés.

La composition peut contenir au moins un polymère filmogène destiné à augmenter le gainage des cils. La quantité de polymère filmogène peut aller de 0,1 à 12 %, de préférence de 5 à 10 % et mieux de 6 à 8 % en poids, par rapport au poids total de la composition.

Parmi les polymères filmogènes pouvant entrer dans la composition de l'invention figurent le polybutène, l'éthylcellulose et les copolymères de la vinylpyrolidone (VP) tels que la VP/eicosène ou la VP/hexadécène, et leurs mélanges.

Parmi les polymères filmogènes, on pourra encore citer les polymères de cellulose tels que l'hydroxyéthylcellulose, les polymères vinyliques comme les polyvinylpyrrolidones, les gommes arabiques, la gomme de guar, les dérivés du xanthane et leurs mélanges.

Les compositions peuvent contenir des adjuvants habituels dans le domaine cosmétique, tels que les tenioactifs, les gélifiants hydrophiles ou lipophiles, les actifs hydrophiles ou lipophiles, les composés gras sous forme de pâte, les conservateurs, les antioxydants, les ajusteurs de pH et les parfums.

Les tensioactifs utilisés préférentiellement dans la composition selon l'invention sont choisis par exemple parmi les éthers oxyéthylénés et/ou oxypropylénés, les esters d'acide gras et de polyéthylène glycol, les polycondensats polyéthylène glycol/polypropylène glycol, les esters et éthers

d'acides gras et de sucrose ou de sorbitan, les esters d'acides gras et de glycérol ou de sorbitol, tels que le stéarate de glycéryle et les sels d'acides gras comme le stéarate de triéthanolamine. On préférera utiliser le stéarate de triéthanolamine dans le cadre de la présente invention.

La présente demande décrit un ensemble de conditionnement et d'application d'un mascara qui peut ou non contenir une des compositions décrites précédemment. Ledit ensemble comprend:

- un récipient creux destiné à contenir le mascara et comportant une paroi définissant un espace intérieur et une ouverture, au moins une première partie de la paroi étant rigide, et au moins une deuxième partie de la paroi étant plus flexible que la première partie rigide et apte à être mue d'une position expansée à une position forcée,
- des moyens de fermeture destinés à obturer de manière amovible ladite ouverture, et
- une tête applicatrice portée par une tige solidaire des moyens de fermeture, ladite tête applicatrice étant montée de manière à être, en position fermée des moyens de fermeture, apte à être mise en contact avec le mascara à l'intérieur dudit récipient creux.

Le fait d'exercer une pression sur la deuxième partie flexible de la paroi permet à l'utilisatrice de malaxer le mascara, qui est généralement thixotrope, afin de casser sa viscosité de repos et d'en assurer une fluidification efficace, donc un chargement satisfaisant de la brosse en mascara et une meilleure répartition du mascara dans le récipient.

On comprend que les termes « rigide » et « flexible » s'entendent relativement l'un par rapport à l'autre, c'est-à-dire que la première partie rigide est plus rigide que la deuxième partie flexible et que la deuxième partie flexible est plus flexible que la première partie rigide. En outre, une partie rigide est une partie configurée pour rester sensiblement au repos et conserver sa forme lorsqu'un utilisateur exerce une pression manuelle sur cette partie. Par exemple, la déformation de la partie rigide lorsque l'on exerce une pression manuelle dessus peut être invisible à l'œil nu. Une déformation peut être considérée comme invisible à l'œil nu si elle est inférieure à un demi-millimètre. La pression manuelle peut être une pression apte à être exercée, par exemple, par les doigts d'une utilisatrice, notamment par deux doigts opposés.

Une partie flexible est une partie configurée pour se déformer sensiblement, notamment de manière visible à l'œil nu, lorsqu'on exerce une pression manuelle dessus. Ainsi, la position expansée et la position forcée peuvent être distinguées à l'œil nu. De préférence, la position expansée et la

position forcée sont séparées, au moins en un point, d'une distance au moins égale à un demi-millimètre.

Optionnellement, la première partie rigide présente au moins une fenêtre obturée par la deuxième partie flexible. Au niveau de la fenêtre, la paroi est donc flexible. L'utilisatrice sait dont facilement où elle peut exercer une pression pour obtenir l'effet de malaxage précédemment expliqué.

Optionnellement, la première partie rigide délimite la fenêtre axialement et circonférentiellement. On comprend que la fenêtre est entièrement entourée par la première partie rigide, ce qui assure que le récipient maintient sa forme malgré les déformations possibles de la deuxième partie flexible de la paroi.

Optionnellement, la tige est configurée de sorte qu'en position fermée des moyens de fermeture, la tête applicatrice soit au moins en partie en regard, axialement, de la fenêtre. En d'autres termes, dans ladite position fermée, la tête applicatrice est positionnée axialement de façon à être en regard de la fenêtre. Grâce à ces dispositions, l'effet de malaxage peut être obtenu directement au voisinage de la tête applicatrice. De plus, la pression exercée sur la deuxième partie flexible peut permettre à l'utilisatrice de déposer directement du produit sur l'applicateur. De préférence, en position fermée des moyens de fermeture, la tête applicatrice peut également être entièrement en regard, axialement, de la fenêtre.

La première partie rigide est assemblée à la deuxième partie flexible de manière étanche de façon à former une paroi étanche pour le récipient. Selon un exemple, la deuxième partie flexible peut être thermoscellée sur la première partie rigide.

Optionnellement, la paroi comprend un corps tubulaire formant la première partie rigide.

Optionnellement, la paroi comprend une membrane formant la deuxième partie flexible.

Optionnellement, la membrane est assemblée sur le corps tubulaire radialement à l'extérieur du corps tubulaire. Dans certains modes de réalisation, la deuxième partie flexible peut former l'extérieur de la paroi. Ces dispositions facilitent la fabrication du récipient et améliorent son aspect.

Optionnellement, le corps tubulaire comprend une bague et une jupe en retrait, radialement, par rapport à ladite bague. La jupe peut s'étendre axialement à partir de la bague. Selon un exemple, la bague et la jupe peuvent être liées par une portion tronconique et/ou un épaulement. Le cas échéant, la fenêtre peut être prévue dans la jupe. La membrane peut être disposée dans le

prolongement axial de la bague, radialement à l'extérieur de la jupe.

Optionnellement, l'ensemble comprend en outre au moins un col solidaire de ladite paroi.

Optionnellement, l'ensemble comprend en outre au moins un moyen d'essorage solidaire dudit col.

Optionnellement, ladite tête applicatrice est une plume floquée, un feutre, une brosse, ou un pinceau.

Optionnellement, la première partie rigide comprend un matériau choisi dans le groupe formé par les polyéthylènes tels que les polyéthylènes basse densité, les polyéthylènes haute densité, et les mélanges de polyéthylènes de densités différentes; les polyoxyméthylènes; le polypropylène; le poly (chlorure de vinyle); les polyesters; les polyamides; les Nylon ; et les mélanges d'autres plastiques tels que les mélanges de polycarbonate et de polypropylène; et leurs mélanges. De préférence, ledit matériau est du polyoxyméthylène.

Optionnellement, la deuxième partie flexible comprend un matériau élastomère ou thermoplastique, tel qu'un silicone, un silicone fluoré, un caoutchouc butyl, un caoutchouc nitrile, le VITON , un copolymère acétate de vinyl - éthylène (EVA), un copolymère séquencé amide polyéther, un élastomère polyester, un caoutchouc d'éthylène et de propylène, un polyuréthanne, un styrène -éthylène styrène (SES), un styrène - butadiène - styrène (SBS), un styrène isoprène - styrène, un styrène / butylène-éthylène / styrène, un latex, synthétique ou non, et un caoutchouc, et leurs mélanges.

Selon un mode de réalisation, un ensemble de conditionnement et d'application du mascara comprend un récipient creux destiné à contenir le mascara, des moyens de fermeture dudit récipient et une tête applicatrice.

Le récipient creux comporte une paroi définissant un espace intérieur et une ouverture, l'ouverture étant en l'espèce définie par un col. La paroi comprend une première partie relativement rigide et une deuxième partie relativement flexible. La première partie relativement rigide est formée, en l'espèce, par un corps tubulaire. Dans ce mode de réalisation, le corps tubulaire s'étend le long d'une direction axiale et comprend successivement, dans la direction axiale, le col précité, une bague, une jupe et une paroi de fond.

Dans ce mode de réalisation, la bague est sensiblement cylindrique. On rappelle qu'un cylindre est une surface définie par une droite de direction fixe (génératrice) décrivant une courbe fermée de forme quelconque. En l'espèce, la bague peut être un tronc de cylindre à base circulaire.

Des fenêtres sont ménagées dans le corps tubulaire, plus précisément dans la jupe. Dans ce mode de réalisation, deux fenêtres sont ménagées dans la

jupe. Toutefois, un nombre quelconque de fenêtres pourrait être prévu. Dans ce mode de réalisation, les fenêtres sont diamétralement opposées dans une direction radiale, c'est-à-dire dans une direction perpendiculaire à la direction axiale précitée. Par ailleurs, chaque fenêtre peut être de forme courbe ou polygonale avec des angles arrondis ou non. Par exemple, une fenêtre peut être de forme rectangulaire, ovale, oblongue ou elliptique.

Dans ce mode de réalisation, hormis la présence des fenêtres, la jupe est sensiblement cylindrique, par exemple à base circulaire.

La paroi de fond est prévue à une extrémité axiale du corps tubulaire, notamment de la jupe, du côté opposé au col. La paroi de fond bouche le corps tubulaire. La paroi de fond peut s'étendre sensiblement radialement. La paroi de fond peut être plane, au moins du côté donnant vers l'intérieur du récipient, de façon à éviter l'accumulation de mascara dans des zones inaccessibles. Le côté de la paroi de fond donnant sur l'extérieur du récipient peut être plan ou présenter une forme désirée, par exemple pour améliorer la stabilité du récipient.

Par ailleurs, la deuxième partie relativement flexible est formée, en l'espèce, par une membrane, de préférence une membrane élastique. On comprend que la limite d'élasticité de la membrane est telle que la membrane demeure dans son domaine de déformation élastique lorsqu'elle est sollicitée entre la position expansée et la position forcée.

Dans le présent mode de réalisation, la membrane obture les fenêtres prévues dans le corps tubulaire. Ainsi, au niveau des fenêtres, la paroi du récipient est réduite à sa deuxième partie flexible. Plus particulièrement, au niveau des fenêtres, la paroi du récipient est constituée uniquement par la membrane.

Comme indiqué précédemment, la deuxième partie flexible est apte à être mue d'une position expansée à une position forcée. Cette mise en mouvement de la deuxième partie flexible peut être réalisée directement ou indirectement. Selon un exemple, les fenêtres sont prévues plus larges qu'un doigt humain moyen, au moins dans une direction, de façon qu'un doigt puisse exercer une pression en appuyant sur la membrane. Par exemple, les fenêtres peuvent s'étendre au moins sur sensiblement un centimètre en largeur. Selon un autre exemple, la pression peut être exercée sur la deuxième partie flexible de manière indirecte par l'intermédiaire de boutons mobiles, articulés ou non, transmettant, éventuellement avec démultiplication, une force ou un déplacement à la deuxième partie flexible.

Dans ce mode de réalisation, notamment pour faciliter l'assemblage de la membrane au corps tubulaire, la membrane est configurée pour épouser au

moins en partie la forme extérieure du corps tubulaire, et au moins en partie la portion du corps tubulaire qui comprend les fenêtres. Plus particulièrement, ici, la membrane épouse la forme de la jupe et de la paroi de fond, en particulier à l'extérieur de celles-ci. On comprend que la membrane ne comprend pas d'ouverture là où sont prévues les fenêtres, de façon à garantir l'étanchéité de la paroi du récipient.

En l'espèce, la membrane est de forme sensiblement à symétrie de révolution. Dans cet exemple, la membrane comprend un tronçon cylindrique et un disque de fermeture prévu à l'extrémité du tronçon cylindrique. Le tronçon cylindrique est prévu dans le prolongement axial de la bague du corps tubulaire. En outre, l'intérieur du tronçon cylindrique est en contact avec l'extérieur de la jupe. Ainsi, la jupe est en retrait, radialement, par rapport à la bague, d'une distance sensiblement égale à l'épaisseur radiale de la membrane, notamment du tronçon cylindrique. Ces dispositions contribuent à l'effet esthétique de l'ensemble.

Pour améliorer encore l'esthétique de l'ensemble, l'épaisseur de la membrane peut varier, en particulier en regard des fenêtres. Selon un exemple, la deuxième partie flexible peut être amincie en regard des fenêtres. Par ailleurs, la deuxième partie de la paroi peut comprendre des motifs décoratifs, par exemple dessinés, gravés, imprimés, ou réalisés par toute autre méthode connue en soi.

Comme indiqué précédemment, la paroi forme un ensemble étanche en soi. Ainsi, la première partie rigide est assemblée à la deuxième partie flexible de manière étanche. Plus particulièrement, le corps tubulaire et la membrane sont assemblés de manière étanche, par exemple thermoscellés l'un à l'autre.

Les moyens de fermeture destinés à obturer de manière amovible ladite ouverture peuvent être, par exemple, un capuchon à clipser, visser ou engager sur le récipient, notamment sur son col. Le cas échéant, le récipient ou le col peut comprendre des moyens de clipsage, visage ou engagement complémentaires. D'autres moyens de fermeture sont connus de l'homme du métier. Ces moyens de fermeture peuvent comprendre des moyens d'étanchéité, dont des exemples sont connus de l'homme du métier.

Comme indiqué précédemment, la tête applicatrice est portée par une tige solidaire des moyens de fermeture, ladite tête applicatrice étant montée de manière à être, en position fermée des moyens de fermeture, apte à être mise en contact avec le mascara à l'intérieur dudit récipient creux.

La présente demande décrit encore un produit de maquillage des cils comprenant un conditionnement contenant une composition conforme à un des aspects du premier objet de l'invention décrit plus haut.

Plus en détail, la présente invention décrit un produit de mascara comprenant :

- une composition de mascara comprenant au moins une phase liquide, des cires, des particules solides d'un polymère, et des pigments,

la phase liquide représentant de 30 à 60% en poids,

les cires représentant de 15 à 40% en poids, de préférence de 20 à 35% en poids,

les pigments représentant de 5 à 15% en poids,

le polymère étant choisi parmi les polyméthylsilsesquioxanes, les polyméthylméthacrylates réticulés et les polyuréthanes réticulés, et le polymère représentant entre 0,01 et 5% en poids,

les pourcentages étant exprimés par rapport au poids de la composition, et

- un ensemble de conditionnement et d'application présentant une paroi flexible qui peut être déformée en exerçant une pression de la main, de manière à créer un malaxage de ladite composition qu'il contient.

Le conditionnement peut être conforme à la description qui en a été faite précédemment.

Les ingrédients de la composition peuvent également être conformes à la description qui en a été faite précédemment.

Une autre partie de la description de la présente demande porte sur un procédé de maquillage des cils comprenant l'application sur lesdits cils de la composition selon la présente demande.

Ce procédé peut consister en un procédé de maquillage qui comprend au moins les étapes suivantes :

- la fourniture à un utilisateur d'une composition de mascara conditionnée dans un ensemble de conditionnement et d'application comprenant i) un récipient doté d'un moyen d'essorage et d'une partie flexible sur au moins une de ses surfaces internes ou externes et ii) un bouchon duquel est solidaire une brosse d'application qui est plongée dans la composition, ladite composition étant conforme une des descriptions qui en a été faire plus haut.
- la pression par l'utilisateur de ladite partie flexible de manière à malaxer la composition qu'il contient,
- l'ouverture du tube et l'essorage de la brosse recouverte de composition

par retrait du bouchon, et

- le brossage des cils.

La brosse peut être une brosse chargeante connue de l'homme de l'art, comme une brosse de type goupillon constituée de fibres de nylon® maintenues par un fil torsadé, ou une brosse obtenue par moulage thermoplastique de matériaux synthétiques (HDPE, LDPE, dérivés siliconés, POM). La brosse peut être reliée au bouchon par une tige flexible.

Dans les exemples ci-après, tous les pourcentages sont donnés en poids par rapport au poids de la composition, la température est en degrés Celsius, la pression est la pression atmosphérique, sauf indication contraire.

Exemple 1: COMPOSITION DE MASCARA

On a préparé la composition de mascara suivante. Le pourcentage massique des ingrédients et leur ordre d'incorporation dans la composition sont détaillés dans le Tableau 1.

Tableau 1

	INGREDIENTS (INCI)	% EN POIDS
A1	AQUA	Qsp 100
	TRIETHANOLAMINE	2,0
A2	GOMME ARABIQUE	2,0
	HYDROXYETHYLCELLULOSE	0,5
B1	BEESWAX	10,0
	PARAFIN	8,0
	STEARIC ACID	4,0
	GLYCERYL STEARATE	4,0
	CARNAUBA WAX	5,0
	VP/EICOSENE COPOLYMER	2,0
	POLYBUTENE	2,0
B2	BLACK IRON OXIDE	8,0
	HDI/TRIMETHYLOL HEXYLLACTONE CROSSPOLYMER	0,3
	POLYMETHYLSILSESQUIOXANE (Tospearl®)	0,10

• Procédé de préparation

La composition a été préparée selon le procédé suivant.

• Phase grasse B:

Faire fondre B1 dans le bécher principal sous agitation Staro au bain-marie à 85°C. Une fois le mélange fondu, ajouter B2.

• Phase aqueuse A liquide:

Dans un second bécher, peser A1, mettre au bain marie à 85°C sous agitation Staro. Une fois le mélange homogène, disperser A2 sous agitation.

• Réalisation de l'émulsion :

Ajouter la phase aqueuse A dans le bécher principal B à 85°C pendant 5min. Arrêter la chauffe et laisser refroidir la formule en diminuant progressivement l'agitation.

• Propriétés de maquillage

Le produit de l'exemple 1 de l'invention a été évalué par un panel, selon un test en aveugle, pour une durée d'utilisation d'une semaine, une fois par jour, dans des conditions d'applications classiques, et comparé à un produit de référence. Le panel était constitué de 59 femmes âgées de 26 à 45 ans, réparties équitablement, utilisatrices régulières de mascaras du marché sélectif.

Lors de ce test, les propriétés du produit de l'invention ont été comparée à celles d'un produit de référence ne comprenant ni le HDI/TRIMETHYLOL HEXYLLACTONE CROSSPOLYMER, ni le POLYMETHYLSILSESQUIOXANE. La quantité totale des deux composés omis a été reportée sur la quantité d'eau, dans le produit de référence.

Voici la synthèse des appréciations qui ont été recueillies pour le produit de l'invention. Il a été vérifié que la moyenne des valeurs numériques obtenues est significative.

- Application : le mascara recouvre uniformément les cils de la racine à la pointe, se recouvre bien d'application en application, la frange des cils est immédiatement recouverte

- Effet volume : la texture est ultra-volumisante, l'effet volumateur est immédiat et spectaculaire et reste constant du matin au soir

- Résultat global du maquillage : les cils sont bien recouverts, beaucoup plus épais, bien allongés et bien courbés.

- Résultat de maquillage: la charge satisfaisante à la 1ère application, elle est obtenue rapidement, les cils sont souples, doux et confortables.

Pour ce qui est de la comparaison avec le produit de référence, les consommatrices ont trouvé la texture plus enrobante (90% versus 76%), les cils plus allongés (86% versus 68%), la tenue du volume du matin au soir meilleure (84% versus 64%), la texture beaucoup plus volumatrice (72% versus 59%), le résultat volume bien plus spectaculaire (62% versus 39%).

Exemple 2 : COMPOSITION DE MASCARA

On a préparé la composition de mascara suivante. Le pourcentage massique des ingrédients et leur ordre d'incorporation dans la composition sont détaillés dans le Tableau 2.

Tableau 2

	INGREDIENTS (INCI)	% EN POIDS
A1	AQUA	QSP 100
	AMINOMETHYL PROPANEDIOL	1,0
A2	HYDROXYETHYLCELLULOSE	1,0
A3	SYNTRAN PE 5760	12,0
B1	PEG-12 CARNAUBA	9,3
	PEG-8 BEESWAX	8,1
	STEARIC ACID	4,5
	PARAFFIN	3,6
	STEARYL ALCOHOL	2,9
	VP/EICOSENE COPOLYMER	2,0
B2	BLACK IRON OXIDE	8,0
	POLYMETHYLSILSESQUIOXANE (Tospearl®)	0,1
	HDI/TRIMETHYLOL HEXYLLACTONE CROSSPOLYMER	0,1

La composition a été préparée selon le procédé suivant.

• Phase grasse B :

Faire fondre B1 dans le bécher principal sous agitation Staro au bain-marie à 85°C. Une fois le mélange fondu, ajouter B2.

• Phase aqueuse A liquide:

Dans un second bécher, peser A1, mettre au bain marie à 85°C sous agitation Staro. Une fois le mélange homogène, disperser A2 sous agitation. Quand mélange homogène, ajouter A3 à 85°C avant émulsion.

• Réalisation de l'émulsion :

Ajouter la phase aqueuse A dans le bécher principal B à 85°C pendant 5min. Arrêter la chauffe et laisser refroidir la formule en diminuant progressivement l'agitation.

Exemple 3 : COMPOSITION DE MASCARA

On a préparé la composition de mascara suivante. Le pourcentage massique des ingrédients et leur ordre d'incorporation dans la composition sont détaillés dans le Tableau 3.

Tableau 3

	INGREDIENTS (INCI)	% EN POIDS
A1	POLYBUTENE	2,0
	CARNAUBA WAX	7,5
	BEESWAX	13,5
	PARAFFIN	5,0
	VP/ EICOSENE COPOLYMER	2,0
A2	BLACK IRON OXIDE	8,0
	POLYMETHYLSILSESQUIOXANE (Tospearl®)	0,2
	HDI/TRIMETHYLOL HEXYLLACTONE CROSSPOLYMER	0,2
B	ISODODECANE	QSP 100
	DISTEARDIMONIUM HECTORITE	5,1
	PROPYLENE CARBONATE	1,5
C	WATER	5,0
	PHENOXYETHANOL	0,3

La composition a été préparée selon le procédé suivant :

- Préparation de la phase A :

Dans un bécher principal, faire fondre A1 au bain-marie (90°C). Quand la phase est fondue et homogène, A2. Homogénéiser rapidement à chaud et replonger le bécher dans le bain-marie (90°C) jusqu'à obtention d'une pâte homogène.

- Préparation de la Phase B liquide :

Dans un bécher secondaire, disperser, à froid et sous Rayneri, l'hectorite modifiée dans l'Isododécane. Quand la phase est homogène, ajouter le Propylène Carbonate. Disperser sous Rayneri jusqu'à obtention d'un gel homogène.

- Ajouter la Phase B dans la phase A et homogénéiser rapidement à la spatule. Passer 3 fois le mélange au tricylindre jusqu'à obtenir une formule lisse et brillante.
- Ajouter la phase C. Homogénéiser sous Rayneri jusqu'à obtenir une formule lisse et brillante.

REVENDICATIONS

1. Composition de mascara comprenant de 30 à 60% en poids d'au moins une phase liquide, de 15 à 40% en poids de cires, et de 5 à 20% en poids pigments, et comprenant en outre des microsphères d'un premier polymère de polyuréthane réticulé et des microsphères d'un deuxième polymère de polyméthylsilsesquioxane réticulé, la somme de la quantité du premier polymère et de la quantité du deuxième polymère étant comprise entre 0,01 et 5% en poids, les pourcentages étant exprimés par rapport au poids de la composition.

2. Composition de mascara selon les revendications 1 ou 2, caractérisée en ce que les microsphères ont une taille moyenne allant de 1 à 40 microns.

3. Composition de mascara selon l'une des revendications précédentes, caractérisée en ce que la somme de la quantité du premier polymère et de la quantité du deuxième polymère est comprise entre 0,1 et 2%.

4. Composition de mascara selon l'une des revendications précédentes, caractérisée en ce que le premier polymère est un polyuréthane réticulé obtenu par copolymérisation d'un diisocyanate aliphatique linéaire, d'un triol aliphatique et d'une lactone.

5. Composition de mascara selon l'une des revendications précédentes, caractérisée en ce que la phase liquide est l'eau ou l'isododécane.

6. Composition de mascara selon l'une des revendications précédentes, caractérisée en ce que le premier polymère et le deuxième polymère sont dispersés dans les cires.

7. Produit de mascara comprenant :

- une composition de mascara selon l'une des revendications 1 à 6, et
- un ensemble de conditionnement et d'application présentant une paroi flexible qui peut être déformée en exerçant une pression de la main, de manière à créer un malaxage de ladite composition qu'il contient.

8. Procédé de maquillage qui comprend au moins les étapes suivantes:

- la fourniture à un utilisateur d'une composition de mascara conditionnée dans un ensemble de conditionnement et d'application comprenant i) un récipient doté d'un moyen d'essorage et d'une partie flexible sur au moins une de ses surfaces internes ou externes et ii) un bouchon duquel est solidaire une brosse d'application qui est plongée dans la composition, ladite composition étant conforme à l'une des revendications 1 à 6.

- la pression par l'utilisateur de ladite partie flexible de manière à malaxer la composition qu'il contient,

- l'ouverture du tube et l'essorage de la brosse recouverte de composition par retrait du bouchon, et

- le brossage des cils.

INTERNATIONAL SEARCH REPORT

International application No
PCT/FR2017/053851

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61Q1/10 A61K8/87 A61K8/891
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61Q A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/067960 A1 (RUSS JULIO G [US] ET AL) 30 March 2006 (2006-03-30) paragraph [0002] example 7 paragraphs [0005] - [0006] -----	1-8
X	US 2006/067904 A1 (RUSS JULIO G [US] ET AL) 30 March 2006 (2006-03-30) page 1; example 2 paragraph [0034] -----	1,4,5

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 March 2018	26/03/2018

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Durand-Oral, Ilknur

2

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Emulsifying Bg: "Product Name/Identifier SilDerm Emulsifying BG Product Code 30314 Recommended Use Topical Cosmetic Use Restrictions on Use None Supplier/Manufacturing Site Active Concepts Safety Data Sheet", , 23 January 2015 (2015-01-23), XP055396498, Retrieved from the Internet: URL:http://activeconceptsllc.com/wp-content/uploads/2015/12/30314-SilDerm®-Emulsifying-BG-GHS-SDS-v4.pdf [retrieved on 2017-08-07] <section 3: Composition/information of ingredients; page 2 -----	1

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/FR2017/053851

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2006067960 A1	30-03-2006	NONE	
US 2006067904 A1	30-03-2006	NONE	

RAPPORT DE RECHERCHE INTERNATIONALE

Demande internationale n°
PCT/FR2017/053851

A. CLASSEMENT DE L'OBJET DE LA DEMANDE
INV. A61Q1/10 A61K8/87 A61K8/891
ADD.

Selon la classification internationale des brevets (CIB) ou à la fois selon la classification nationale et la CIB

B. DOMAINES SUR LESQUELS LA RECHERCHE A PORTE

Documentation minimale consultée (système de classification suivi des symboles de classement)
A61Q A61K

Documentation consultée autre que la documentation minimale dans la mesure où ces documents relèvent des domaines sur lesquels a porté la recherche

Base de données électronique consultée au cours de la recherche internationale (nom de la base de données, et si cela est réalisable, termes de recherche utilisés)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie*	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
X	US 2006/067960 A1 (RUSS JULIO G [US] ET AL) 30 mars 2006 (2006-03-30) alinéa [0002] exemple 7 alinéas [0005] - [0006] -----	1-8
X	US 2006/067904 A1 (RUSS JULIO G [US] ET AL) 30 mars 2006 (2006-03-30) page 1; exemple 2 alinéa [0034] -----	1,4,5

-/--

[X] Voir la suite du cadre C pour la fin de la liste des documents

[X] Les documents de familles de brevets sont indiqués en annexe

* Catégories spéciales de documents cités:

"A" document définissant l'état général de la technique, non considéré comme particulièrement pertinent

"E" document antérieur, mais publié à la date de dépôt international ou après cette date

"L" document pouvant jeter un doute sur une revendication de priorité ou cité pour déterminer la date de publication d'une autre citation ou pour une raison spéciale (telle qu'indiquée)

"O" document se référant à une divulgation orale, à un usage, à une exposition ou tous autres moyens

"P" document publié avant la date de dépôt international, mais postérieurement à la date de priorité revendiquée

"T" document ultérieur publié après la date de dépôt international ou la date de priorité et n'appartenant pas à l'état de la technique pertinent, mais cité pour comprendre le principe ou la théorie constituant la base de l'invention

"X" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme nouvelle ou comme impliquant une activité inventive par rapport au document considéré isolément

"Y" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme impliquant une activité inventive lorsque le document est associé à un ou plusieurs autres documents de même nature, cette combinaison étant évidente pour une personne du métier

"&" document qui fait partie de la même famille de brevets

Date à laquelle la recherche internationale a été effectivement achevée	Date d'expédition du présent rapport de recherche internationale
14 mars 2018	26/03/2018

Nom et adresse postale de l'administration chargée de la recherche internationale	Fonctionnaire autorisé
Office Européen des Brevets, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Durand-Oral, Ilknur

2

Formulaire PCT/ISA/210 (deuxième feuille) (avril 2005)

C(suite). DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie*	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
A	Emulsifying Bg: "Product Name/Identifier SilDerm Emulsifying BG Product Code 30314 Recommended Use Topical Cosmetic Use Restrictions on Use None Supplier/Manufacturing Site Active Concepts Safety Data Sheet", , 23 janvier 2015 (2015-01-23), XP055396498, Extrait de l'Internet: URL:http://activeconceptsllc.com/wp-content/uploads/2015/12/30314-SilDerm®-Emulsifying-BG-GHS-SDS-v4.pdf [extrait le 2017-08-07] <section 3: Composition/information of ingredients; page 2 -----	1

2

RAPPORT DE RECHERCHE INTERNATIONALE

Renseignements relatifs aux membres de familles de brevets

Demande internationale n°
PCT/FR2017/053851

Document brevet cité au rapport de recherche	Date de publication	Membre(s) de la famille de brevet(s)	Date de publication
US 2006067960 A1	30-03-2006	AUCUN	
US 2006067904 A1	30-03-2006	AUCUN	

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 380 557 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
26.10.2011 Bulletin 2011/43

(21) Application number: **10731199.5**

(22) Date of filing: **08.01.2010**

(51) Int Cl.:
A61K 8/87 *(2006.01)* ***A61Q 1/00*** *(2006.01)*
A61Q 1/02 *(2006.01)* ***A61Q 1/12*** *(2006.01)*
A61Q 5/00 *(2006.01)* ***A61Q 15/00*** *(2006.01)*
A61Q 17/04 *(2006.01)* ***A61Q 19/00*** *(2006.01)*
A61Q 19/10 *(2006.01)* ***C11D 3/12*** *(2006.01)*
C11D 3/37 *(2006.01)* ***C11D 17/06*** *(2006.01)*
C11D 17/08 *(2006.01)*

(86) International application number:
PCT/JP2010/050124

(87) International publication number:
WO 2010/082530 (22.07.2010 Gazette 2010/29)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR

(30) Priority: **15.01.2009 JP 2009006875**

(71) Applicants:
- **Konishi Co., Ltd.**
  Chuo-ku
  Osaka-shi
  Osaka 541-0045 (JP)
- **Shiseido Co., Ltd.**
  Tokyo 104-8010 (JP)

(72) Inventors:
- **ORIGUCHI Toshiki**
  Osaka-shi
  Osaka 538-0053 (JP)
- **NAKAYAMA Yoshitaka**
  Osaka-shi
  Osaka 538-0053 (JP)
- **KURAHASHI Takuma**
  Yokohama-shi
  Kanagawa 224-8558 (JP)
- **YAGI Katsuhiko**
  Yokohama-shi
  Kanagawa 224-8558 (JP)
- **MURAKAMI Yuki**
  Yokohama-shi
  Kanagawa 224-8558 (JP)

(74) Representative: **HOFFMANN EITLE**
Patent- und Rechtsanwälte
Arabellastraße 4
81925 München (DE)

(54) COSMETIC

(57) It is provided cosmetics to prevent to come off and keep long. The cosmetic comprises specific polyurethane particles with a cosmetic base. The specific polyurethane particle consists of a body of the polyurethane particle and hydrophilic fine silica powders existing on the body. The body is obtained by three-dimensionally polymerizing an isocyanate-terminated urethane prepolymer with trifunctional or more functional amines. The isocyanate-terminated urethane prepolymer is obtained by reacting polyisocyanates and polyols including a poly(tetramethylene ether)glycol. The polyurethane particles are obtained by spray-drying a mixed aqueous dispersion in which the hydrophilic fine silica powders and the polyurethane spheres are dispersed in a water.

EP 2 380 557 A1

Description

Technical Field

[0001] The present invention relates to contain polyurethane particles, especially, which superiorly absorb sebums.

Background Art

[0002] It is used cosmetics consisting of polyurethane particles so as to smooth a skin or hide small wrinkles and pores. For example, the patent reference 1 discloses polyurethane particles which consist of a hexamethylene diisocyanate/trimethylol hexyllactone crosspolymer and silica.

[0003]

Patent reference 1: JP2005-3114300 (the paragraph 0023 is referred.)

Summary of Invention

Technical Problem

[0004] The inventors have discovered that a specific polyurethane particle superiorly absorbs sebums (tokugan 2008-310341). Containing the polyurethane particles as one component of cosmetics, the inventors have assumed that the cosmetics give a smooth skin or hide small wrinkles and pores and keep long for superiorly absorbing sebums. So, experimenting with the cosmetics containing the polyurethane particles, the inventors have discovered that the cosmetics keep long. Therefore, the invention is a use invention for the cosmetics on the tokugan 2008-310341.

Solution to Problem

[0005] The inventors is relates to the cosmetics containing polyurethane particles. Each surface of the bodies of the polyurethane particles is covered with hydrophilic fine silica powders. The body of the polyurethane particle is obtained by three-dimensionally polymerizing an isocyanate-terminated urethane prepolymer with trifunctional or more functional amines. And the isocyanate-terminated urethane prepolymer is obtained by reacting polyisocyanates and polyols including a poly(tetramethylene ether)glycol.

[0006] The polyurethane particle means one particle in the polyurethane particles. The polyurethane particle consists of the body of the polyurethane particle and the hydrophilic fine silica powders on the body.

[0007] The invention relates to the cosmetics containing polyurethane particles. The polyurethane particle is formed by covering the surface of the body with the hydrophilic fine silica powders.

[0008] The hydrophilic fine silica powder consists of mainly SiO_2, and has not substantially hydrophobic groups on the surface of it. The hydrophilic fine silica powders are well known, and sold by Nippon Aerosil Co. as AEROSIL 200, 200V, 200CF, 200FAD, 300, 300CF, 380, 50, 90G, 130, OX50, MOX80, MOX170, COK84 and etc.. Such hydrophilic fine silica powders are used in the invention. A particle size of the hydrophilic fine silica powder is finer than the particle size of the obtained polyurethane particle to cover the body of the polyurethane particle with the hydrophilic fine silica powders. Concretely, an average particle size of the obtained polyurethane particles is 1-50 μm, and an average particle size of the hydrophilic fine silica powders is 5-40 nm. Therefore, it is preferable that the particle size of the polyurethane particle is 20 or more times larger than the particle size of the hydrophilic fine silica powder. The average particle size of the hydrophilic fine silica powders is decided in nominal value.

[0009] It is used as the polyisocyanates for producing a polyurethane to be well known compounds which have two or more isocyanate groups in a molecule. It is preferably used alicyclic polyisocyanates or aliphatic polyisocyanates. Concretely, it is used an isophorone diisocyanate, a 1,6-hexamethylene diisocyanate and a hydrated MDI.

[0010] It is used as the polyols for producing a polyurethane to be a poly(tetramethylene ether)glycol. The other polyols may be mixed with the poly(tetramethylene ether)glycol. It may be used as the other polyols to be well known polyols for producing a polyurethane. A number average molecular weight of poly(tetramethylene ether)glycol is not limited, but preferably 650-3000.

[0011] Trifunctional or more functional amines for producing a polyurethane are used to three-dimensionally polymerize a urethane prepolymer obtained by reacting the polyols and the polyisocyanates. It is used a diethylenetriamine, triethylenetetramine, tetraethylenepentamine and 3,3'-diaminodipropylamine as the trifunctional or more functional amines.

[0012] The polyurethane particle of the invention is obtained by the following method with the above compound.

[0013] The method comprises; a process to obtain an isocyanate-terminated urethane prepolymer by reacting polyisocyanates and polyols including a poly(tetramethylene ether)glycol, a process to obtain an oil-in-water emulsion by adding

and mixing the isocyanate-terminated urethane prepolymer to an aqueous solution in which a dispersant dissolves, a process to obtain polyurethane spheres in the oil-in-water emulsion by that the isocyanate-terminated urethane prepolymer in oil droplets is three-dimensionally polymerized by adding the trifunctional or more functional amines in the oil-in-water emulsion, a process to obtain an aqueous polyurethane dispersion in which the polyurethane spheres disperse by removing the dispersant from the oil-in-water emulsion. a process to obtain a mixed aqueous dispersion by mixing the aqueous polyurethane dispersion with an aqueous silica dispersion in which hydrophilic fine silica powders disperse in a water, and a process to spray-dry the mixed aqueous dispersion in a high temperature atmosphere with a spray-dryer. Thereby, the water is vaporized in the mixed aqueous dispersion, the polyurethane spheres are converted to bodies of the polyurethane particles, and each surface of the bodies of the polyurethane particles is covered with the hydrophilic fine silica powders. The polyurethane particles are obtained by the above method.

[0014] The processes of the method are more described as the followings. The isocyanate-terminated urethane prepolymer is obtained by reacting conventionally the polyisocyanates and the polyols including a poly(tetramethylene ether)glycol. Then, an amount by mole of NCO group of the polyisocyanates exceeds an amount by mole of OH group of the polyols to terminate at the NCO group in the urethane prepolymer. The amount by mole of NCO group is conventionally 1.5-3.0 times to the amount by mole of OH group. Generally, the polyisocyanates and polyols are dissolved in an organic solvent such as ethyl acetate or methyl ethyl ketone, and react with a tin catalyst such as dibutyl tin dilaurate or an amine catalyst such as 1,8-diazabicyclo[5.4.0]undec-7-ene.

[0015] Conventionally, it is used only the poly(tetramethylene ether)glycol as the polyols, but may be mixed with the other polyols. It may be used a polyalcohol, polyetherpolyol, polyesterpolyol, polycarbonatepolyol, polyolefinpolyol, polyacrylicpolyol or castor oil as the other polyols. Mixing with the other polyols, it is preferable that the poly(tetramethylene ether)glycol occupies 50 or more mass% in the polyols. Less than 50 mass%, the polyurethane particle is insufficient to absorb sebums because the paly(tetramethylene ether)glycol is a component to absorb sebums. Using only the poly (tetramethylene ether)glycol, the body of the polyurethane particle tends to be soft. Mixing with the polycarbonatepolyol as the other polyols, the body of the polyurethane particle tends to be gradually hard with increase of the content.

[0016] The content of the isocyanate group (NCO group) of the isocyanate-terminated urethane prepolymer is 2.0-10 mass%, and preferably 2.5-3.5 mass%. More than 10 mass% in the content, the polyurethane particle is insufficient to absorb sebums because a content of urethane linkage is much. Less than 2.0 mass% in the content, it may be difficult to treat the isocyanate-terminated urethane prepolymer because it becomes high molecular weight and high viscosity.

[0017] The obtained isocyanate-terminated urethane prepolymer is added and mixed to an aqueous solution in which a dispersant is dissolved to obtain an oil-in-water emulsion. Concretely, the oil-in-water emulsion is obtained by the following process.

[0018] It is prepared the aqueous solution in which the dispersant is dissolved. The dispersant is to emulsify the isocyanate-terminated urethane prepolymer in a water. For example, as the dispersant, it is used general surfactants such as nonionic surfactant or usual polymeric dispersants such as polyvinyl alcohol. The dispersant is dissolved in the water to obtain the aqueous solution. Dissolving the dispersant, it is preferable to heat the water so as to dissolve easily. After the dispersant is entirely dissolved in the water, it is preferable to cool the aqueous solution at room temperature. A temperature of the heated water is decided at a solubility of the dispersant. For example, using the polyvinyl alcohol having a saponification degree of about 86.5-89.0 mol%, the temperature of the heated water is about 90°C. A concentration of the dispersant is decided so as to emulsify the isocyanate-terminated urethane prepolymer in the water. It is conventionally about 3-20 mass%.

[0019] The isocyanate-terminated urethane prepolymer is added and mixed in the aqueous solution cooled at room temperature. An addition mass of the isocyanate-terminated urethane prepolymer is conventionally about 3-20 parts by mass to 100 parts by mass of the aqueous solution. The machine and degree for mixing are decided so as to emulsify the isocyanate-terminated urethane prepolymer in the water. It is used a homomixer, a homogenizer, a high-pressure homogenizer or an ultrasonic homogenizer as the machine for mixing. Using the homomixer, the degree for mixing is about 5 minutes at about 8000 rpm. Adding and mixing are conventionally executed at room temperature, but may be executed at a little heating temperature so as to mix easily.

[0020] A trifunctional or more functional amine is added in the oil-in-water emulsion. The trifunctional or more functional amine is used to obtain polyurethane having network structure by three-dimensionally polymerizing the isocyanate-terminated urethane prepolymer as described in paragraph 0011. It is used various poly-functional amine as the trifunctional or more functional amine. The poly-functional amine is added in itself or in solution dissolving it in a solvent such as water. An addition mass of the poly-functional amine is preferably chemical equivalent to the isocyanate group of the isocyanate-terminated urethane prepolymer in the oil-in-water emulsion. That is, the poly-functional amine is preferably added such as an amino group of the poly-functional amine is Chemical equivalent to the isocyanate group of the isocyanate-terminated urethane prepolymer. Thereby, the isocyanate group reacts with the amino group to three-dimensionally polymerize. The addition mass of the poly-functional amine may be from 0.8 to less than the chemical equivalent to restraint three-dimensional polymerization. Furthermore, the addition mass of the poly-functional amine may be to 1.2 from more than the chemical equivalent to be densely three-dimensional polymerization.

[0021] Not only the poly-functional amine such as the trifunctional or more functional amine but also a difunctional amine or polyalcohol may be added with the poly-functional amine to react with isocyanate group. Using the difunctional amine or polyalcohol, it may be controlled to three-dimensionally polymerize the isocyanate-terminated urethane prepolymer.

[0022] Three-dimensionally polymerizing the isocyanate-terminated urethane prepolymer in oil droplets with the addition of the poly-functional amine, the oil-in-water emulsion is conventionally heated to quicken the reaction of the polymerization. The temperature of the oil-in-water emulsion is decided on the reactivity of the poly-functional amine. For example, using the 3,3'-diaminodipropylamine as the poly-functional amine, the oil-in-water emulsion is heated at about 80 ˚C, then the three-dimensional polymerization has finished for about 20 hours.

[0023] After the three-dimensional polymerization is finished, the oil droplets in the oil-in-water emulsion are converted to the polyurethane spheres. That is, the polyurethane spheres are dispersed to be in a dispersion. The dispersant in the dispersion is removed. The method of removing the dispersant is the following. The polyurethane spheres are collected with filtering or centrifugal separating the dispersion. The collected polyurethane spheres are dispersed in a water again. The polyurethane spheres are again collected with filtering or centrifugal separating the second dispersion. By repeating the above process, it is obtained an aqueous polyurethane dispersion in which the polyurethane spheres disperse as dispersion medium of water.

[0024] It is prepared the aqueous silica dispersion in which the hydrophilic fine silica powders disperse into a water. It is easily prepared to add and mix the hydrophilic fine silica powders in the water. It is decided the condition of adding and mixing or the content of the powders so as to disperse the powders informally in the water, not cohering. For example, using the trade mark 「Aerosil® 200」 which are the hydrophilic fine silica powders and dispersing them in a content of 5 mass%, the aqueous silica dispersion is easily obtained by mixing with a water for 10 minutes at 10000 rpm by a homomixer.

[0025] Mixing the above aqueous silica dispersion with the above aqueous polyurethane dispersion, the mixed aqueous dispersion is obtained. The mixing ratio of the both is decided on the ratio of the solid content of the both. Mixing the both, it is preferable to add a water so as to prevent that the hydrophilic fine silica powders and polyurethane spheres cohere. The addition mass of the water is optionally decided, conventionally being about equal to the mass of the aqueous polyurethane dispersion. Adding the water, it is preferable to mix so as to prevent coherence.

[0026] The mixed aqueous dispersion is dried with the spray-dryer having nozzles or disks. Using the spray-dryer having nozzles, the mixed aqueous dispersion is spray-dried through each nozzle in the high temperature atmosphere to dry. Using the spray-dryer having disks, the mixed aqueous dispersion is dropped on each rotating disk and spray-dried on the centrifugal force of each disk in the high temperature atmosphere to dry. The spray-drying in the invention is characterized by spraying in remaining the form of each polyurethane sphere in the mixed aqueous dispersion, that is, not atomizing the polyurethane sphere. Because the polyurethane sphere is three-dimensionally polymerized in the mixed aqueous dispersion. Spraying the mixed aqueous dispersion, it is sprayed the polyurethane spheres and the hydrophilic fine silica powders with the water. Drying the water, the hydrophilic fine silica powders adhere onto each surface of the polyurethane spheres. The polyurethane spheres being softer, the hydrophilic fine silica powders adhere on the surface in implanting.

[0027] The condition of spraying is not strict because the polyurethane spheres are not atomized at spraying. It is not strict the condition of the pressure, centrifugal force and aperture of the nozzle for atomization. Therefore, the spray-dryer having nozzles or disks may be used. The condition of the high temperature atmosphere to dry after spraying is decided so as to vapor the spraying water. The condition is conventional, for example, the inlet of a hot air may be the temperature of about 140˚C and the temperature of about 70˚C into the dryer. Spraying and drying the polyurethane spheres, each body of the polyurethane particles is formed with one of them or joining two or more. The polyurethane sphere being softer or more stick surface, the body of the polyurethane particles tends to be formed with two or more of the polyurethane spheres. The polyurethane spheres being harder, the body of the polyurethane particles tends to be formed with one of the polyurethane spheres.

[0028] Spray-drying the mixed aqueous dispersion, the polyurethane sphere is converted to the body of the polyurethane particle, covering the surface of the body with the hydrophilic fine silica powders. The hydrophilic fine silica powders adhere on the body. Being softer the polyurethane sphere or the body of the polyurethane particle, the hydrophilic fine silica powders adhere on the body in implanting. An average particle size of the polyurethane particles is decided on an average particle size of the polyurethane sphere in the mixed aqueous dispersion, a softness or stickiness of the body or the condition of spray-drying. The average particle size of the polyurethane particles is conventionally about 1-50 μm. The average particle size is measured with the following method. 100 polyurethane particles are picked up, and each particle size is measured with an optical microscope or an electron microscope. The average particle size is calculated on a number average. The picked up polyurethane particle cohering with two or more, the cohered particle is separated one by one and measured.

[0029] The polyurethane particles may be compounded with a cosmetic base as it is or after applying a hydrophobic treatment such as siliconization or fluoridization to them. The polyurethane particle superiorly absorbs the sebums and

oleic acids, but partly absorbs other oils. Therefore, it may be permitted to absorb and hold various oils, medicinal properties, ultraviolet absorbers, moisturizing agents, emollient agents, perfumed oils, germicidal agents or antioxidants in the polyurethane particles so as not to lower an absorbent capacity of sebums. The containing mass of the polyurethane particles is optionally decided, conventionally 0.1-30 parts by mass, preferably 1-20 parts by mass, more preferably 3-15 parts by mass to the amount of the cosmetic.

[0030] It is used a general base as the cosmetic base in the invention. It is preferably used the cosmetic base which is difficult to absorb oils because the polyurethane particles partly absorb oils. The form of the cosmetic is optionally decided, generally is selected from the group consisting of solid, powder, gel and liquid. A solid cosmetic has somewhat volume by molding the cosmetic base. The solid cosmetic is used as a face-wash or foundation. A powder cosmetic is observed as powders, and the containing mass of the powders is 80 or more parts by mass to the amount of the powder cosmetic. The powder cosmetic is used as a foundation, face powder, eye shadow, rouge, body powder, deodorant powder or fragrance powder. A gel cosmetic is used as a hairdressing, foundation materials or hand cream. A liquid cosmetic is observed as an aqueous solution or emulsion. The liquid cosmetic is used as a toner, milky lotion, foundation materials or hairdressing. It may be used as a sheet-like cosmetic which contains the solid cosmetic or the liquid cosmetic in a sheet such as non-woven fabric. Wiping a skin with the sheet-like cosmetic, the solid cosmetic or the liquid cosmetic is applied to the skin.

[0031] The cosmetics may be used with the polyurethane particles absorbing a well known active ingredient. For example, the cosmetics may be used as a make-up preparations, skin care preparations, pimple care preparations, antiperspirants, ultraviolet protective preparations, hair cosmetics, face packs or fragrance cosmetics. The cosmetics keep long because the active ingredient is gradually released from the polyurethane particles.

Advantageou Effects of invention

[0032] The cosmetics contain the polyurethane particles which superiorly absorb the sebums. Applying the cosmetics to a skin or hair, the secreted sebums on the skin or hair are superiorly absorbed. Therefore, a makeup is prevented to come off because the sebums are difficult to pile up between the cosmetics and the skin or hair. That is, applying the cosmetics of the invention, the makeup is prevented to come off and keep long.

Examples

[0033] The invention is described on the basis of the following examples, but the invention is not limited to the example. The invention must be constructed on the discovery that the specific polyurethane particle superiorly absorbs the sebums.

Producing example 1 for polyurethane particles 1

[Preparing an isocyanate-terminated urethane prepolymer]

[0034] 20 parts by mass of ethyl acetate and 300 parts by mass of poly(tetramethylene ether)glycol having a number average molecular weight of 1000 were charged in a four-necked flask fitted with a stirrer, nitrogen inlet, thermometer and condenser. 104.6 parts by mass of isophorone diisocyanate and 0.04 parts by mass of dibutyl tin dilaurate were added and reacted under a nitrogen stream at 75-80 ˚C for 5 hours to obtain the isocyanate-terminated urethane prepolymer containing 3.6% of isocyanate group.

[Preparing an oil-in-water emulsion]

[0035] 900 parts by mass of deionized water and 100 parts by mass of polyvinyl alcohol having a saponification degree of 86.5-89.0 mol% as a dispersant which was sold as a trade name of PVA-205 by Kuraray Co., Ltd. were charged and heated at 90˚C to obtain an aqueous solution of polyvinyl alcohol. 100 parts by mass of the above prepared isocyanate-terminated urethane prepolymer were added in the aqueous solution of polyvinyl alcohol, and they were mixed at 8000 rpm for 5 minutes with a homomixer to obtain the oil-in-water emulsion in which oils are consisted of the isocyanate-terminated urethane prepolymer.

[Preparing an aqueous polyurethane dispersion]

[0036] 35.7 parts by mass of 10% aqueous solution of 3,3'-diaminodipropylamine were added in the above oil-in-water emulsion. They were heated at 80 ˚C with stirring, remained at the temperature and reacted for 20 hours. The isocyanate-terminated urethane prepolymer reacted with the 3,3'-diaminodipropylamine to be three-dimensionally polymerized, and polyurethane spheres were formed. The polyurethane spheres were sunk and collected with a centrifu-

gation. The polyurethane spheres were again dispersed in a water and were sunk and collected with a centrifugation. Sixth dispersing and collecting were carried out to remove the polyvinyl alcohol as the dispersant from the water. It is obtained the aqueous polyurethane dispersion comprising the polyurethane spheres of 40% by mass.

[Preparing an aqueous silica dispersion]

[0037] 95 parts by mass of deionized water were charged and stirred at 10000 rpm in a homomixer. 5 parts by mass of hydrophilic fine silica powders having an average particle size of 20 nm which was sold as a trade name of AEROSIL 200 by Nippon Aerosil Co., Ltd. were added in the deionized water and mixed for 10 minutes to obtain the aqueous silica dispersion.

[Preparing a mixed aqueous dispersion]

[0038] 100 parts by mass of the above aqueous polyurethane dispersion, 80 parts by mass of the above aqueous silica dispersion and 110 parts by mass of deionized water were mixed to obtain the mixed aqueous dispersion.

[Producing polyurethane particles 1]

[0039] Spray-drying the above mixed aqueous dispersion with a spray-dryer which was sold as a trade name of L-81 by Ohkawara Kakohki Co., Ltd., the polyurethane particles were obtained. Each condition of the spray-drying was as the following. A pressure of spraying was 0.3MPa, a temperature of an inlet of a hot air was 140 °C and a temperature into a dryer was 70 °C. Vaporizing the water in the mixed aqueous dispersion by the spray-drying, the polyurethane spheres were converted to bodies of the polyurethane particles and the hydrophilic fine silica powders were adhered to each surface of the bodies of the polyurethane particles in implanted. Therefore, each body of the polyurethane particles was covered with the hydrophilic fine silica powders to be the polyurethane particle. The polyurethane particles were not cohered and smooth because of separating from each one. An average particle size of the polyurethane particles is about 12μm.

Producing example 2 for polyurethane particles 2

[Preparing an isocyanate-terminated urethane prepolymer]

[0040] The isocyanate-terminated urethane prepolymer containing 2.5% of isocyanate group was obtained with the same method of the Producing example 1 except that a poly(tetramethylene ether)glycol having a number average molecular weight of 3000 was used in place of the number average molecular weight of 1000 and 45.0 parts by mass of isophorone diisocyanate were used in place of the 104.6 parts by mass.

[Preparing an oil-in-water emulsion]

[0041] The oil-in-water emulsion was obtained with the same method of the Producing example 1 except that the above isocyanate-terminated urethane prepolymer was used.

[Preparing an aqueous polyurethane dispersion]

[0042] The aqueous polyurethane dispersion was obtained with the same method of the Producing example 1 except that the above oil-in-water emulsion was used and 24.5 parts by mass of 10% aqueous solution of 3,3'-diaminodipropylamine were used in place of the 35.7 parts by mass.

[Preparing an aqueous silica dispersion]

[0043] The aqueous silica dispersion was obtained with the same method of the Producing example 1.

[Preparing a mixed aqueous dispersion]

[0044] The mixed aqueous dispersion was obtained with the same method of the Producing example 1 except that the above aqueous polyurethane dispersion was used.

[Producing polyurethane particles 2]

[0045] The polyurethane particles were obtained with the same method of the Producing example 1 except that the above mixed aqueous dispersion was used. The properties of the polyurethane particles were the same as them of the polyurethane particles 1. An average particle size of the polyurethane particles is about 15 μm.

Example 1

[0046] It was obtained a powder cosmetic consisting of the following composition. The powder cosmetic was used as a foundation.

the polyurethane particles 1	5 masts%
mica treated by silicon	20 mass%
mica	5mass%
titanium oxide coated with polymethylhydrosiloxane	10 mass%
fine particle of titanium oxide	5 mass%
iron oxide treated by alkyl	3.44 mass%
silicone elastomer as trade name KSP-100 by Shin-Etsu Chemical Co., Ltd.	8 mass%
activated zinc oxide	8.5 mass%
mica with barium sulfate and aluminum oxide	6 mass%
chlorphenesin	0.2 mass%
olefin oligomer	1 mass%
poly(methylphenylsiloxane)	2 mass%
diisostearyl malate	2.5 mass%
2-ethylhexyl paramethoxycinnamate	3 mass%
sorbitan sesquiisostearate	1.2 mass%
tocopherol	0.02 mass%
talc coated with poly(methylhydrosiloxane)	residue

Example 2

[0047] A powder cosmetic was obtained with the same method of the Example 1 except that the blending quantities of the polyurethane particles 1 and the silicone elastomer were changed as the followings.

the polyurethane particles 1	10 mass%
silicone elastomer as trade name KSP-100 by Shin-Etsu Chemical Co., Ltd.	3 mass%

Example 3

[0048] A powder cosmetic was obtained with the same method of the Example 1 except that the blending quantity of the polyurethane particles 1 was changed as the following, and the silicone elastomer was not used.

the polyurethane particles 1	13 mass%
silicone elastomer as trade name KSP-100 by Shin-Etsu Chemical Co., Ltd.	not used

Comparative Example 1

[0049] A powder cosmetic was obtained with the same method of the Example 1 except that the polyurethane particles 1 were not used, and the blending quantity of the silicone elastomer was changed as the following.

the polyurethane particles 1	not used
silicone elastomer as trade name KSP-100 by Shin-Etsu Chemical Co., Ltd.	13 mass%

Comparative Example 2

[0050] A powder cosmetic was obtained with the same method of the Example 1 except that polyurethane particles sold as trade name PLASTIC POWDES D-400 by Toshiki Pigment Co., Ltd. were used in place of the polyurethane particles 1. The polyurethane particles (PLASTIC POWDES D-400) consist of a hexamethylene diisocyanate/trimethylol hexyllactone crosspolymer and silica, and an average particle size of them is about 13 μm.

[0051] 20 experts used each powder cosmetic of the example 1-3, the comparative example 1 and 2. They evaluated a keeping after 2 hours, a spreading in putting make-up, a smoothness and a hiding small wrinkles and pores on the basis of the following scores.

a score of 5: very superior
a score of 4: superior
a score of 3: medium
a score of 2: inferior
a score of 1: very inferior

[0052] Each average score was calculated. A practical evaluation was decided on the basis of the following. The result was shown in the table 1.

◎: more than 4.4 of the average score.
○: 3.5-4.4 of the average score
△: 2.6-3.5 of the average score
×: less than 2.6 of the average score

[0053]

[Table 1]

	Keeping	Spreading	Smoothness	Hiding
Example 1	○	○	○	○
Example 2	◎	◎	◎	◎
Example 3	◎	◎	◎	◎
Compar.Ex.1	△	○	○	○
Compar.Ex.2	△	△	△	△

[0054] The table 1 shows that the powder cosmetics of the example 1-3 using the polyurethane particles 1 is superior in the keeping to the comparative example 1 not using the polyurethane particles 1 and the comparative example 2 using the other sold polyurethane particles. That shows to prevent that a makeup comes off because the polyurethane particles 1 much absorb sebums.

Example 4

[0055] It was obtained a powder cosmetic consisting of the following composition. The powder cosmetic was used as a loose powder.

the polyurethane particles 2	8.5 mass%
mica treated by silicon	20 mass%
iron oxide	0.05 mass%
activated zinc oxide	1 mass%
zinc myristate	4 mass%
talc coated with poly(methylhydrosiloxane)	residue

Comparative Example 3

[0056] A powder cosmetic was obtained with the same method of the Example 4 except that polyurethane particles sold as trade name PLASTIC POWDES D-400 by Toshiki Pigment Co., Ltd. were used in place of the polyurethane

particles 2. The polyurethane particles (PLASTIC POWDES D-400) consist of a hexamethylene diisocyanate/trimethylol hexyllactone crosspolymer and silica, and an average particle size of them is about 13 μm.

Comparative Example 4

[0057] A powder cosmetic was obtained with the same method of the Example 4 except that the silicone elastomer sold as trade name KSP-100 by Shin-Etsu Chemical Co., Ltd. was used in place of the polyurethane particles 2.

[0058] Each powder cosmetic of the example 4, the comparative example 3 and 4 was evaluated on the same, and shown in the table 2.

[0059]

[Table 2]

	Keeping	Spreading	Smoothness	Hiding
Example 4	◎	○	◎	○
Compar.Ex.3	△	○	△	○
Compar.Ex.4	△	○	○	○

[0060] The table 2 shows that the powder cosmetic of the example 4 using the polyurethane particles 2 is superior in the keeping to the comparative example 3 using the other sold polyurethane particles and the comparative example 4 using the sold silicone elastomer. That shows to prevent that a makeup comes off because the polyurethane particles 2 much absorb sebums.

Example 5

[0061] It was obtained a powder cosmetic consisting of the following composition. The powder cosmetic was used as a powdery foundation.

the polyurethane particles 1	5 mass%
polydimethylsiloxane	5 mass%
isostearic acid	0.5 mass%
diisostearyl malate	3 mass%
triethylhexanoin	1 mass%
sorbitan sesquiisostearate	1 mass%
mica coated with spherical PMMA (polymethyl methacrylate)	6 mass%
pearl agent	1 mass%
fine particle of zinc oxide	0.5 mass%
fine particle of titanium oxide	2 mass%
synthetic fluotphlogopite	2 mass%
talc treated by soap scum	8 mass%
vitamin E acetate	0.1 mass%
δ -tocopherol	0.1 mass%
ethylparaben	appropriate mass%
trimethoxycinnamic acid methylbis(trimethylsiloxy)silylisopentyl	1 mass%
2-ethylhexyl p-methoxycinnamate	1 mass%
spherical powders of polyalkyl acrylate	6 mass%
sericite coated with poly(methylhydrosiloxane)	20 mass%
titanium oxide coated with poly(methylhydrosiloxane)	15 mass%
pigment coated with poly(methylhydrosiloxane) [colorant]	5 mass%
talc coated with poly(methylhydrosiloxane)	residue

Example 6

[0062] It was obtained a powder cosmetic consisting off the following composition. The powder cosmetic was used

as a powdery foundation.

the polyurethane particles 1	8 mass%
particles of synthetic hydrocarbon wax	2 mass%
polydimethylsiloxane	6 mass%
purified lanolin	5 mass%
triethylhexanoin	2 mass%
sorbitan sesquiisostearate	0.5 mass%
needle-like particles of titanium oxide	5 mass%
fine particles of zinc oxide	1 mass%
particles sinterring iron oxide and titanium oxide coated with silicone	7 mass%
barium sulfate	8 mass%
mica deoxidized by titanium [titanium pearl pigment]	2 mass%
synthetic fluorphlogopite coated with silicone	5 mass%
talc coated with silicone	2 mass%
mica coated with silicone	15 mass%
stearyl glycyrrhetinate	0.1 mass%
ascorbyl dipalmitate	0.1 mass%
D- α-tocopherol acetate	0.1 mass%
Do- δ -tocopherol	0.1 mass%
paraoxy benzoic acid ester	appropriate mass%
2-ethylhexyl paramethoxycinnamate	3 mass%
bengara coated with silicone	1 mass%
yellow iron oxide coated with silicone	1 mass%
black iron oxide	1mass%
spherical powders of polyalkyl acrylate	3 mass%
perfume	appropriate mass%
calcined sericite	residue

Example 7

[0063] It was obtained a liquid, cosmetic consisting of the following composition. The liquid cosmetic was used as a toner.

the polyurethane particles 1	3 mass%
ethanol	5 mass%
glycerol	1 mass%
1,3-butanediol	5 mass%
polyoxyethylene polyoxypropylene decyltetradecyl ether	0.2 mass%
sodium hexametaphosphate	0.03 mass%
trimethylglycine	1 mass%
poly(sodium aspartate)	0.1 mass%
α -tocopherol-2-L-ascorbate diesterpotassium phosphate	0.1 mass%
thiotaurine	0.1 mass%
green tea extract	0.1 mass%
peppermint extract	0.1 mass%
iris germanica florentina extract	0.1 mass%
EDTA3Na	0.1 mass%
carboxyvinyl polymer	0.05 mass%
potassium	0.02 mass%
phenoxyethanol	appropriate mass%
perfume	appropriate mass%
purified water	residue

Example 8

[0064] It was obtained a liquid cosmetic consisting of the following composition. The liquid cosmetic was used as a toner.

the polyurethane particles 1.	mass%
ethanol	10 mass%
glycerol	2 mass%
poly(oxyethylene · oxypropylene) · methylpolysiloxane copolymer	1 mass%
lauryl dimethyl aminoacetic acid betaine	0.1 mass%
citric acid	0.02 mass%
sodium citrate	0.08 mass%
sodium hexametaphosphate	0.01 mass%
hypotaurine	0.1 mass%
chamomile extract	0.1 mass%
lavender oil	0.001 mass%
phenoxyethanol	appropriate mass%
active hydrogen water	1 mass%
purified water	residue

Example 9

[0065] It was obtained a liquid cosmetic consisting of the following composition. The liquid cosmetic was used as a toner.

the polyurethane particles 1	mass%
ethanol	40 mass%
dipropylenglycol	1 mass%
polyoxyethylene polyoxypropylene decyltetradecyl ether	0.1 mass%
anhydrous silicic acid	1 mass%
salicylic acid	0.1 mass%
sodium citrate	0.2 mass%
zinc p-phenolsulfonate	0.2 mass%
dipotassium glycyrrhizinate	0.1 mass%
pyridoxine hydrochloride	0.1 mass%
1-menthol	0.05 mass%
EDTA3Na	0.05 mass%
bentonite	0.8 mass%
purified water	residue

Example 10

[0066] It was obtained a powder cosmetic consisting of the following composition. The powder cosmetic was used as a deodorant spray.

the polyurethane particles 1	1.5 mass%
aluminum potassium sulfate (an average particle was 20 μm.)	3 mass%
zeolite supporting silver ion, zinc ion and ammonium ion (an average particle was bout 5 μm, and the particles more than 15 μm of a particle size were less 1 mass%.)	2 mass%
zinc oxide	0.2 mass%
(oil components)	
polv(oxyethylene)nonylphenylether	0.5 mass%
dimetnylpolysiloxane (20 mPa - s, 25 °C)	0.1 mass%
isopropyl myristate	0.5 mass%
(addition agents)	

(continued)

polyoxyethylene sorbitan monooleate	0.1 mass%
perfume	0.1 mass%
(propellant)	
liquefied petroleum gas	92 mass%

The deodorant spray was obtained by the following method. Powder components were mixed with a kneader. The oil components were mixed with a blender. The addition agents were absorbed into the mixed oil components. The mixed powder components and the mixed oil components absorbing the addition agents each were charged in a spray can, and the propellant was charged in the spray can to obtain the deodorant spray.

Example 11

[0067] It was obtained a powder cosmetic consisting of the following composition. The powder cosmetic was used as a loose powder.

the polyurethane particles 1	20 mass%
titanated mica coated with an alkyl modified silicone resin	25 mass%
sericite coated with an alkyl modified silicone resin	30 mass%
sapindus mukurossi peel extract	0.01 mass%
hemp cellulose powders	0.1 mass%
talc coated with an alkyl modified silicone resin	residue

Example 12

[0068] It was obtained a liquid cosmetic consisting of the following composition. The liquid cosmetic was used as a makeup base of water-in-oil emulsion.

the polyurethane particles 1	3 mass%
dimethylpolysiloxane (6 mPa · s)	5 mass%
decamethylcyclopentasiloxane	30 mass%
polyoxyethylene · methylpolysiloxane copolymer	3 mass%
dodecamethylcyclohexasiloxane	1 mass%
glycerol	5 mass%
dipropylglycol	5 mass%
sage oil	0.1 mass%
talc	0.1 mass%
titanated mica	0.1 mass%
polymethylsilsesquioxane powders	10 mass%
tocopherol acetate	0.1 mass%
δ - tocopherol	0.1 mass%
thiotaurine	0.1 mass%
peppermint extract	0.1 mass%
p-oxybenzoic acid ester	appropriate mass%
phenoxyethanol	appropriate mass%
edetate trisodium	appropriate mass%
colored pigment	appropriate mass%
dimethyl distearyl ammonium hectorite	1.5 mass%
purified water	residue

Example 13

[0069] It was obtained a liquid cosmetic consisting of the following composition. The liquid cosmetic was used as a

milky foundation.

the polyurethane particles 1	4 mass%
microcrystalline wax	1 mass%
dimethylpolysiloxane	15 mass%
decamethylcyclohexasiloxane	2 mass%
1,3-butanediol	6 mass%
candelilla wax	3 mass%
isostearic acid	1 mass%
ethylene glycol fatty acid ester	0.1 mass%
octyldodecyl lanolate	0.5 mass%
2-alkyl-N-carboxymethyl-N-hydroxyethyl imidazolinium betaine	4 mass%
titanium oxide	14.5 mass%
barium sulfate	5 mass%
talc	3 mass%
(dim.ethicone/vinyldimethicone)crosspolymer	powders 0.1 mass%
sodium metaphosphate	0.1 mass%
hydroxypropyl- β -cyclodextrin	0.1 mass%
DL- α'tocopherol acetate	0.1 mass%
hamamelis virginiana (witch hazel) extract liquid	0.1 mass%
peony root extract	0.1 mass%
sodium chondroitin sulfate	0.1 mass%
sodium hyaluronate	0.1 mass%
p-oxybenzoic acid ester	appropriate mass%
bengara	appropriate mass%
yellow iron oxide	appropriate mass%
black iron oxide	appropriate mass%
xanthan gum	0.2 mass%
carboxymethyl cellulose	0.2 mass%
melilot extract	2 mass%
purified water	residue

Example 14

[0070] It was obtained a gel cosmetic consisting of the following composition. The gel cosmetic was used as a hair styling wax.

the polyurethane particles 1	10 mass%
microcrystalline wax	5 mass%
ceresin	10 mass%
sunflower oil	1 mass%
diglycerolsorbitan pentaoctanoate	10 mass%
lipophilic glyceryl monostearate	5 mass%
self-emulsified glyceryl monostearate	5 mass%
silanized silicic anhydride	5 mass%
pentaerythritol Tetra-2-ethylhexanoate	residue

Example 15

[0071] It was obtained a powder cosmetic consisting of the following composition. The powder cosmetic was used as a powder-type body soap.

the polyurethane particles 1	3 mass%

(continued)

sodium cocoyl ethyl ester sulfonate	10 mass%
sodium methyl lauroyl taurate	1 mass%
potassium N-myristoyl-L-glutamate	10 mass%
sodium N-lauroyl-L-glutamate	20 mass%
POLYMER JR-400 sold by Union Carbide Co.	0.2 mass%
talc	10 mass%
hydroxypropyl methyl cellulose	0.2 mass%
dipotassium glycyrrhiznate	0.1 mass%
trimethylglycine	0.1 mass%
sophora flavescens extract	appropriate mass%
saxifraga sarmentosa extract	appropriate mass%
perilla extract	appropriate mass%
D-mannitol	residue

Example 16

[0072] It was obtained a gel cosmetic consisting of the following composition. The gel cosmetic was used as a gel-type makeup base.

the polyurethane particles 1	7 mass%
ethanol	4 mass%
1,3-butanediol	7 mass%
glycerol	8 mass%
hydrophobic modifies polyetherurethane	2 mass%
succinoglucan	0.15 mass%
citric acid	0.02 mass%
sodium citrate	0.08mass%
iron oxide	0.01 mass%
phenoxyethanol	0.5 mass%
edetate trisodium	0.1 mass%
purified water	residue

Example 17

[0073] It was obtained a liquid cosmetic consisting of the following composition. The liquid cosmetic was used as a sunscreen preparation.

the polyurethane particles 1	5 mass%
decamethylcyclopentasiloxane	20 mass%
trimethylsiloxysilicic acid	1 mass%
polyoxyethylene methylpolysiloxane copolymer	2 mass%
dipropylglycol	4 mass%
squalane	5 mass%
fine particles titanium oxide coated with silicone (an average size was 20 nm)	10 mass%
talc (hydrophobic treatment)	6 mass%
paraben	appropriate mass%
phenoxyethanol	appropriate mass%
edetate trisodium	0.02 mass%
4-t-butyl-4'-methoxydibenzoylmethane	0.1 mass%
2-ethylhexyl p-methoxycinnamate	7 mass%
diparamethoxycinnamic acid mono-2-ethylhexanoic acid glyceryl	0.5 mass%

(continued)

dimethyl distearyl ammonium hectorite	1 mass%
perfume	appropriate mass%
purified water	residue

[0074] Using each cosmetic of the Example 5-17, it was prevented to come off and kept long.

Claims

1. Cosmetics containing polyurethane particles wherein;
each surface of the bodies of the polyurethane particles is covered with hydrophilic fine silica powders,
the body of the polyurethane particle is obtained by three-dimensionally polymerizing an isocyanate-terminated urethane prepolymer with trifunctional or more functional amines, and the isocyanate-terminated urethane prepolymer is obtained by reacting polyisocyanates and polyols including a poly(tetramethylene ether)glycol.

2. The cosmetics according to the claim 1, wherein;
each surface of the bodies of the polyurethane particles is covered with hydrophilic fine silica powders which are implanted on the surface.

3. The cosmetics according to the claim 1, wherein;
a number average molecular weight of poly(tetramethylene ether)glycol is 650-3000.

4. The cosmetics according to the claim 1, wherein;
an isophorone diisocyanate is used as the polyisocyanates and the poly(tetramethylene ether)glycol is used as the polyols.

5. The cosmetics according to the claim 1, wherein;
a 3,3'-diaminodipropylamine is used as trifunctional amines.

6. The cosmetics according to the claim 1, wherein;
a particle size of the polyurethane particle is 20 or more times larger than a particle size of the hydrophilic fine silica powder.

7. The cosmetics according to the claim 1, wherein;
an average particle size of the polyurethane particles is 1-50μm.

8. The cosmetics according to the claim 1, wherein;
the polyurethane particles are containing 0.1-30 parts by mass in the cosmetics.

9. The cosmetics according to the claim 1, wherein;
the form of the cosmetics is selected from the group consisting of solid, powder, gel and liquid.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/050124

A. CLASSIFICATION OF SUBJECT MATTER
A61K8/87(2006.01)i, *A61Q1/00*(2006.01)i, *A61Q1/02*(2006.01)i, *A61Q1/12*(2006.01)i, *A61Q5/00*(2006.01)i, *A61Q15/00*(2006.01)i, *A61Q17/04*(2006.01)i, *A61Q19/00*(2006.01)i, *A61Q19/10*(2006.01)i, *C11D3/12*(2006.01)i,
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61K8/87, A61Q1/00, A61Q1/02, A61Q1/12, A61Q5/00, A61Q15/00, A61Q17/04, A61Q19/00, A61Q19/10, C11D3/12, C11D3/37, C11D17/06, C11D17/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2010
Kokai Jitsuyo Shinan Koho 1971-2010 Toroku Jitsuyo Shinan Koho 1994-2010

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2001-323070 A (Catalysts & Chemicals Industries Co., Ltd.), 20 November 2001 (20.11.2001), claims; paragraphs [0001], [0008], [0022]; examples 1 to 5 & US 2001/0028890 A1 & US 2003/0215474 A1 & FR 2806004 A1 & KR 10-2001-0088428 A	1-9
A	WO 2007/139114 A1 (Shiseido Co., Ltd.), 06 December 2007 (06.12.2007), claims (particularly, claims 3, 5); paragraph [0031] & JP 2007-320906 A & US 2009/0238877 A1 & EP 2042159 A1 & KR 10-2009-0013821 A & CN 101460140 A	1-9

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 April, 2010 (06.04.10)	13 April, 2010 (13.04.10)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/050124

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2007/029761 A1 (Kao Corp.), 15 March 2007 (15.03.2007), claims & JP 2007-320906 A & US 2009/0238877 A1 & EP 2042159 A1 & KR 10-2009-0013821 A & CN 101460140 A	1-9
A	JP 2008-239542 A (Dainichiseika Color & Chemicals Mfg. Co., Ltd.), 09 October 2008 (09.10.2008), claims (Family: none)	1-9
A	JP 2000-191441 A (Kose Corp.), 11 July 2000 (11.07.2000), paragraph [0007]; paragraphs [0009] to [0010], refer to 'art pearl C-800' (Family: none)	1-9

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/050124

Continuation of A. CLASSIFICATION OF SUBJECT MATTER
(International Patent Classification (IPC))

C11D3/37(2006.01)i, *C11D17/06*(2006.01)i, *C11D17/08*(2006.01)i

(According to International Patent Classification (IPC) or to both national classification and IPC)

Form PCT/ISA/210 (extra sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/050124

<Regarding Coverage of Search>

Although the polyisocyanates and tri- or higher functional amines in the invention of claims 1-9 include a very large number of polyisocyanates and polyfunctional amines having various structures, only isophorone diisocyanate for the former and 3,3'-diaminopropylamine for the latter are specifically disclosed in the description within the meaning of PCT Article 5. In other words, only a few compounds among the claimed compounds are disclosed by the description within the meaning of PCT Article 5, and thus the invention of claims 1-9 is not fully supported within the meaning of PCT Article 6.

This international search report therefore covers those supported and disclosed by the description, namely those wherein isophorone diisocyanate or a similar compound is used as the polyisocyanate, and 3,3'-diaminopropylamine or a similar compound is used as the tri- or higher functional amine.

Form PCT/ISA/210 (extra sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 20053114300 B **[0003]**

PTO/SB/08a (01-22)
Approved for use through 05/31/2024. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM
Art Unit	1699
Examiner Name	Brian M GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4404296	A	1983-09-13	SCHAEPEL DIETMAR	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20150197610	A1	2015-07-16	PETERSON BRUCE W, et al.	
	2	20050276770	A1	2005-12-15	FILIPPI, et al.	
	3	20090081137	A1	2009-03-26	NGUYEN KIM, et al.	
	4	20080287604	A1	2008-11-20	WIBAUX	

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM
Art Unit	1699
Examiner Name	Brian M GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

	1	2016090081	WO	A1	2016-06-09	LUBRIZOL ADVANCED MAT INC		☐
	2	2759572	EP	A1	2014-07-30	TEKNOR APEX CO, et al.		☐
	3	2008201698	JP	A	2008-09-04	LINTEC CORP	English Abstract	☒
	4	2011178693	JP	A	2011-09-15	KOSE CORP, et al.	English Abstract	☒
	5	H04320457	JP	A	1992-11-11	KUBO YASUSHI, et al.	English Abstract	☒
	6	2017114773	JP	A	2017-06-29	OREAL	English Abstract	☒
	7	2018199653	JP	A	2018-12-20	TOSHIKI PIGMENT KK, et al.	English Abstract	☒
	8	2008039466	WO	A1	2008-04-03	DU PONT, et al.		☐
	9	2380557	EP	A1	2011-10-26	KONISHI CO LTD, et al.		☐
	10	2365024	EP	A1	2011-09-14	KONISHI CO LTD		☐
	11	2008260722	JP	A	2008-10-30	DAINICHISEIKA COLOR CHEM, et al.	English Abstract	☒

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	18066105
	Filing Date	2022-12-14
	First Named Inventor	Anna K. CROOM
	Art Unit	1699
	Examiner Name	Brian M GULLEDGE
	Attorney Docket Number	GRAN-1012-U-D

	12	2008239542	JP	A	2008-10-09	DAINICHISEIKA COLOR CHEM, et al.	English Abstract	☒
	13	H05262622	JP	A	1993-10-12	NEGAMI KOGYO KK	English Abstract	☒
	14	2018122532	WO	A1	2018-07-05	LVMH RECH	English Abstract	☒
	15	3778689	EP	A1	2021-02-17	MITSUI CHEMICALS INC		☐
	16	3778690	EP	A1	2021-02-17	MITSUI CHEMICALS INC		☐

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	MUTLU et al., "Castor oil as a renewable resource for the chemical industry." Eur. J. Lipid Sci. Technol., 112: 10-30 (2010).	☐
	2	SRIVASTAVA et al., "Gel Point Prediction of Metal-filled Castor Oil-based Polyurethanes System." Polym. Adv. Technol., 13: 1055-1066 (2002).	☐
	3	International Search Report issued in International Application No. PCT/US2020/041540, mailed October 16, 2020.	☐
	4	Extended European Search Report for Corresponding European Application No. 20855942.7, November 8, 2023, 13 Pages.	☐

If you wish to add additional non-patent literature document citation information please click the Add button Add

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	18066105
	Filing Date	2022-12-14
	First Named Inventor	Anna K. CROOM
	Art Unit	1699
	Examiner Name	Brian M GULLEDGE
	Attorney Docket Number	GRAN-1012-U-D

EXAMINER SIGNATURE			
Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM
Art Unit	1699
Examiner Name	Brian M GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

CERTIFICATION STATEMENT

Please see 37 CFR 1.97(e) to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☒ A certification statement is not submitted herewith.

FEE

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

COPIES

☐ An identification of an earlier application pursuant to 37 CFR 1.98 (d) (1) is attached.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Michael N. Mercanti/	Date (YYYY-MM-DD)	2025-01-09
Name/Print	Michael N. Mercanti	Registration Number	33966

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Europäisches Patentamt
European Patent Office
Office européen des brevets

Espacenet

JPH05262622A null

Applicants:

Inventors:

Classifications:

IPC ***A61K8/18; A61K8/72; A61K8/87; A61Q1/00; A61Q1/02; A61Q1/04; A61Q1/12; C08J3/14; C08J3/20; C08L75/00; C08L75/04;*** (IPC1-7): A61K7/00; A61K7/02; C08J3/14; C08J3/20; C08L75/04;

Priorities: JP3484391A 1991-02-28

Application: JP3484391A·1991-02-28

Publication: JPH05262622A·1993-10-12

Published as: JPH05262622A

null

Abstract

PURPOSE:To provide a cosmetic having excellent covering power, adhesiveness, adsorptivity and miscibility, free from safety problem because of little stimulation to the skin, giving soft and smooth feeling to the skin and exhibiting excellent slipperiness and feeling. CONSTITUTION:The objective cosmetic contains (A) fine powder of spherical polyurethane having an average particle diameter of < =30mum (or containing 0-10wt.% of particles of 30-74m diameter and having an average particle diameter of < =25mum), preferably polyurethane powder having particle diameter range of 1-15mum and uniform particle size distribution and preferably further (B) pigments such as titanium oxide, zinc oxide, Pigment Blue 15 and talc or functional fillers such as ultraviolet absorber, antioxidant and humectant. The cosmetic exhibits the above effects such as excellent covering power to mask the spots, pimples, etc., on the skin surface, adsorptivity and adhesion to the skin, absorbability of sweat and secreted material and miscibility with other cosmetic base and has excellent slipperiness and feeling to the skin compared with conventional, cosmetics containing organic fine powder.

【発行国】

日本国特許庁（ＪＰ）

【公報種別】 (19)日本国特許庁（ＪＰ） (12)公開特許公報（Ａ） (11)特許出願公開番号

特開平5－262622

(43)公開日 平成５年(1993)10月12日

公開特許公報（Ａ）

(51)Int.Cl.[5]		識別記号	庁内整理番号	ＦＩ	技術表示箇所
Ａ６１Ｋ	7/02		P 9165－4C		
	7/00		J 9165－4C		
// Ｃ０８Ｊ	3/14	ＣＦＦ	9268－4F		
	3/20		C 9268－4F		
		ＣＦＦ	B 9268－4F		

【公開番号】 特開平５－２６２６２２

審査請求 未請求 請求項の数３(全 5 頁) 最終頁に続く

(21)出願番号 特願平3－34843

【公開日】 (22)出願日 平成３年(1991)２月28日

平成５年（１９９３）１０月１２日

(71)出願人 390028048
根上工業株式会社
石川県能美郡根上町道林町ロ22
(72)発明者 菅野 俊司
石川県加賀市大聖寺上福田町ホ－45
(72)発明者 新谷 正喜
石川県能美郡川北町田子島マ－110
(74)代理人 弁理士 志賀 正武 （外２名）

【発明の名称】

化粧料

(54)【発明の名称】 化粧料

【国際特許分類第５版】

A61K 7/02
7/00
// C08J 3/14
3/20

CFF B 9268-4F

C08L 75/04 NFX 8620-4J

NFY 8620-4J

(57)【要約】

【構成】 化粧料に、弾力性に富む球状ポリウレタン微粉末を配合する。

【効果】 皮膚表面のシミ、ソバカス等を隠す被覆性、皮膚への吸着性、付着性、汗、分泌物の吸収性、他の化粧用基材との混合性に優れるとともに、皮膚への刺激が殆どなく、安全面で問題がない化粧料が得られる。特に、皮膚に使用した際にその感触が柔らかく滑らかであり、滑り性、感触性を向上させることができる。

【審査請求】未請求

【請求項の数】３

【全頁数】５

【特許請求の範囲】
【請求項１】　平均粒子径が３０μm以下である球状ポリウレタン微粉末を含有してなることを特徴とする化粧料。
【請求項２】　上記球状ポリウレタン微粉末が顔料含有球状ポリウレタン微粉末であることを特徴とする請求項１記載の化粧料。
【請求項３】　上記球状ポリウレタン微粉末が機能性フィラー含有球状ポリウレタン微粉末であることを特徴とする請求項１記載の化粧料。
【発明の詳細な説明】
【０００１】
【産業上の利用分野】本発明は有機系微粉末を含有する化粧料に関するもので、特に皮膚に対する滑り性、感触性に優れた化粧料に関する。
【０００２】
【従来の技術】従来、微粉末の形態で化粧料に使用されるものとしては二酸化チタン、亜鉛華、タルク、カオリン、沈降性炭酸カルシウム、塩基性マグネシウム等の無機系粉末、あるいはナイロン樹脂、架橋スチレン樹脂、アクリル樹脂、酢酸綿、Ｎ－アシルリジン、セルロース誘導体等の有機系粉末が知られている。
【０００３】これらの化粧料用微粉末に要求される性能は、（１）皮膚表面のシミ、ソバカス等を隠す被覆性、（２）皮膚に塗布する際の延び、滑り性、感触、（３）皮膚への吸着性、付着性、（４）皮膚への刺激がないこと、（５）汗、分泌物の吸収性、（６）他の化粧用基材との混合性、分散安定性、（７）安全面で問題がないこと等が挙げられる。
【０００４】
【発明が解決しようとする課題】しかしながら、二酸化チタン等の無機粉末では良好な被覆力、感触性が得られるが親水性が高く、油性基材との配合が困難であった。また、ナイロン樹脂等の有機粉末は微小球状形態がもたらす滑り性の良さ、安全性の高さ、付着性、混合性等に優れ皮膚への刺激も殆どないが、硬い粒子であるため皮膚に塗布した際の感触性に劣る面があった。
【０００５】この発明は前記事情に鑑みてなされたもので、皮膚に対する滑り性、感触性に優れた有機系微小球状粉末含有化粧料を提供することを目的とする。
【０００６】
【課題を解決するための手段】この発明の化粧料は、平均粒子径が３０μm以下である球状ポリウレタン微粉末を含有してなることを前記課題の解決手段とした。
【０００７】さらに詳しくは平均粒子径が３０μm以下、もしくは３０μm以上７４μm以下の粒子が０～１０重量％存在し、かつ平均粒子径が２５μm以下である球状ポリウレタン微粉末であり、より好ましくは粒子径１～１５μmで均一な粒度分布を有する球状ポリウレタン微粉末を含有してなるものである。
【０００８】以下、本発明について詳しく説明する。
【０００９】ここでのポリウレタンはイソシアネート基を有する化合物と、そのイソシアネート化合物と反応する活性水素を有する基、例えば水酸基、アミノ基、カルボキシル基を有する化合物とを反応させて得られる重合体であり、弾力性に富むものである。
【００１０】また、本発明でのポリウレタン微粉末は種々の製造方法で得ることができ、特に製造方法については限定されないが、例えば本発明者が先に提案した特願平２－３１４６９６号に記載の方法がある。この製造方法は、懸濁安定剤を含む水中に粒状にポリイソシアネートプレポリマーを単独で、あるいはそれにポリウレタンまたはポリウレタンポリオールを添加し、撹拌速度を調整して目的の粒径の懸濁液を調製し、次いで加温して反応を開始させて球状微粉末を生成させ、これを固液分離、洗浄、乾燥することによって球状ポリウレタン微粉末を製造するものである。ここで懸濁安定剤の量、種類、撹拌速度等を変化させることにより球状ポリウレタン微粉末の粒度、粒度分布を調節することができる。この製造方法によれば、球状ポリウレタン微粉末の粒度の調節が容易であるとともに、効率よく、かつ安定して再現性よく所望の球状ポリウレタン微粉末を得ることができる。
【００１１】この他、種々の公知の製造方法によって製造することができ、例えば米国特許明細書３５２７７２９号、特公昭５０－８１１６号公報、特開平３－２２６６号公報等に開示されている方法によっても本発明で使われるポリウレタン微粉末を製造することができる。
【００１２】尚、本発明において平均粒子径を３０μm以下と規定するのは、これが３０μmを越えると微粉末の皮膚に対する異物感や不快感が発現するとともに、皮膚に対する付着性、被覆力が著しく低下するという問題を解決するためである。
【００１３】また請求項２記載の顔料含有球状ポリウレタン微粉末は前記ポリウレタン微粉末中に顔料が含まれているものであり、前記球状ポリウレタン微粉末同様の方法で製造される。ここで用いられる顔料としては球状ポリウレタン微粉末の生成反応を阻害せず、かつ生成した顔料含有球状ポリウレタン微粉末を化粧料として使用した場合に、安全性に問題ないものであればよく、有機系、無機系いずれのものも使用することができる。例えば酸化チタン、亜鉛華、ピグメントブルー１５（フタロシアニン系ブルー顔料）、タルク等が使用できる。
【００１４】また請求項３記載の機能性フィラー含有球状ポリウレタン微粉末は前記球状ポリウレタン微粉末中に機能性フィラーが含まれているものであり、前記球状ポリウレタン微粉末同様の方法で製造される。ここで用いられる機能性フィラーとしては紫外線吸収剤、酸化防止剤、保湿剤等、化粧料として有用なフィラーであり、球状ポリウレタン微粉末の生成反応を阻害せず、かつ生

成した顔料含有球状ポリウレタン微粉末を化粧料として使用した場合に、安全性に問題ないものであればよく、有機系、無機系いずれのものも使用することができる。例えばペンタエリスリチル－テトラキス［３－（３，５－ジーターシャリブチル４－ヒドロキシフェニル）プロピオネート］、ビス（２，２，６，６テトラメチル－４－ピペリジル）セバケート、コラーゲン、キトサン、微粉状酸化チタン、微粉状酸化鉄等が使用できる。

【００１５】

【実施例】以下、本発明の実施例について説明する。尚、本発明は以下の実施例に限定されるものではない。

【００１６】（実施例１）２Ｌ撹拌機付きセパラブルフラスコに水９６５ｇを仕込み、この中へ、メトローズ９０ＳＨ－１００（信越化学工業株式会社製、メチルセルロース）３５ｇを溶解して分散媒を調製した。

【００１７】一方、窒素ガスで充分に置換し、乾燥させた２ＬオートクレーブにアデカポリエーテルＧ－７００（水酸基価２２５ｍｇ／ＫＯＨｇ；旭電化工業株式会社製、グリセリンＰＯ付加物）７４８ｇとヘキサメチレンジイソシアネート（以下、ＨＭＤＩと記載）１００８ｇを仕込み、さらに窒素ガスにて、充分に上方置換させた後密閉し、１２０℃で２０時間撹拌、混合し反応させた。その後、減圧下で未反応のＨＭＤＩを除去した後、トルエンを加えて不揮発分９０重量％の合成物（以下、合成物（Ｉ）と記載）を得た。このものはイソシアネート含有量８．７３％で粘度１５００ｃｐｓであった。

【００１８】６００ｒｐｍ撹拌下において、上記分散媒に、上記合成物（Ｉ）２８０ｇをトルエン１２０ｇで希釈した溶液を加え懸濁液を調製した。撹拌を継続させた状態でこの懸濁液を６０℃に昇温させ、１．５時間反応させた後、室温になるまで冷却し、次いで固液分離して水で充分洗浄した後、７０℃にて２０時間乾燥を行い、平均粒子径５μｍの球状ウレタン微粉末を得た。

【００１９】このようにして得られた球状ポリウレタン微粉末を用いて粉白粉を調製した。

球状ポリウレタン微粉末（平均粒子径５μｍ）	４０重量部
タルク	４０
カオリン	１１
ステアリン酸マグネシウム	６
香料	１
色素	２

ボールミルを用い、上記の配合比に基づいて各種粉末原料を混合粉砕し、粉白粉を調製した。ここで得られた粉白粉は皮膚に対する吸着力に優れ、伸びもよく、膚への感触も異物感がなくて柔らかく、滑らかであった。

【００２０】（実施例２）実施例１と同様にして得られた球状ポリウレタン微粉末を用いてプレストパウダーを調製した。

球状ポリウレタン微粉末（平均粒子径５μｍ）	４５重量部
タルク	２５
カオリン	１０
ステアリン酸亜鉛	５
トラガントガム水溶液（結合剤）	７
ピロリドンカルボン酸ナトリウム（結合剤）	３
香料	１
色素	２

ボールミルを用い、上記の配合比に基づいて各種粉末原料を混合粉砕し、粉白粉を調製した。次いで、結合剤としてトラガントガム水溶液およびピロリドンカルボン酸ナトリウムを加え、プレス成型してプレストパウダーとした。ここで得られたプレストパウダーは成型加工が容易で、ひび割れしにくく、膚への感触も異物感がなくて柔らかく、滑らかであった。

【００２１】（実施例３）２Ｌ撹拌機付きセパラブルフラスコに水９６５ｇを仕込み、この中へ、メトローズ９０ＳＨ－１００（信越化学工業株式会社製、メチルセルロース）３５ｇを溶解して分散媒を調製した。６００ｒｐｍ撹拌下で、この分散媒に合成物（Ｉ）２８０ｇ、トルエン９２ｇ、およびレジノカラーＵＤ－５２２Ａ（レジノカラー工業株式会社製、白色顔料）６０ｇからなる混合液を加え、懸濁液を調製した。撹拌を継続させた状態で懸濁液を６０℃に昇温し、１．５時間反応させた後、室温まで冷却し、次いで固液分離して水で充分洗浄した後、２０時間乾燥して、平均粒子径５μｍの顔料含有球状ウレタン微粉末を得た。

【００２２】このようにして得られた顔料含有球状ポリウレタン微粉末を用いて練り白粉を調製した。

顔料含有球状ポリウレタン微粉末（平均粒子径５μｍ）	５５重量部
グリセリン	１０
ピロリドンカルボン酸ナトリウム	３

精製水	29
香料	1
色素	2

乳化機を用い、上記配合比に基づいて、各種原料を混練し、練り白粉を調製した。ここで得られた練り白粉は皮膚に対する伸び、被覆力に優れ、膚への感触も異物感がなくて柔らかく、滑らかであった。

【００２３】（実施例４）２Ｌ撹拌機付きセパラブルフラスコに水９７０ｇを仕込み、この中へ、メトローズ９０ＳＨ－１００（信越化学工業株式会社製、メチルセルロース）３０ｇを溶解して分散媒を調製した。６００ｒｐｍ撹拌下で、この分散媒に合成物（Ｉ）２８０ｇをトルエン９２ｇ、レジノカラーＵＤ－５２２Ａ（レジノカラー工業株式会社製、白色顔料）６０ｇからなる混合液を加え、懸濁液を調製した。撹拌を継続させた状態で懸濁液を６０℃に昇温し、１．５時間反応させた後、室温まで冷却し、次いで固液分離して水で充分洗浄した後、２０時間乾燥して、平均粒子径１５μｍの顔料含有球状ウレタン微粉末を得た。

【００２４】このようにして得られた顔料含有球状ポリウレタン微粉末を用いてボディパウダーを調製した。

顔料含有球状ポリウレタン微粉末（平均粒子径１５μｍ）	４４重量部
重炭酸ナトリウム	20
カオリン	29
ステアリン酸亜鉛	4
ミンクオイル	2
香料	1

混合機を用い、上記配合比に基づいて、各種原料を充分に撹拌、混合した後、さらに撹拌しつつオイル、香料を加えてボディーパウダーを調製した。ここで得られたボディーパウダーは皮膚に対する伸び、付着性、吸着性が良好で、膚への感触も異物感がなくて柔らかく、滑らかであった。

【００２５】（実施例５）２Ｌ撹拌機付きセパラブルフラスコに水９７０ｇを仕込み、この中へ、メトローズ９０ＳＨ－１００（信越化学工業株式会社製、メチルセルロース）３０ｇを溶解して分散媒を調製した。６００ｒｐｍ撹拌下で、この分散媒に合成物（Ｉ）２８０ｇをトルエン１２０ｇで希釈した溶液を加え、懸濁液を調製した。撹拌を継続させた状態で懸濁液を６０℃に昇温させ、１．５時間反応させた後、室温まで冷却し、次いで固液分離して水で充分洗浄した後、２０時間乾燥して、平均粒子径１５μｍの球状ウレタン微粉末を得た。

【００２６】このようにして得られた球状ポリウレタン微粉末を用いて口紅を調製した。

球状ポリウレタン微粉末（平均粒子径１５μｍ）	２０重量部
ヒマシ油	30
カルナバワックス	6
ミツロウ	11
ラノリン	20
オレイルアルコール	10
色素	2
香料	1

混合機を用い、上記配合比に基づいて、球状ポリウレタン微粉末、色素、香料、を充分に撹拌、混合した後、さらにヒマシ油、オレイルアルコールを加え、混合、撹拌した。この混合物を溶融したオイル、ワックスに入れ、分散させた後、成型機に流し込み冷却して口紅を調製した。ここで得られた口紅は唇に対する伸び、付着性が良好であり、その感触も異物感がなくて柔らかく、滑らかであった。

【００２７】（実施例６）２Ｌ撹拌機付きセパラブルフラスコに水９７０ｇを仕込み、この中へ、メトローズ９０ＳＨ－１００（信越化学工業株式会社製、メチルセルロース）３０ｇを溶解して分散媒を調製した。６００ｒｐｍ撹拌下で、この分散媒に合成物（Ｉ）２８０ｇ、トルエン１２０ｇおよびサノールＬＳ７７０（三共株式会社製、紫外線吸収剤）５．６ｇからなる溶液を加え、懸濁液を調製した。撹拌を継続させた状態で懸濁液を６０℃に昇温させ、１．５時間反応させた後、室温まで冷却し、次いで固液分離して水で充分洗浄した後、２０時間乾燥して、平均粒子径１５μｍの紫外線吸収剤含有球状ウレタン微粉末を得た。

【００２８】このようにして得られた紫外線吸収剤含有球状ポリウレタン微粉末を用いてアイシャドウを調製した。

紫外線吸収剤含有球状ポリウレタン微粉末（平均粒子径１５μｍ）	１０重量部
タルク	1

顔料	１２
雲母	１８
白色ワセリン	１２
ラノリン誘導体	５
マイクロクリスタリンワックス	１５
スクワラン	２
流動パラフィン	２７

乳化機を用い、上記配合比に基づいて、各種原料を充分に混練し、アイシャドウを調製した。ここで得られたアイシャドウは、皮膚に対する伸び、吸着性に優れ、膚への感触も異物感がなくて柔らかく、滑らかであった。

【００２９】

【発明の効果】以上説明したようにこの発明の化粧料は、ポリウレタン樹脂を平均粒子径が３０μｍ以下である球状微粉末の形態で含有してなるものである。したがって、弾力性に富む球状ポリウレタン微粉末を配合することによって被覆性、付着性、吸着性、混合性に優れるとともに、皮膚への刺激も殆どなく、安全性にも問題がない化粧料が得られる。特に、皮膚に使用した際にその感触が柔らかく滑らかであり、従来の有機系微小球状粉末含有化粧料に比較して滑り性、感触性を向上させることができる。

フロントページの続き

(51)Int.Cl.[5]	識別記号	庁内整理番号	ＦＩ	技術表示箇所
ＣＯ８Ｌ　75/04	ＮＦＸ	8620－4Ｊ		
	ＮＦＹ	8620－4Ｊ		

Espacenet

JP2011178693A BEAUTY METHOD

Applicants: KOSE CORP,NITTO DENKO CORP

Inventors: FUKUSHIMA YUKO,ISSHIKI TAKASHI,NAKAYAMA JUNKO,TAKAHASHI HISANORI,KONNO MASAYUKI,SUZUKI KIYOSHI

Classifications:
IPC ***A61K8/02; A61K8/06; A61K8/33; A61K8/34; A61K8/37; A61Q19/00;***

Priorities: JP2010042873A 2010-02-26

Application: JP2010042873A·2010-02-26

Publication: JP2011178693A·2011-09-15

Published as: JP2011178693A

BEAUTY METHOD

Abstract

PROBLEM TO BE SOLVED: To provide a beauty method that moisturizes parts of wrinkle occurrence such as tail of eyes, lips, forehead, or neck part, or parts having possibility of wrinkle occurrence and improves wrinkles or suppresses wrinkle occurrence. SOLUTION: The beauty method includes coating the skin with an emulsified cosmetic containing 5-50 mass% of an oily component and sticking a sheet for skin adhesion which has a sheet substrate layer and an adhesive layer to be adhered to the skin surface and has a steam transmittance of the whole sheet containing the sheet substrate layer and the adhesive layer of 200-2,000 g/m2/24 hours. Preferably the tensile strength of the whole sheet containing the sheet substrate layer and the adhesive layer is 20-200 N/cm, the sheet substrate layer is a polyurethane, the thickness of the sheet substrate layer is 30-250 μm and the adhesive layer is a gel-based adhesive containing an organic liquid component. COPYRIGHT: (C)2011,JPO&INPIT

(19)日本国特許庁(JP)　(12)公開特許公報(A)　(11)特許出願公開番号
特開2011-178693
(P2011-178693A)
(43)公開日　平成23年9月15日(2011.9.15)

(51)Int.Cl.			F I		テーマコード（参考）
A61K	8/34	(2006.01)	A61K	8/34	4C083
A61K	8/37	(2006.01)	A61K	8/37	
A61K	8/33	(2006.01)	A61K	8/33	
A61K	8/06	(2006.01)	A61K	8/06	
A61K	8/02	(2006.01)	A61K	8/02	

審査請求 未請求　請求項の数 9　ＯＬ　（全 27 頁）　最終頁に続く

(21)出願番号　特願2010-42873 (P2010-42873)
(22)出願日　平成22年2月26日 (2010.2.26)

(71)出願人　000145862
株式会社コーセー
東京都中央区日本橋３丁目６番２号
(71)出願人　000003964
日東電工株式会社
大阪府茨木市下穂積１丁目１番２号
(74)代理人　100107984
弁理士　廣田　雅紀
(74)代理人　100102255
弁理士　小澤　誠次
(74)代理人　100096482
弁理士　東海　裕作
(74)代理人　100123168
弁理士　大▲高▼　とし子

最終頁に続く

(54)【発明の名称】美容方法

(57)【要約】
【課題】目尻、口元、額、首部など、皺が発生している、あるいは発生するおそれのある部位の保湿を行って、皺の改善又は発生抑制を図るための美容方法を提供すること。
【解決手段】皮膚上に、油性成分を５～５０質量％含有する乳化化粧料を塗布した後、シート基材層と皮膚表面に粘着可能な粘着剤層を有し、かつ、シート基材層と粘着剤層を含むシート全体の水蒸気透過度が２００～２，０００ｇ／ｍ^2・２４ｈｒｓである皮膚貼付用シートを貼付することからなる美容方法である。シート基材層と粘着剤層を含むシート全体の引張強度が２０～２００Ｎ／ｃｍ、シート基材層がポリウレタン、シート基材層の厚みが３０～２５０μｍ、粘着剤層が有機液状成分を含有するゲル系粘着剤であることなどが好ましい。
【選択図】なし

【特許請求の範囲】
【請求項１】
皮膚上に、油性成分を５～５０質量％含有する乳化化粧料を塗布した後、シート基材層と皮膚表面に粘着可能な粘着剤層を有し、かつ、シート基材層と粘着剤層を含むシート全体の水蒸気透過度が２００～２，０００ｇ／ｍ^2・２４ｈｒｓである皮膚貼付用シートを貼付することからなる美容方法。
【請求項２】
皮膚の皺を改善又は皺の発生を抑制する美容方法である請求項１記載の美容方法。
【請求項３】
シート基材層と粘着剤層を含むシート全体の引張強度が２０～２００Ｎ／ｃｍであることを特徴とする請求項１又は２記載の美容方法。
【請求項４】
シート基材層がポリウレタンからなることを特徴とする請求項１～３のいずれかに記載の美容方法。
【請求項５】
シート基材層の厚みが３０～２５０μｍであることを特徴とする請求項１～４のいずれかに記載の美容方法。
【請求項６】
粘着剤層が、有機液状成分を含有するゲル系粘着剤からなることを特徴とする請求項１～５のいずれかに記載の美容方法。
【請求項７】
油性成分中に抱水性油性成分を１０～８０質量％含有することを特徴とする、請求項１～６のいずれかに記載の美容方法。
【請求項８】
乳化化粧料が、高級アルコール、脂肪酸モノグリセリル及びグリセリンアルキルエーテルから選ばれる一種又は二種以上の両親媒性物質を０．５～６質量％含有することを特徴とする請求項１～７のいずれかに記載の美容方法。
【請求項９】
シート基材層、皮膚表面に粘着可能な粘着剤層及び剥離層を有し、かつ水蒸気透過度が２００～２，０００ｇ／ｍ^2・２４ｈｒｓである皮膚貼付用シート、及び、油性成分を５～５０質量％含有する乳化化粧料を有する美容キット。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は、目尻、口元、額、首部など、皺が発生している、あるいは発生するおそれのある部位の保湿を行って、皺の改善又は発生の抑制を図るための美容方法に関する。本発明は、純粋な美容に関する発明であり、治療を対象とするものではない。
【背景技術】
【０００２】
従来、医療、衛生、化粧等様々な用途に対して皮膚に接着するテープやシートが開発されてきた。例えば、弾性を少なくとも１２ヶ月間維持するエラストマー繊維を組合せたものを含み、少なくとも２００％の伸張性を有するオレフィン樹脂のブレンドを含む、身体適合性の高い整形外科用キャスティングテープ（特許文献１参照）や、肌追従型薄層フィルムである支持体の上面に膏体層が形成され、該膏体層の上面に、一対の剥離ライナーからなる剥離材が重ね合わされた、肌への追従性がよく、全体的に薄く、膏体層を均一にでき、屈曲部位に貼り付けても皺ができずに剥がれにくい貼付剤（特許文献２参照）が報告されている。
【０００３】
また、皺を物理的に伸ばすために、シートを用いる例も知られており、例えば、粘着性を有する、外観が透明または半透明のシート状製剤であって、同シートの内部またはその

表面に、開口率が十分に大きい編織布及び／又は不織布を厚み方向に積層させてあることを特徴とする、目尻、口元、額、首部の皺を伸ばして固定する目的の皺伸ばしシート（特許文献３参照）や、ストレッチ性のある基材層に粘着剤を３５ｇ／ｍ^{2}以上の厚塗りで塗布したことを特徴とする、皮膚の表面の皺を引っ張って伸ばし固定するストレッチ・テープ（特許文献４参照）が報告されている。

【０００４】

ところで、これらの医療、衛生用の粘着テープやシートは、発汗により生じた水分を外部へ逃がし、ムレを防ぐために透湿性に優れていることが通常要求される。そのため、例えば、ジオール成分として、ポリオキシテトラメチレングリコール、ブタンジオール、ポリエチレングリコール及びポリプロピレングリコールからなる群から選ばれる少なくとも一種と、イソシアネート成分として、メタンジフェニレンジイソシアネートとから得られるエーテル系ウレタン樹脂から成ることを特徴とする皮膚貼付材用フィルム基材（特許文献５参照）や、４０℃の水に５分間浸漬した際の長さ変化で表される水膨潤率が５％以下であることを特徴とする厚みが１０μｍ～５０μｍであるウレタン系樹脂からなる皮膚貼付材用フィルム基材（特許文献６参照）や、厚みが１０μｍ～５０μｍのエーテル系ウレタン樹脂からなり、少なくとも一方向の引張強度が５～３０Ｎ／２０ｍｍ幅、少なくとも一方向の伸びが４００～１，０００％、少なくとも一方向の引裂強度が４００～１，０００Ｎ／ｃｍ厚であることを特徴とする皮膚貼付材用フィルム基材（特許文献７参照）であって、それぞれ透湿度が、８００～４，０００ｇ／ｍ^2・２４ｈｒｓであるフィルム基材が提案されている。

【０００５】

かかるシートの皮膚に対する接着性を高めること等を目的として、粘着剤の開発も行われており、アクリル系重合体１００質量部と、この重合体と相溶する室温で液状ないしはペースト状の成分が３０～１００質量部からなる粘着剤組成物であって、この液状ないしはペースト状の成分が、炭素数８～１８の一塩基酸ないしは多塩基酸と炭素数が１４～１８の分岐アルコールのエステル及び／又は炭素数が１４～１８の不飽和脂肪酸ないしは分岐酸と４価以下のアルコールのエステルからなり、且つ上記アクリル系重合体の４０～８０質量％が架橋により不溶化されていることを特徴とする医療用粘着剤を支持体の少なくとも片面に設けてなる医療用外用材（特許文献８参照）や、基材フィルムの片面に感圧性接着剤層を設けてなる貼付材であって、前記接着剤層はアクリル酸又はメタクリル酸のアルキルエステル単量体４０～８０質量％、アルコキシル基含有エチレン性不飽和単量体１０～５０質量％及びカルボキシル基含有エチレン性不飽和単量体１～１０質量％からなる共重合体を主体とし、該共重合体のガラス転移点が２５０Ｋ以下であり、且つ乾燥後の共重合体のゲル分率が２５％以上であることを特徴とする外用貼付材（特許文献９参照）や、アルキル基の炭素数が４以上の（メタ）アクリル酸アルキルエステルを主成分として共重合した共重合体および当該共重合体と相溶する液体成分とを含む架橋ゲル層が支持体の少なくとも片面に形成されてなり、当該共重合体と当該液体成分との含有質量比が、１．０：０．６～１．０：１．８であり、かつベークライト板への接着力が２５０ｇ／１２ｍｍ幅以下であるアクリル系ゲル材（特許文献１０参照）や、支持体の少なくとも片面にアクリル酸エステル系重合体と、該重合体と相溶する液状成分とを含む粘着剤層を形成してなる粘着シートであって、粘着剤層は剪断応力を加えた場合に凝集破壊または界面破壊が生じない弾性体であると共に、剪断応力を加えた際のずれ変形移動完了距離が粘着剤層の厚みの０．５～６倍であることを特徴とするアクリル系粘着シート（特許文献１１参照）や、エラストマーフィルムの片面に担持フィルムを設けてなる積層フィルムのエラストマーフィルム側に、粘着剤層が形成された粘着シートであって、該粘着剤層はアクリル系重合体を主成分としており、この重合体と相溶する常温で液状ないしはペースト状の成分が、上記粘着剤層および担持フィルムの両方に存在しており、担持フィルムが剥離可能な状態でエラストマーフィルムの片面に形成されていることを特徴とする皮膚貼付用粘着シート（特許文献１２参照）が報告されている。

【０００６】

また、ポリオール成分が、繰返し単位がポリオキシアルキレン骨格を有するポリエーテルポリオールを少なくとも１種類含んでおり、前記ポリオール成分とポリイソシアネート成分とを反応させて得られるポリエーテルウレタンからなるフィルム上に、アクリル酸エステル系ポリマーと、該アクリル酸エステル系ポリマーに対して相溶可能であり、常温で液状もしくはペースト状である、炭素数が１６以上のカルボン酸エステルと、架橋剤成分とを含む樹脂組成物から形成した粘着剤層を有し、４０℃、３０％ＲＨの雰囲気下で２４時間保存したときの透湿度が８００ｇ／ｍ^2・２４ｈ・４０℃・３０ＲＨ以上、２，４００ｇ／ｍ^2・２４ｈ・４０℃・３０ＲＨ以下であることを特徴とする皮膚貼着用粘着シート（特許文献１３参照）や、屈折率が１．４５以上１．５５以下であるポリウレタンを含有する樹脂シート上に、アクリル系粘着剤、シリコーン系粘着剤及びポリウレタン系粘着剤の一種以上を含有する粘着層を有する皮膚のたるみを改善するために用いられる粘着シート（特許文献１４参照）や、ポリエチレンとポリスチレンを共重合したジェル状の皮膚保護用シートの片面、又はシリコンジェルシートの片面にポリウレタンフィルムを貼り着け、さらに当該片面の反対側の面は剥離紙を貼り着けたことを特徴とする皮膚保護用シート（特許文献１５参照）などが提案されている。

【０００７】

その他、化粧用シートとしては、可撓性の熱可塑性エラストマ若しくはゴムからなり、ラジウムを含む湯の花を含有するラジウム放射性セラミックスが混練されている、シリコーンゴム又はポリウレタンからなることを特徴とする、人の肌に被せて使用する美肌シート（特許文献１６参照）や、皮膚表面に粘着可能な粘着層を設けてなる基材シートの粘着層に剥離可能な離型シートが接合されてなる化粧シートにおいて、該離型シートには、ループ状の切離し線が形成されており、該切離し線は基材シートの輪郭線の内側に設けられ、かつ、該基材シートへの皮膚外用剤又は薬液の塗布、含浸域に相当することを特徴とする、物理的な引張りによって、皮膚を引き締めて活性化すると同時に、薬剤を速やかに皮膚面に浸透させ、パックを短時間で完結させるための機能を具備する化粧シート（特許文献１７参照）や、液体を含浸させて顔面に載置される化粧用シート体において、顔面の左右の頬のそれぞれに対向する第１及び第２の頬対向部と、前記第１及び第２の頬対向部のそれぞれに連続して顔面の左右の鼻翼のそれぞれに対向する第１及び第２の鼻翼対向部と、横方向の中央部に形成されて前記第１及び第２の鼻翼対向部を互いに分離する分離形状と、を設けた化粧用シート体（特許文献１８参照）などが提案されている。

【０００８】

一方、皮膚の保湿性を高めることを目的とする乳化化粧料としては、プロピレン又は１－ブテンをモノマーとする単独重合体であるオレフィン重合体と２０℃でペースト状を示す抱水性油剤を含有することを特徴とし、抱水性油剤が、Ｎ－ラウロイル－Ｌ－グルタミン酸（コレステリル又はフィトステリル・ベヘニル・オクチルドデシル）、ジペンタエリトリット脂肪酸エステル、マカデミアンナッツ油脂肪酸フィトステリル、ヒドロキシステアリン酸コレステリル等からから選ばれる保湿効果とその持続性が高い乳化化粧料（特許文献１９参照）や、ダイマー酸とダイマージオールとのエステル、Ｎ－アシルグルタミン酸のジエステル、（ピロリドンカルボン酸／脂肪酸）グリセリル等の抱水性の液状油性成分を含有するマイクロエマルション剤形の粘度１０００～４０００ｍＰｓの液状化粧料を含む化粧料セット（特許文献２０参照）や、２－メタクリロイルオキシエチルホスホリルコリンの単独重合体または、２－メタクリロイルオキシエチルホスホリルコリンと疎水性モノマーとの共重合体から選ばれる一種又は二種以上と、抱水性油剤を１～５０質量％含有することを特徴とする乳化化粧料（特許文献２１参照）や、コレステロールエステル等の抱水性油分を抱水性組成物全量中の５～８０質量％含有する抱水組成物含有する乳化化粧料（特許文献２２参照）や、油溶性Ｎ－長鎖アシル酸性アミノ酸モノ又はジエステルなどの、５０℃で抱水させ室温に戻したとき自重の１３５％以上の水を抱水することが可能な抱水性油分を０．１～９０質量％含むほか、水膨潤性粘土鉱物を第四級アンモニウム塩で処理して得られる有機変性粘土鉱物と水とを含有してなる油中水型乳化組成物（特許文献２３参照）などが報告されている。

【０００９】
さらに、化粧料を皮膚に塗布した後にテープやシートを貼付する組合せに関するものとして、ヒアルロン酸を必須有効成分とし、ビオセラミド、ソウハクヒ抽出液、アミノカプロン酸、ローヤルゼリー、イノシット、海洋性コラーゲン、酵母エキス、グリチルリチン酸ジカリウムの中から一成分、あるいは二成分以上を補助成分として、スクワランを用いてクリーム状にし、これを適用部位に塗布した後、絹不織布シートで保温する基礎化粧方法（特許文献２４参照）や、皮膚上の前記エマルジョンの上に貼付される感圧接着剤物品が、前記皮膚に直接貼付される前記感圧接着剤テープの接着力のレベルの少なくとも約５０％で接着する油中水エマルジョン（特許文献２５参照）が報告されている。

【先行技術文献】

【特許文献】

【００１０】

【特許文献１】特開平８－３０８９１９号公報
【特許文献２】特開２００４－１８８００５号公報
【特許文献３】特開２００１－３３５４３０号公報
【特許文献４】特開２００４－３１３２７７号公報
【特許文献５】特開２００５－２１８４９４号公報
【特許文献６】特開２００５－２１８４９５号公報
【特許文献７】特開２００５－２１８４９６号公報
【特許文献８】特許第２５３９３３０号公報
【特許文献９】特許第２５８４８６６号公報
【特許文献１０】特許第２７００８３５号公報
【特許文献１１】特許第２９７１９９８号公報
【特許文献１２】特許第３８０８７７１号公報
【特許文献１３】特許第３８８４９９５号公報
【特許文献１４】特開２００８－１４３８７６号公報
【特許文献１５】特開２００８－２６６２３２号公報
【特許文献１６】特開２００４－３５７８３３号公報
【特許文献１７】特開２００５－１８５３９１号公報
【特許文献１８】特開２００８－１８８０８５号公報
【特許文献１９】特開２００８－２４７８３３号公報
【特許文献２０】特開２００７－９９６５４号公報
【特許文献２１】特開２００４－１４３０６３号公報
【特許文献２２】特開平９－２０８４２３号公報
【特許文献２３】特開平８－２０５２９号公報
【特許文献２４】特開２００６－１８８４８０号公報
【特許文献２５】特表２００５－５１７５１８号公報

【発明の概要】

【発明が解決しようとする課題】

【００１１】
これまで、目尻、口元、額、首部などの皮膚の皺を改善のためには、シートやテープを貼付して引っ張る方法、保湿用化粧料を塗布する方法、保湿用化粧料を含浸したシートを貼付する方法、保湿用化粧料を塗った後、シートで被覆する方法などがあったが、いずれも、皺の改善に充分な効果を奏していないか、あるいは手間が掛かり過ぎるという問題点があった。そこで、本発明は、皺を充分に改善し、併せて皺の発生を抑制することのできる簡便な美容方法を提供することを目的とする。

【課題を解決するための手段】

【００１２】
本発明者らは、鋭意検討を行った結果、皮膚の皺の改善が必要な部位に保湿用化粧料として乳化化粧料を塗った後、水蒸気透過性が比較的低い皮膚貼付用粘着シートを貼付して

、適用部位の保湿を行うことにより皮膚を充分に改善することができることを見出した。さらに皮膚貼付用粘着シートの粘着剤として、一般的に用いられているようなアクリル系粘着剤やゴム系粘着剤を使用した場合には、化粧料を塗布した部位へ貼付した際にはがれやすいのに対して、有機液状成分を含有するゲル系粘着剤を用いた場合には、乳化化粧料を塗布した部位に貼付した際にもはがれにくい点で好ましいことを見出し、本発明の美容方法を完成した。

【００１３】

すなわち本発明は、

（１）皮膚上に、油性成分を５～５０質量％含有する乳化化粧料を塗布した後、シート基材層と皮膚表面に粘着可能な粘着剤層を有し、かつ、シート基材層と粘着剤層を含むシート全体の水蒸気透過度が２００～２，０００ｇ／ｍ^2・２４ｈｒｓである皮膚貼付用シートを貼付することからなる美容方法、

（２）皮膚の皺を改善又は皺の発生を抑制する美容方法であることを特徴とする上記（１）記載の美容方法、

（３）シート基材層と粘着剤層を含むシート全体の引張強度が２０～２００Ｎ／ｃｍであることを特徴とする上記（１）又は（２）記載の美容方法、

（４）シート基材層がポリウレタンからなることを特徴とする上記（１）～（３）のいずれかに記載の美容方法、

（５）シート基材層の厚みが３０～２５０μｍであることを特徴とする上記（１）～（４）のいずれかに記載の美容方法、

（６）粘着剤層が、有機液状成分を含有するゲル系粘着剤からなることを特徴とする上記（１）～（５）のいずれかに記載の美容方法、

（７）油性成分中に抱水性油性成分を１０～８０質量％含有することを特徴とする、上記（１）～（６）のいずれかに記載の美容方法、及び、

（８）乳化化粧料が、高級アルコール、脂肪酸モノグリセリル及びグリセリンアルキルエーテルから選ばれる一種又は二種以上の両親媒性物質を０．５～６質量％含有することを特徴とする上記（１）～（７）のいずれかに記載の美容方法に関する。

【００１４】

また、本発明は、

（９）シート基材層、皮膚表面に粘着可能な粘着剤層及び剥離層を有し、かつ水蒸気透過度が２００～２，０００ｇ／ｍ^2・２４ｈｒｓである皮膚貼付用シート、及び、油性成分を５～５０質量％含有する乳化化粧料を有する美容キットに関する。

【発明の効果】

【００１５】

本発明の方法により、顕著な皺の改善・発生の抑制、皺改善期間の短縮化が図れる。

【図面の簡単な説明】

【００１６】

【図１】本発明の皮膚貼付用シートの具体例を示す図である。

【発明を実施するための形態】

【００１７】

以下、本発明の詳細について説明する。

（皮膚貼付用シート）

本発明において使用する皮膚貼付用シートは、シート基材層と皮膚表面に粘着可能な粘着剤層を有する。粘着剤層側には、剥離可能な剥離層を設け、使用前に剥離するようにしてもよい。また、シート基材層における粘着剤層形成面と反対側には印刷層などを有していてもよい。剥離層を設ける場合は、剥離層を皮膚貼付用シート１枚ごとに設けてもよいし、１枚の剥離シートに複数枚の皮膚貼付用シートを設けるようにしてもよい。

【００１８】

また、本発明における皮膚貼付用シートは、乳化化粧料中の水分が容易に蒸発しない程度に水蒸気透過性が比較的小さいものが使用され、水蒸気透過度（Ｄｒｙ法）が２００～

２，０００ｇ／ｍ^2・２４ｈｒｓであり、好ましくは２００～１，５００ｇ／ｍ^2・２４ｈｒｓである。ここで、水蒸気透過度とは、所定の条件下におけるシートの１ｍ^{2}当りの水蒸気の透過量であり、所定量の水を所定の口径を有する容器内部に入れた後、容器の口をシートで覆い、温度４０℃、相対湿度３０％Ｒ．Ｈ．の条件下で２４時間放置したときの水の減少量を１ｍ^{2}当りに換算した値である。水蒸気透過性が小さすぎると長時間貼付時に皮膚がふやけ角層水分量が上昇しバリア機能の低下を招き、赤斑やかゆみが生じる場合がある。さらに、貼付した皮膚表面と本発明の皮膚貼付用シートとの間が湿潤状態になりやすく、粘着力の低下を招いて皮膚面からの脱落を生じやすくなる。一方、水分透過性が高すぎると皺改善効果が低下する傾向を示す。

【００１９】

本発明における皮膚貼付用シートは、貼付する部位の皮膚全体のカーブに追従する程度の柔らかさを有するが、皮膚の皺の凹凸や微細な表情の動きがあっても、それに追従して凹凸を作らない程度の硬さを有する必要がある。皮膚の皺の凹凸や微細な表情の動きに合わせて湾曲すると皺の改善効果が少なくなる。上記水蒸気透過性及び硬さを有するため、シート全体の厚さは、通常、３０～２５０μｍであり、５０～２００μｍが好ましい。また、本発明の皮膚貼付用シートは、皮膚上の適用部位に応じて、適宜、サイズを設定すればよい。

【００２０】

上記皮膚貼付用シートの硬さの指標としては、ＪＩＳ　Ｌ１０９６に規定する剛軟性Ａ法による剛軟度（４５°カンチレバー法、基材幅２０ｍｍ、基材長さ１５０ｍｍ）を、１５～２５ｍｍの範囲とすることによって、貼付使用中の皮膚面の動きや皺の凹凸に対する追従性や取扱性、貼付中の違和感低減に効果的である。

【００２１】

（シート基材層）

本発明において使用するシート基材層は、上記のとおり、乳化化粧料中の水分が容易に蒸発しない程度に水蒸気透過度が大きくないことが必要であると共に、貼付する部位の皮膚全体のカーブに追従する程度の柔らかさを有し、かつ、皮膚の皺の凹凸や微細な表情の動きには追従しない程度の硬さを有する必要がある。このようなシート基材層を構成するための材質としては、ポリエチレンやポリプロピレンなどのポリオレフィン、ポリテトラエチレンテレフタレートなどのポリエステル、ポリエーテルポリウレタンやポリエステルポリウレタンなどのポリウレタン、ポリアミド、ポリ酢酸ビニル、エチレン－酢酸ビニル共重合体、エチレン－ビニルアルコール共重合体、ポリ塩化ビニル、ポリ塩化ビニリデンなどの各種プラスチック材料の単層体もしくは積層体を用いることができる。これらのうち、皮膚追従性等の優れた柔軟性を発揮させるためには、特にポリウレタンが好ましい。本発明のシート基材層として用いられるポリウレタンは、主鎖の繰り返し単位中にウレタン結合（－ＮＨＣＯＯ－）を有する重合体であって、本発明の皮膚貼付用シートとして使用しうるものであれば特に制限はないが、主として、イソシアネート類とポリヒドロキシ化合物との反応により製造されるポリエーテル系、ポリエステル系の重合体である。

【００２２】

イソシアネート類としては、トリレンジイソシアネート、４，４’－ジフェニルメタンジイソシアネート（ＭＤＩ）、１，５－ナフチレンジイソシアネート（ＮＤＩ）、トリジンジイソシアネート、１，６－ヘキサメチレンジイソシアネート（ＨＤＩ）、イソホロンジイソシアネート（ＩＰＤＩ）、キシレンジイソシアネート（ＸＤＩ）、トリイソシアネート、テトラメチルキシレンジイソシアネート（ＴＭＸＤＩ）、１，８－ジイソシアネートメチルオクタン、リジンエステルトリイソシアネート、ビシクロヘプタントリイソシアネート等を例示することができ、これらの中でも、入手のし易さや機械的強度に優れたポリマー構造が得られる点から、４，４’－ジフェニルメタンジイソシアネート（ＭＤＩ）を用いることが好ましい。

【００２３】

また、ポリヒドロキシ化合物としては、エチレングリコール、１，３－プロピレングリ

コール、１，２－プロピレングリコール、１，３－ブタンジオール、１，４－ブタンジオール、１，５－ペンタンジオール、１，６－ヘキサンジオール、３－メチル－１，５－ペンタンジオール、ネオペンチルグリコール、１，８－オクタンジオール、１，９－ノナンジオール、ジエチレングリコール、１，４－シクロヘキサンジメタノール、グリセリン等の脂肪族ポリオール、１，４－ジメチロールベンゼン、ビスフェノールＡのエチレンオキサイド付加物、プロピレンオキサイド付加物などの芳香族グリコール等を例示することができ、これらの中でも、水膨潤性を抑制しつつ高透湿性を確保することができるという点からは、ポリオキシテトラメチレングリコールと、ポリエチレングリコールおよび／またはポリプロピレングリコールのランダム重合体を用いることが好ましく、ポリオキシテトラメチレングリコール、ポリエチレングリコール、ポリプロピレングリコールは、用途に応じて適当な分子量を有するものが選択されることが好ましいが、例えば質量平均分子量が５００～３０００のものが好ましいものとして挙げられる。

【００２４】

これらのうち、ポリウレタンとしては、イソシアネート類としてＭＤＩを用い、ポリヒドロキシ化合物としてポリオキシテトラメチレングリコールとポリエチレングリコールおよび／またはポリプロピレングルコールを用いることが好ましく、ポリエーテル系ポリウレタン中にポリヒドロキシ化合物として、ポリオキシテトラメチレングリコール５～６０質量％、ポリエチレングリコール１０～５０質量％含有させることがさらに好ましく、特にポリエーテル系ポリウレタン中にポリヒドロキシ化合物として、ポリオキシテトラメチレングリコール５～４５質量％、ポリエチレングリコール２０～４５質量％を含有することが好ましい。さらに、鎖延長剤を使用することができ、鎖延長剤としては従来公知の材料を用いることができるが、例えば、エチレングリコール、プロピレングリコール、ブタンジオール等のジオール類、エチレンジアミン、トリレンジアミン等のジアミン類を挙げることができる。また、ポリウレタンの基材の厚さとしては、通常３０～２５０μｍであり、特に、５０～１５０μｍが好ましい。また、引張強度として、２０～２００Ｎ／ｃｍの範囲、特に、２０～１００Ｎ／ｃｍの範囲とすることが、貼付時の違和感の低減や皺伸ばし効果の点から好ましい。

【００２５】

本発明に使用されるポリウレタンは、上記イソシアネート類とポリヒドロキシ化合物を原料として公知の製造法により製造することができるが、例えば、特開２００５－２１８４９５号公報などに記載された方法により製造することができる。即ち、本発明に使用されるポリウレタンは、例えば、ワンショット法又はプレポリマー法を用いて重合することができる。また、溶剤を使用しないバルク重合であっても、粘度低減のために溶液中で重合を行ってもよい。このうち、バルク重合について説明すると以下のとおりである。反応容器にポリヒドロキシ化合物を投入し、温度が５０～８０℃になるように調整し攪拌しつつ、イソシアネート類を添加してウレタン化を起こさせる。さらに鎖延長剤を添加して反応させた後、反応生成物をトレーに移動して、１００～１５０℃で４時間以上保持し、反応を完結させることによって、塊状のポリウレタンを得ることができる。

【００２６】

次に、塊状のポリウレタンを粉砕してペレット化し、この樹脂ペレットを溶融させた後、Ｔダイ押出し機やインフレーションダイ押出機を用いて、シート状に押出すことにより、ポリウレタンからなるフィルム基材を形成することができる。なお、シート状に押出されたフィルム基材は、通常、巻き取られる。あるいは、カレンダー加工により、２本の加熱したロール間でポリウレタンを圧延、伸展し、シート化することによりポリウレタンからなるフィルム基材が形成され、フィルム基材は必要に応じて巻き取られる。あるいはまた、樹脂ペレットをＮ，Ｎ－ジメチルアミド等の溶剤に溶解し、この溶液をバーコーター等を用いて例えばポリエステルフィルム等の剥離ライナー上に塗布し、乾燥させて溶剤を除去することにより、ポリウレタンからなるフィルム基材を形成してもよい。

【００２７】

必要に応じて、フィルムに通常使用される添加剤、例えば紫外線吸収剤、老化防止剤、

充填剤、顔料、着色剤、難燃剤、帯電防止剤などを添加することができる。これらの添加剤は、その種類に応じて通常の量で用いられる。

【００２８】

（粘着剤層）

本発明の粘着剤層に使用される粘着剤は、シート基材層に塗布でき、かつ、貼着した皮膚に対して粘弾性を有し、皮膚に対して刺激の少ないものであることが必要である。さらに、乳化化粧料中の水分が容易に蒸発しない程度に水蒸気透過性が小さいことが必要であると共に、貼付する部位の皮膚全体のカーブに追従する程度の柔らかさを有し、かつ、皮膚の皺の凹凸に追従しない硬さを有する必要がある。そのため、粘着剤層に使用される粘着剤としては、その材料について特に限定されるものではなく、アクリル系粘着剤やゴム系粘着剤、シリコーン系粘着剤などを用いることができる。これらのうち、粘着特性の調整、皮膚低刺激性などの観点から、アクリル系粘着剤を用いることが好ましい。また、粘着剤の性状の点からは皮膚面への低刺激性や乳化化粧料との相性（相溶性等）の観点から、ゲル系粘着剤が好ましく、特に、有機液状成分を含有するゲル系粘着剤が好ましい。

【００２９】

ゲル系粘着剤としては、一般的にヒドロゲル系粘着剤、オルガノゲル系粘着剤などがあるが、本発明では皮膚面上に塗布した乳化化粧料上に皮膚貼付用シートを貼付し、しかも貼付中はしっかりと粘着固定しておく必要があるので、水分を保持しているヒドロゲル系粘着剤よりも貼付中での粘着特性の変動が少ないオルガノゲル系粘着剤を用いることが好ましい。

【００３０】

このようなオルガノゲル系粘着剤としては、有機液状成分を多く含んだアクリル系粘着剤を用いることが好ましく、有機液状成分とアクリル系粘着剤が相溶することによって粘着剤層の凝集力が低下する場合には、凝集力の低下を防止するために架橋剤によって架橋する。それにより、含有する有機液状成分の相分離や、粘着剤層中からの溶出を防止することが出来る。

【００３１】

粘着剤層において使用するアクリル系粘着剤に用いるモノマー混合物は、皮膚接着性（粘着性）を付与するための（メタ）アクリル酸アルキルエステルを主モノマーとし、凝集力等を付与するための共重合可能な不飽和モノマーを副モノマーとし、これらを共重合させてアクリル系粘着剤とする。

【００３２】

上記（メタ）アクリル酸アルキルエステルの具体例としては、アクリル酸またはメタクリル酸のアルキルエステル、具体的には炭素数が１～１２、好ましくは４～９のアルキルエステルを１種類もしくは２種類以上併用して用いることができる。

上記（メタ）アクリル酸アルキルエステルと共重合する不飽和モノマーとしては、アルコキシ基含有エチレン性不飽和モノマーや、カルボキシル基含有エチレン性不飽和モノマーなどを用いることができる。

【００３３】

アルコキシ基含有エチレン性不飽和モノマーは、粘着剤層に親水性や透湿性を付与するために含有させることが好ましく、具体的には、メトキシポリエチレングリコール（メタ）アクリレート、エトキシジエチレングリコール（メタ）アクリレート、ブトキシジエチレングリコール（メタ）アクリレート、メトキシエチル（メタ）アクリレート、エトキシエチル（メタ）アクリレート、ブトキシエチル（メタ）アクリレートなどの炭素数が１～４のアルコキシ基を有するアルコキシアルキル（メタ）アクリレートを用いることが好ましい。

また、カルボキシル基含有エチレン性不飽和モノマーとしては、粘着剤層に凝集性を与えたり、粘着剤を架橋処理する際の反応点を確保するため含有させることが好ましく、具体的には、アクリル酸、メタクリル酸、イタコン酸、クロトン酸、フマール酸、（無水）マレイン酸が挙げられる。これらのうち、共重合性や取り扱い性などの点から、アクリル

酸やメタクリル酸を用いることが好ましい。

【００３４】

さらに粘着剤層に親水性の付与が必要な場合、共重合性モノマーとして、スチレンや酢酸ビニル、Ｎ－ビニル－２－ピロリドン、２－ヒドロキシエチルアクリレート、２－ヒドロキシプロピルアクリレートなどのモノマーも必要に応じて適宜共重合してもよい。

【００３５】

アクリル系粘着剤からなる粘着剤層をオルガノゲル系粘着剤にする場合には、得られるオルガノゲル粘着剤中のアクリル系共重合体の質量平均分子量は１５０万以下、好ましくは５０万～１００万程度に調整することが、粘着剤層の凝集性付与の点から望ましいものである。

また、貼付する皮膚面の凹凸に対する粘着剤層表面の密着性を向上させ、さらに耐汗接着性を発揮させる観点からは、アクリル系粘着剤１００質量部に対して２０～１２０質量部の有機液状成分を含有させてオルガノゲル状の粘着剤を作製することが好ましい。

【００３６】

有機液状成分とは油状成分であって、代表的には脂肪酸エステルやカルボン酸エステル、グリセリンエステルなどが挙げられる。脂肪酸エステルとしては、前記アクリル系重合体に親和性、相溶性を示すと共に、発汗時の水分に対しても親和性を示すものであって、具体的には、ミリスチン酸エチル、ミリスチン酸イソプロピル、パルミチン酸イソプロピル、ステアリン酸ブチル、イソステアリン酸イソプロピル、ラウリル酸ヘキシル、乳酸セチル、乳酸ミリスチル、フタル酸ジエチル、ミリスチン酸オクチルドデシル、オレイン酸オクチルドデシル、ジメチルオクタン酸ヘキシルデシル、２－エチルヘキサン酸セチル、２－エチルヘキサン酸イソセチル、２－エチルヘキサン酸ステアリル、コハク酸ジオクチルなどの一価アルコールを用いたカルボン酸エステルや、ジカプリル酸プロピレングリコール、ジカプリン酸プロピレングリコール、ジイソステアリン酸プロピレングリコール、モノカプリル酸グリセリル、トリカプリル酸グリセリル、トリ２－エチルヘキサン酸グリセリル、トリカプリン酸グリセリル、トリラウリン酸グリセリル、トリイソステアリン酸グリセリル、トリオレイン酸グリセリル、トリ２－エチルヘキサン酸トリメチロールプロパンなどの二価以上の多価アルコールを用いたカルボン酸エステルを用いることができる。

【００３７】

上記のカルボン酸エステルのうち、酸化劣化を防止するという観点から不飽和二重結合を有さない飽和脂肪酸を用い、皮膚への低刺激性や経済性の点からグリセリンエステルとすることが望ましい。従って、飽和脂肪酸としては、カプリル酸やカプリン酸、２－エチルヘキサン酸などの飽和脂肪酸と、一価もしくは多価アルコールとのエステル化物を用いることが好ましく、最も好ましくはカプリル酸トリグリセリル、２－エチルヘキサン酸トリグリセリルを用いることが望ましい。

【００３８】

上記、カルボン酸エステルのうち、不飽和結合を有するものを用いた場合、大気中の酸素によって酸化劣化して物性変化を起こし、所望の特性を発揮しない恐れがあるので、このような場合には酸化防止剤を粘着剤中に配合しておくことが好ましい。

【００３９】

上記組成物を含むオルガノゲル系粘着剤におけるアクリル系共重合体は、その３０～８０質量％、好ましくは３５～７０質量％が不溶化（ゲル化）するものであることが好ましい。なお、ここでの「不溶化」とは、具体的にはトルエンに溶解しないという意味である。また、不溶化率は、乾燥したサンプルをトルエン中に常温で７日間浸漬し、平均孔径０．２μｍのポリテトラフルオロエチレン膜（日東電工社製、ＮＴＦ膜）にて不溶分を濾別、乾燥して浸漬前の乾燥サンプル質量との比率で算出した値である。

【００４０】

上記不溶化率が３０質量％に満たない場合は形成した粘着層の内部凝集力が不十分となって、皮膚面への貼付中にずれが生じたり、皮膚面から剥離したときに皮膚面に粘着剤が

残留する、所謂糊残り現象を生じる恐れがある。

【００４１】

一方、不溶化率が８０質量％を超える場合には、皮膚接着性が極端に低下し、貼付使用中に端部剥がれや、剥離脱落現象を生じる恐れがある。

【００４２】

また、アクリル系粘着剤を不溶化する方法として、一般的に架橋処理を施す方法を採用することができる。架橋処理としては、有機過酸化物やイソシアネート化合物、有機金属塩、金属アルコラート、金属キレート、エポキシ化合物、一級アミノ化合物等の架橋剤を用いた化学的架橋や、電子線や紫外線等の電離性放射線を照射してなる架橋を行うことができる。

【００４３】

さらに、上記のようにして得られた粘着剤に対して、必要に応じてグリセリンやポリエチレングリコール、ポリプロピレングリコールなどの多価アルコールに代表される可塑剤や、ポリアクリル酸、ポリアクリル酸架橋体、ポリビニルピロリドンに代表される水溶性もしは吸水性の樹脂、ロジン系樹脂、テルペン系樹脂、石油系樹脂に代表される粘着性付与樹脂、各種軟化剤、各種充填剤、顔料などの各種添加剤を配合してもよい。

【００４４】

粘着剤層の厚さとしては、通常５～８０μｍであり、特に、１０～５０μｍが好ましい。

さらに、皮膚に対する粘着力は以下の測定方法で０．２～１．５Ｎ／１０ｍｍが好ましい。

【００４５】

測定方法：前腕内側部に０．０２ｇの乳化化粧料を塗布。その後、シート貼付部を意識し、人指し指で往復１０回擦り込む。化粧料を塗りこんだ肌に皮膚貼付用シート（２ｃｍ×５ｃｍ）を貼付し、指で軽く圧着した。１５分間腕を動かさないよう安静にし、その後はがしたときの抵抗を引張試験機で９０°ピールをし、最大値の値を粘着力とした。測定機器はテンシロン型引張試験機を用いた。（剥離速度３００ｍｍ／分、ｎ＝３）本測定方法における乳化化粧料としては、後述の実施例の「２乳化化粧料の製造」において調製されたものを使用した。

【００４６】

（シート形状）

本発明に使用されるシート形状としては、皮膚下の筋肉に沿った形状であることが望ましい。筋肉に沿った形状でない場合は、微細な表情の動きに追随してシート自体が波打つことにより物理的な力による皺伸ばし効果が減少するからである。特に顔への貼付に関しては表情筋にそった形が望ましく、目じりの周辺の皺に関しては、眼輪筋に沿った形状が好ましい。一つの具体例を図１に示す。

【００４７】

（乳化化粧料）

本発明の乳化化粧料における油性成分としては、動物油、植物油、合成油等の起源を問わず、炭化水素類、エステル類、脂肪酸類、シリコーン油類、フッ素系油類等を挙げることができ、具体的には、流動パラフィン、スクワラン、ワセリン、ポリブテン、ポリイソブチレン等の炭化水素油類；オリーブ油、ヒマシ油、ミンク油、マカデミアンナッツ油等の油脂類；イソオクタン酸セチル、ミリスチン酸イソプロピル、パルミチン酸イソプロピル、ミリスチン酸オクチルドデシル、トリオクタン酸グリセリル、オレイン酸オレイル、オレイン酸オクチルドデシル、オレイン酸デシル、イソステアリン酸イソセチル、イソノナン酸イソトリデシル、ステアリン酸イソセチル、パルミチン酸イソプロピル、パルミチン酸－２－エチルヘキシル、パルミチン酸－２－ヘキシルデシル、ミリスチン酸オクチルドデシル、ミリスチン酸ミリスチル、オクタン酸セチル、テトラ－２－エチルヘキサン酸セチル、コハク酸－２－エチルヘキシル、モノイソステアリン酸アルキレングリコール、ジ－２－エチルヘキサン酸エチレングリコール、ジカプリン酸ネオペンチルグリコール、

トリ－２－エチルヘキサン酸トリメチロールプロパン、テトラ－２－エチルヘキサン酸ペンタエリスリトール、ジペンタエリスリトール脂肪酸エステル、ジイソステアリン酸ポリグリセリル、イソステアリン酸ジグリセリル、トリイソステアリン酸グリセリル、トリベヘン酸グリセリル、リンゴ酸ジイソステアリル、テトラ－２－エチルヘキサン酸ペンタエリトリット、ロジン酸ペンタエリトリットエステル、ジオクタン酸ネオペンチルグリコール、１２－ヒドロキシステアリン酸コレステリル、Ｎ－ラウロイル－Ｌ－グルタミン酸ジ（コレステリル・ベヘニル・オクチルドデシル）エステル等のエステル類；低重合度ジメチルポリシロキサン、高重合度ジメチルポリシロキサン、メチルフェニルポリシロキサン、デカメチルシクロペンタシロキサン、オクタメチルシクロテトラシロキサン、フッ素変性ポリシロキサン等のシリコーン類；パーフルオロデカン、パーフルオロオクタン、パーフルオロポリエーテル等のフッ素系油剤類を挙げることができ、これらは一種又は二種以上用いることができる。油性成分を配合することにより、水分だけでなく皮膚への油分の浸透を促し柔らかくしたり、シート除去時に皮膚がひっぱられて感じる痛みを緩和したり、シート除去後に皮膚の乾燥を防ぎ保護する他、皮膚を柔軟にすることにより皺伸ばし効果を持続させる。なかでも分子量３００～４００の油性成分を配合すると皺改善効果がさらに高くなり好ましい。分子量３００～４００の油剤としては、ジカプリン酸プロピレングリコール、ジ－２－エチルヘキサン酸ネオペンチルグリコール、イソノナン酸イソトリデシル、２－エチルヘキサン酸セチル、パルミチン酸オクチル、コハク酸ジ２－エチルヘキシル、オレイン酸エチルなどが挙げられる。

【００４８】

本発明に用いられる乳化化粧料における油性成分の含有量は、乳化化粧料全量中の５～５０質量％が好ましく、５～３０質量％がより好ましい。５質量％未満では、充分な弾力性、ツヤや潤い感、効果感が得られず、５０質量％を超えると適度で均一な膜厚感や密着感が得られず好ましくない。また先に記載の分子量３００～４００の油剤の配合量は限定されないが、好ましくは、３～２０質量％であり、更に好ましくは５～１０質量％である。

【００４９】

上記油性成分の中でも、自重と等量以上の水を抱え込むことのできる抱水性油性成分が肌への親和性を高めるために含まれることが好ましい。本発明で用いる「抱水性」とは、以下の抱水力試験により測定される抱水力（％）が１００％以上を示すものである。抱水力試験方法は、５０℃に加熱した試料（油性成分）１０ｇを２００ｍＬビーカーに秤り取り、ディスパーミキサーにて３０００ｒｐｍで攪拌しながら、５０℃の水を徐々に、水が試料から排液してくるまで添加し、水が排液しない最大量（質量）を測定し、この数値を試料１０ｇで除し、１００倍して抱水力（％）として評価している。本発明ではこのような抱水性油性成分のなかでも、とりわけＮ－ラウロイル－Ｌ－グルタミン酸ジ（コレステリル・ベヘニル・オクチルドデシル）エステル、Ｎ－ラウロイル－Ｌ－グルタミン酸ジ（フィトステリル・ベヘニル・オクチルドデシル）エステル、Ｎ－ラウロイル－Ｌ－グルタミン酸ジ（コレステリル・オクチルドデシル）エステル、Ｎ－ラウロイル－Ｌ－グルタミン酸ジ（フィトステリル・オクチルドデシル）エステル、ダイマー酸ジリノール酸（フィトステリル／イソステアリル／セチル／ステアリル／ベヘニル）、ヒドロキシステアリン酸コレステリル、ヒドロキシステアリン酸フィトステリル、ヘキサ（ヒドロキシステアリン酸／ステアリン酸／ロジン酸）ジペンタエリスリチル、ステアリン酸硬化ヒマシ油、マカデミアンナッツ脂肪酸コレステリル、トリイソステアリン酸ジグリセリル等が好ましい。抱水性油性成分の含有量は、油性成分中の１０～８０質量％が好ましく、３０～７０質量％がより好ましい。

【００５０】

本発明に用いられる乳化化粧料には、乳化を安定させるために高級アルコール、脂肪酸モノグリセリル、及び、グリセリンアルキルエーテルから選ばれる分子内に親水性基と親油性基の両方を有している両親媒性物質を用いることが好ましい。なかでも２５℃において固形の両親媒性物質は、べたつき感を与えずに、化粧膜に柔軟性を与え、化粧膜を厚く

することにより潤い感を高め、さらには皺を改善又は皺の発生を抑制する効果も期待することができ、特に好ましいものである。

【００５１】

このような高級アルコールとして、炭素原子数１４～３０の直鎖飽和高級アルコールを挙げることができ、具体的には、ベヘニルアルコール、トリデシルアルコール、ミリスチルアルコール、ペンタデシルアルコール、セチルアルコール、セトステアリルアルコール、ヘプタデシルアルコール、ステアリルアルコール等の直鎖飽和脂肪族アルコールやラノリンアルコール等を例示することができる。

【００５２】

脂肪酸モノグリセリルとしては、炭素原子数は１６～１８のものであり、具体的には、ステアリン酸グリセリル、パルミチン酸グリセリル等を例示することができる。

グリセリンアルキルエーテルとしては、炭素原子数は１６～１８のものであり、具体的には、グリセリンモノステアリルエーテル、グリセリンモノセチルエーテル等を例示することでできる。これらは必要に応じて１種、又は２種以上用いることができる。

【００５３】

両親媒性物質の含有量は、乳化化粧料全量中、０．５～６質量％であり、より好ましくは２～６質量％である。この範囲とすることにより、乳化化粧料の安定性が向上し、また塗布時の使用感に優れるものとなる。

【００５４】

本発明においては、前記抱水性油性成分と、前記両親媒性物質の含有質量比[抱水性油性成分量]／[両親媒性物質量]が０．８～５の範囲とすることで、皺改善の効果として好ましく、２～４の比率とすることで、さらに皺改善の効果に優れるものとすることができる。

【００５５】

本発明に用いられる乳化化粧料に配合される界面活性剤としては、油性成分を安定に乳化する目的のために配合され、通常化粧料に用いられている界面活性剤であれば特に限定されず、例えば、非イオン性界面活性剤、アニオン性界面活性剤、両性界面活性剤、カチオン性界面活性剤を挙げることができる。

【００５６】

上記非イオン性界面活性剤としては、グリセリン脂肪酸エステル及びそのアルキレングリコール付加物、ポリグリセリン脂肪酸エステル及びそのアルキレングリコール付加物、プロピレグリコール脂肪酸エステル及びそのアルキレングリコール付加物、ソルビタン脂肪酸エステル及びそのアルキレングリコール付加物、ソルビトールの脂肪酸エステル及びそのアルキレングリコール付加物、ポリアルキレングリコール脂肪酸エステル、蔗糖脂肪酸エステル、ポリオキシアルキレンアルキルエーテル、グリセリンアルキルエーテル、ポリオキシエチレンアルキルフェニルエーテル、ポリオキシエチレン硬化ヒマシ油、ラノリンのアルキレングリコール付加物、ポリオキシアルキレンアルキル共変性シリコーン、ポリエーテル変性シリコーンを例示することができる。

【００５７】

上記アニオン性界面活性剤としては、アルキルベンゼン硫酸塩、アルキルスルホン酸塩、α－オレフィンスルホン酸塩、ジアルキルスルホコハク酸塩、α－スルホン化脂肪酸塩、アシルメチルタウリン塩、Ｎ－メチル－Ｎ－アルキルタウリン塩、ポリオキシエチレンアルキルエーテル硫酸塩、ポリオキシエチレンアルキルフェニルエーテル硫酸塩、アルキル燐酸塩、ポリオキシエチレンアルキルエーテル燐酸塩、ポリオキシエチレンアルキルフェニルエーテル燐酸塩、Ｎ－アシルアミノ酸塩、Ｎ－アシル－Ｎ－アルキルアミノ酸塩、Ｏ－アルキル置換リンゴ酸塩、アルキルスルホコハク酸塩を例示することができる。

【００５８】

上記カチオン性界面活性剤としては、アルキルアミン塩、ポリアミン及びアルカノールアミン脂肪酸誘導体、アルキル四級アンモニウム塩、環式四級アンモニウム塩等を例示することができる。

【００５９】
上記両性界面活性剤としては、アミノ酸タイプやベタインタイプのカルボン酸型、硫酸エステル型、スルホン酸型、リン酸エステル型のものがあり、人体に対して安全とされるものが使用できる。例えば、Ｎ，Ｎ－ジメチル－Ｎ－アルキル－Ｎ－カルボキシルメチルアンモニウムベタイン、Ｎ，Ｎ－ジアルキルアミノアルキレンカルボン酸、Ｎ，Ｎ，Ｎ－トリアルキル－Ｎ－スルフォアルキレンアンモニウムベタイン、Ｎ，Ｎ－ジアルキル－Ｎ，Ｎ－ビス（ポリオキシエチレン硫酸）アンモニウムベタイン、２－アルキル－１－ヒドロキシエチル－１－カルボキシメチルイミダゾリニウムベタイン、レシチンを例示することができる。

【００６０】
また、本発明の乳化化粧料の構成成分として、レシチンが配合されることが好ましい。
レシチンは、大豆やその他植物由来でも、卵黄由来でも、水素添加されていてもされてなくとも良い。また、酵素処理でリゾ化していても良い。レシチンの配合により、配合成分の肌への浸透性が高まり、より高い皺改善効果が得られる。

【００６１】
本発明に用いられる乳化化粧料には、上記記載の成分以外にも必要に応じて、保湿剤、防腐剤、酸化防止剤、紫外線吸収剤、エモリエント剤、美容成分、香料、水溶性高分子、保湿顔料、着色顔料、光輝性顔料、有機粉体、疎水化処理顔料、タール色素等通常化粧料に用いられる成分を配合することができる。

【００６２】
本発明の乳化型化粧料の剤型としては、水中油型乳化化粧料又は油中水型乳化化粧料のいずれでもよく、形態としては、液状、低粘度乳液状、クリーム状のいずれも適用できる。また、本発明の乳化型化粧料としては、化粧水、美容液、乳液、クリーム、等の肌に直接適用する化粧料を好適に挙げることができる。

【００６３】
（皮膚の皺を改善する美容方法）
目尻、口元、額、首部など、皺のできている部位あるいはできやすい部位に、まず、上記乳化化粧料を適量塗布する。塗布後、その上に上記皮膚貼付用シートを貼付する。皮膚貼付用シートの貼付時間は、適宜設定しうるが、通常、一回当り１時間～１日、必要ならば繰り返し行う。皮膚貼付用シートは、使用の都度取り替えてもよく、繰り返し使用してもよい。また就寝前に使用し、起床後シートを剥がすといった使用方法が、皮膚の動きが少なくもっとも効果が高い。

【００６４】
（保湿用化粧キット）
本発明は、上記乳化化粧料１種類以上と上記皮膚貼付用シート１枚以上とをセットにしたキットとすることもできる。

【００６５】
以下に実施例を用いて本発明を詳細に説明するが、本発明の範囲は実施例に限定されるものではない。

【実施例】

【００６６】
［実施例１～１０及び比較例１～３］
１　皮膚添付用シートの製造
（１）シート基材の評価
まず、シート基材の違いによる肌への使用性について検討した。
本発明のシート基材を用いた皮膚添付用シートを下記の試験方法に従って皮膚面へ貼付した際の使用感を試験し、下記の表に記載した。また、各シート基材の剛軟度をＪＩＳＬ１０９６に規定する剛軟性Ａ法（４５°カンチレバー法）に従って測定した結果（ｎ＝５）を表１中に併記した。
＜使用感の試験方法＞

前腕内側部の中央部に縦１ｃｍ×横５ｃｍの大きさに裁断した皮膚貼付用シートを貼付し、指で軽く圧着した。貼付圧着後、約５時間経過した際の使用感を以下の判断基準で３段階評価し、その平均点を表１に示した。（ｎ＝５）

＜評価基準＞

３：全く違和感がない。

２：ほとんど違和感がない。

１：やや違和感がある。

【００６７】

【表１】

＜評価結果＞

	シート①	シート②	シート③	シート④	シート⑤	シート⑥
シート基材	ポリウレタン	不織布	ポリウレタン	ポリウレタン	ポリウレタン	ポリウレタン
シート基材厚さ(μm)	100	100	30	70	200	100
剛軟度(mm)	21.8	36.5	10.4	17.9	30.8	55.8
使用感	2.6	1.6	1.8	2.4	2	1.4

【００６８】

上記表から明らかなように、比較的柔軟性を有するポリウレタンシートの中でも、剛軟度が１５～２５ｍｍの厚み範囲にある１００μｍ厚のシート基材や７０μｍ厚のシート基材は使用感に特に優れたものであった。

【００６９】

（２）皮膚貼付用シートの製造

＜粘着剤Ａを使用した皮膚貼付用シート＞

不活性ガス雰囲気下で、イソノニルアクリレート６５部、２－メトキシエチルアクリレート３０部、アクリル酸５部を共重合させて得られたアクリル系共重合体１００部にカプリル酸トリグリセリル１００部、架橋剤として三官能性イソシアネート（日本ポリウレタン社製、コロネートＨＬ）０．１部をトルエン中で配合し、粘着剤の溶液を調製した。得られた粘着剤の溶液をセパレーター上に塗布、乾燥し、粘着剤の厚みが３０μｍになるように調整し、以下の実施例及び比較例における表３～５に示される様に、シート基材の片面に積層、転写した。シート基材は図１に示される形状の物を使用した。

【００７０】

＜粘着剤Ｂを使用した皮膚貼付用シート＞

窒素ガス雰囲気下でアクリル酸５部、アクリル酸２－エチルヘキシルエステル９５部を共重合させて得られたアクリル系共重合体１００部にトリオレイン酸ソルビタン６７部、架橋剤として三官能性イソシアネート（日本ポリウレタン社製、コロネートＨＬ）０．１４部を酢酸エチル中で配合し、粘着剤の溶液を調製した。

得られた粘着剤の溶液をセパレーター上に塗布、乾燥し、粘着剤の厚みが５０μｍになるように調整し、接着剤Ａと同様に、シート基材の片面に積層、転写した。

【００７１】

＜粘着剤Ｃを使用した皮膚貼付用シート＞

窒素ガス雰囲気下でアクリル酸５部、アクリル酸２－エチルヘキシルエステル９５部を共重合させて得られたアクリル系共重合体１００部にトリオレイン酸ソルビタン４０部、架橋剤として三価のエポキシ化合物（日産化学工業社製、テピック－Ｓ）０．０５部を酢酸エチル中で配合し、粘着剤の溶液を調製した。

得られた粘着剤の溶液を、接着剤Ａと同様に、シート基材の片面に直接塗布、乾燥し、不織布より上の粘着剤の厚みが２０μｍになるように調整した。

【００７２】

２　乳化化粧料の製造

表２に示す処方の乳化化粧料（保湿用アイクリーム）を以下に示す方法で調製した。

【００７３】

【表２】

単位：質量％

No.	成分	配合量
1	ﾓﾉｽﾃｱﾘﾝ酸ﾎﾟﾘｴﾁﾚﾝｸﾞﾘｺｰﾙ(40EO)	2
2	ﾓﾉｽﾃｱﾘﾝ酸ｸﾞﾘｾﾘﾙ	1.5
3	ﾍﾞﾍﾆﾙｱﾙｺｰﾙ	1.5
4	ｾﾄｽﾃｱﾘﾙｱﾙｺｰﾙ	2.5
5	ｼﾞｶﾌﾟﾘﾝ酸ﾌﾟﾛﾋﾟﾚﾝｸﾞﾘｺｰﾙ	7
6	ﾄﾘｲｿｽﾃｱﾘﾝ酸ｼﾞｸﾞﾘｾﾘﾙ	11
7	N-ﾗｳﾛｲﾙ-L-ｸﾞﾙﾀﾐﾝ酸ｼﾞ(ｺﾚｽﾃﾘﾙ･ﾍﾞﾍﾆﾙ･ｵｸﾁﾙﾄﾞﾃﾞｼﾙ)	7
8	ﾜｾﾘﾝ	2
9	ｼﾞﾒﾁﾙﾎﾟﾘｼﾛｷｻﾝ(100cs)	0.5
10	ｽｸﾜﾗﾝ	2
11	精製水	20
12	1,3-ﾌﾞﾁﾚﾝｸﾞﾘｺｰﾙ	20
13	ｶﾙﾎﾞｷｼﾋﾞﾆﾙﾎﾟﾘﾏｰ	0.15
14	精製水	15
15	水酸化ﾅﾄﾘｳﾑ	0.05
16	精製水	残分

【００７４】

製法

１．Ｎｏ．１～Ｎｏ．１０を均一に混合し、７０℃に加熱する。

２．Ｎｏ．１１及びＮｏ．１２を７０℃に加熱する。

３．Ｎｏ．１３及びＮｏ．１４をアジディスパーにて、３０００ｒｐｍで２０ｍｉｎ分散する。

４．アジディスパーにて３０００ｒｐｍで撹拌しながら２に１を徐注入し３ｍｉｎ混合する。

５．４を４０℃まで冷却し、３を投入しアジディスパーで１５００ｒｐｍで３ｍｉｎ混合後、Ｎｏ．１５及びＮｏ．１６を注ぎ、さらに３ｍｉｎ混合する。

【００７５】

３　評価試験

女性ボランティア１４名に、夜のお手入れ後に上記２で製造した保湿用アイクリーム（表中では「クリーム１」という）を０．０５ｇ塗布した後、上記２で製造した表３～５に示すような各種の皮膚貼付用シート（図１の形状で実施例１～１０、比較例１～３の組成）を目じりに貼付し、指で軽く圧着した。

【００７６】

そのまま就寝し起床後シートを除去した。これを２週間連続使用し、以下のような評価を行った。

皺の評価に関しては、「皺改善度」、「肌の弾力」、「肌のキメ」、「皮膚粘着性」、「皮膚トラブル」、「はがすときの痛みのなさ」に関して以下のような評価を行った。なお、「はがすときの痛みのなさ」については、シート単独・粘着剤違いの評価のときのみ行った。

【００７７】

「皺改善度」

日本香粧品学会の抗皺製品評価ガイドライン（日本化粧品学会誌　３０（４），３１６－３３６（２００６）より）に基づいて判定し、皺スコアを０～７の８段階のスコアで評価した。初期の皺スコアから２週間使用後の皺スコアの差の４人の平均を皺改善度として表に示す。

【００７８】

「肌の弾力」

１．使用前と変化なし
２．使用前より肌の弾力がわずかに上がった。
３．使用前より肌の弾力が上がった
４．使用前より肌の弾力がかなり上がった。

「肌のキメ」

１．使用前と変化なし
２．使用前より皮溝・皮丘がわずかに鮮明になった。
３．使用前より皮溝・皮丘が鮮明になった。
４．使用前より皮溝・皮丘がかなり鮮明になった。

「皮膚粘着性」

１．使用中シートがはがれることが５回以上であった。
２．使用中シートがはがれることが３回から４回であった。
３．使用中シートがはがれることが２回以内であった。
４．使用中シートがはがれることがなかった。

「皮膚トラブル」

１．皮膚に違和感を感じ、皮膚がかゆくなる若しくは赤くなる。
２．皮膚に違和感を感じることがある。
３．皮膚に違和感をほとんど感じない
４．皮膚に違和感を全く感じない

「はがすときの痛みのなさ」

１．シートをはがすときに強い痛みがあった。
２．シートをはがすときに痛みがあった。
３．シートをはがすときにほとんど痛みはなかった。
４．シートをはがすときにまったく痛みはなかった。

【００７９】

＜評価の判定＞

専門の評価者４名が評価を行い、以下の判定を行った。

◎：評点の平均が３．５以上４以下
○：評点の平均が３以上３．５未満
△：評点の平均が２以上３未満
×：評点の平均が２未満

【００８０】

シート基材層の材質違い、厚さ違い、粘着剤層の粘着剤違いについての評価結果を以下表３～５に示す。

【００８１】

【表３】

（シート基材材質違い）

	実施例１	実施例２	実施例３	比較例１	比較例２	比較例３
塗布クリーム	クリーム１	クリーム１	クリーム１	クリーム１	クリーム１	クリーム１
シート材質	ポリウレタン	ポリウレタン	不織布	ポリオレフィン	不織布	塩化ビニリデン
粘着剤種	A	A	C	B	－	－
シート基材厚さ(μm)	100	100	100	100	300	10
粘着剤厚さ(μm)	30	30	20	50	－	－
引張強度(N/cm)	47	70	20	17	15	12
水蒸気透過度(g/m^2/24hrs)	790	370	880	60	4950	20
皺改善度	0.75	0.675	0.25	0.125	−0.125	0
肌の弾力	◎	◎	◎	○	△	○
肌のキメ	◎	◎	◎	○	△	○
皮膚トラブル	◎	◎	◎	×	◎	△
皮膚粘着性	◎	◎	◎	○	×	×

【００８２】

水蒸気透過性が高いものでは、皺の改善が満足いくものではなく、逆に水蒸気透過性が低い場合は、皮膚トラブルが起こる場合があった。

【００８３】

【表４】

（シート基材厚さ違い）

	実施例１	実施例４	実施例５	実施例６
塗布クリーム	クリーム１	クリーム１	クリーム１	クリーム１
シート材質	ポリウレタン	ポリウレタン	ポリウレタン	ポリウレタン
粘着剤種	A	A	A	A
シート基材厚さ(μm)	100	30	70	200
粘着剤厚さ(μm)	30	30	30	30
引張強度(N/cm)	47	10	30	130
水蒸気透過度(g/m^2/24hrs)	790	1460	940	270
皺改善度	0.75	0.125	0.5	0.5
肌の弾力	◎	○	◎	◎
肌のキメ	◎	○	◎	◎
皮膚トラブル	◎	◎	◎	○
皮膚粘着性	◎	◎	◎	◎

【００８４】

シート基材がポリウレタンの場合、３０μｍ未満のシートは、シートが柔らかいため、シートがよれて、皺に対して高い効果を発揮しにくい。一方、２５０μｍを越えるシートはシートが硬いために、使用時に違和感を感じる場合があった。

【００８５】

【表５】

（シート基材単独・粘着剤違い）

	実施例１	実施例７	実施例８	実施例９	実施例１０
塗布クリーム	クリーム１	クリーム１	クリーム１	クリーム１	クリーム１
シート材質	ポリウレタン	ポリウレタン	ポリウレタン	ポリウレタン	ポリウレタン
粘着剤種	A	A	A	B	アクリル系
シート基材厚さ(μm)	100	100	100	100	100
粘着剤厚さ(μm)	30	10	60	30	30
引張強度(N/cm)	47	30	27	26	25
水蒸気透過度(g/m^2/24hrs)	790	980	750	550	490
粘着力(ベーク板)(N/cm)	0.8	0.68	1.31	0.5	3.92
粘着力(皮膚)(N/cm)	0.8	0.4	1.8	0.5	0.7
皺改善度	0.75	0.25	0.25	0.5	0.25
肌の弾力	◎	○	◎	◎	◎
肌のキメ	◎	○	○	◎	○
皮膚トラブル	◎	◎	○	◎	○
皮膚粘着性	◎	○	◎	◎	○
はがすときの痛みのなさ	◎	◎	○	○	○

【００８６】

粘着剤層の厚さにより皮膚粘着性とはがすときの痛みに差はあるが、使用性には問題がなかった。

粘着剤の種類としては、有機液状成分を含有するアクリル系粘着剤のようなゲル系粘着剤が好ましい。

【００８７】

［実施例１１～２１、比較例４～１０］

目じりに、表６及び７に示される実施例１１～２１、比較例４～１０の水中油型の乳化化粧料保湿用アイクリームを０．０５ｇ塗布し、実施例１と同じゲル系粘着剤の皮膚貼付用シート（ブーメラン型　図１参照）を貼付し指で軽く圧着する。そのまま就寝し起床後シートを除去するといった生活を２週間続けた後、評価を行った。各実施品につきｎ＝４で測定。女性ボランティア３６名対象。比較例１０に関しては、クリーム塗布後、シートを貼付せずに就寝し、シート貼付部と同様に評価を行った。

【００８８】

表６及び７に示す処方のアイクリームは、以下に示す方法で調製した。

１．Ｎｏ．１１及びＮｏ．１２をアジディスパーにて、３０００ｒｐｍで２０ｍｉｎ分散する。

２．Ｎｏ．１～Ｎｏ．９を均一に混合し、７０℃に加熱する。

３．Ｎｏ．１０を７０℃に加熱する。

４．アジディスパーにて３０００ｒｐｍで撹拌しながら、３に２を徐注入し３ｍｉｎ混合する。

５．４を４０℃まで冷却し、１を投入しアジディスパーで１５００ｒｐｍで３ｍｉｎ混合

後、水酸化ナトリウムを溶解させたＮｏ．１４を注ぎ、さらに３ｍｉｎ混合する。

【００８９】

（評価試験）

評価は、「皺改善度」「肌の弾力」「肌のキメ」「皮膚粘着性」の４項目で、各効果の判定についても、実施例１～１０の評価試験と同様に行った。なお、表中、各成分の数値の単位は質量％を示す。

【００９０】

【表６】

（質量％）

No.	成分	実施例11	実施例12	実施例13	実施例14	実施例15	実施例16	実施例17	実施例18	実施例19	実施例20	実施例21
1	モノステアリン酸ポリエチレングリコール(40EO)	2	2	2	2	2	1.5	2	2	2	2	2
2	モノステアリン酸グリセリル	1.5	1.5	1.5	1.5	1.5	0.5	1.5	1.5	1.5	1.5	1.5
3	ベヘニルアルコール	1.5	1.5	1.5	1.5	1.5	0.5	1.5	1.5	1.5	1.5	1.5
4	セトステアリルアルコール	2.5	2.5	2.5	2.5	2.5	1	2.5	2.5	2.5	2.5	2.5
5	Ｎ-ラウロイル-Ｌ-グルタミン酸ジ(コレステリル・ベヘニル・オクチルドデシル)	12	20	-	-	20	0.5	1	5	10	10	10
6	ワセリン	7	-	20	-	10	3	4	15	-	-	-
7	ジカプリン酸プロピレングリコール	-	-	-	20	10	-	-	-	-	-	2
8	流動パラフィン	-	-	-	-	4	-	-	-	14	25	5
9	ジメチルポリシロキサン(100cs)	-	-	-	-	-	-	〃	〃	-	-	4
10	精製水	20	20	20	20	20	20	20	20	20	20	20
11	アクリル酸・メタクリル酸アルキル共重合体(注)	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
12	精製水	15	15	15	15	15	15	15	15	15	15	15
13	水酸化ナトリウム	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
14	精製水	残分	残分	残分	残分	残分	残分	残分	残分	残分	残分	残分
評価項目	皺改善度	0.75	0.625	0.375	0.25	0.75	0.125	0.25	0.625	0.5	0.25	0.625
	肌のキメ	◎	◎	◎	○	◎	○	○	◎	◎	◎	◎
	皮膚粘着性	◎	○	◎	◎	◎	◎	◎	◎	○	○	○
	肌の弾力	◎	◎	○	○	◎	○	○	◎	◎	○	◎

（注）商品名　ペミュレンＴＲ－１（NOVEON社製）

【００９１】

【表７】

（質量％）

No.	成分	比較例4	比較例5	比較例6	比較例7	比較例8	比較例9	比較例10
1	モノステアリン酸ポリエチレングリコール(40EO)	-	-	-	-	2	2	2
2	モノステアリン酸グリセリル	-	-	-	-	1.5	1.5	1.5
3	ベヘニルアルコール	-	-	-	-	1	1.5	1.5
4	セトステアリルアルコール	-	-	-	-	2	2.5	2.5
5	N-ラウロイル-L-グルタミン酸ジ(コレステリル・ベヘニル・オクチルドデシル)	-	-	-	-	-	30	12
6	ワセリン	-	-	100	-	-	-	7
7	ジカプリン酸プロピレングリコール	-	100	-	-	-	-	-
8	流動パラフィン	-	-	-	-	-	25	-
9	ジメチルポリシロキサン(100cs)	-	-	-	100	-	-	-
10	精製水	20	-	-	-	20	20	20
11	アクリル酸・メタクリル酸アルキル共重合体(注)	0.15	-	-	-	0.15	0.15	0.15
12	精製水	15	-	-	-	15	15	15
13	水酸化ナトリウム	0.05	-	-	-	0.05	0.05	0.05
14	精製水	残分	-	-	-	残分	残分	残分
評価項目	皺改善度	-0.125	0	0.125	0	-0.125	0.125	0
	肌のキメ	×	×	×	×	×	×	△
	皮膚粘着性	◎	◎	×	×	◎	△	-
	肌の弾力	×	×	△	△	×	△	△

（注）商品名　ペミュレンＴＲ－１（NOVEON社製）

【００９２】

Ｎ－ラウロイル－Ｌ－グルタミン酸ジ（コレステリル・ベヘニル・オクチルドデシル）やジペンタエリトリット脂肪酸エステルはペースト系油剤であるのとともに抱水性が高く、非常に効果が高かった。

流動パラフィン等非極性油は単独塗布ではゲル系粘着剤の粘着力を低下させるのであるが、実施例１９－２１のように乳化することによって粘着性は向上した。さらに、非極性油も極性油と混合することによって、使用中にはがれないものとなり、皺改善することができた。また被験者の使用後の感想から、ペースト系油剤配合のサンプルは、被験者自身の肌改善効果感が非常に高いことがわかった。

【００９３】

比較例４は、油剤の配合がなくエモリエント効果に欠けたため、肌の弾力改善やキメの回復がなかった。比較例５－７は、水分の配合がされていないため、肌の乾燥を押さえることが不十分であり、スキンケアの基本である保湿効果に欠けた。肌状態が乾燥していると、肌自体の持つ酵素活性などの回復効果が期待できない。比較例８は油剤の配合がないため、シート剥離時にやや痛みが伴ったほか、皺の回復も見られなかった。比較例９は油剤の配合量が多すぎ、粘着テープの粘着力が保てず、就寝中にシートが剥がれ落ちたため良い結果が得られなかった。比較例１０は、クリームだけでも効果実感はあったが、皺改善効果はなかった。

【００９４】

［実施例２２］

表８に示す処方のアイクリーム（油中水型乳化化粧料：乳液）を以下に示す方法で調製した。

【００９５】

【表８】

（質量％）

No.	成分	配合量
1	ｼﾞﾋﾄﾞﾛｷｼｽﾃｱﾘﾝ酸 PEG-30	3
2	ﾄﾘ 2-ｴﾁﾙﾍｷｻﾝ酸ｸﾞﾘｾﾘﾙ	6
3	ﾏｶﾃﾞﾐｱﾝﾅｯﾂ脂肪酸ｺﾚｽﾃﾘﾙ	6
4	ｲｿﾉﾅﾝ酸ｲｿﾄﾘﾃﾞｼﾙ	3.5
5	PEG-9 ﾎﾟﾘｼﾞﾒﾁﾙｼﾛｷｼｴﾁﾙｼﾞﾒﾁｺﾝ	0.5
6	ﾃﾞｶﾒﾁﾙﾍﾟﾝﾀｼﾛｷｻﾝ	4
7	ｽｸﾜﾗﾝ	3
8	塩化ﾅﾄﾘｳﾑ	1
9	ｸﾞﾘｾﾘﾝ	10
10	精製水	残分

【００９６】

製法

１．Ｎｏ．１～Ｎｏ．７を均一に混合する。

２．Ｎｏ．８～Ｎｏ．１０を均一に混合する。

３．アジディスパーにて３０００ｒｐｍで攪拌しながら１に２を徐注入し５ｍｉｎ混合する。

【００９７】

実施例２２の乳液を顔全体に塗布し、気になる皺の部分に適当に大きさを整えた実施例１と同じ皮膚貼付用シートを貼付し、就寝した。翌日シート貼付部を観察したところ、角質層の乾燥状態、キメを改善することができた。２週間連続使用後の皺改善度は０．１２５であった。

【００９８】

［実施例２３］

表９に示す処方のアイクリーム（水中油型乳化化粧料：マッサージクリーム）を以下に示す方法で調製した。

【００９９】

【表９】

(質量%)

No.	成分	配合量
1	N-ステアロイル-L グルタミン酸ナトリウム	0.4
2	グリセリン	10
3	1,3-ブチレングリコール	15
4	精製水	残分
5	モノオレイン酸ポリオキシエチレンソルビタン(20EO)	0.1
6	セスキオレイン酸ソルビタン	0.5
7	ヒドロキシステアリン酸コレステリル	15
8	セトステアリルアルコール	1
9	スクワラン	31
10	ミツロウ	2
11	ジカプリン酸プロピレングリコール	14

【０１００】
製法
１．Ｎｏ．１～Ｎｏ．４を７５℃に加温し均一に混合する。
２．Ｎｏ．５～Ｎｏ．１１を７５℃に加温し均一に混合する。
３．７５℃にてアジディスパーにて３０００ｒｐｍで攪拌しながら１に２を徐注入し５ｍｉｎ混合する。
【０１０１】
実施例２３のマッサージクリームにて目じりをマッサージ後、皮膚貼付用シートを貼付し、就寝した。翌日目じりを観察したところ、小じわの低減が見られ、角質層の乾燥状態、キメを改善が確認できた。２週間連続使用後の皺改善度は０．５であった。
【０１０２】
［実施例２４］
表１０に示す処方のアイクリーム（水中油型乳化化粧料）を以下に示す方法で調製した。
【０１０３】

【表１０】

（質量％）

No.	成分	配合量
1	水素添加大豆リン脂質	2
2	ｸﾞﾘｾﾘﾝ	7
3	1,3-ﾌﾞﾁﾚﾝｸﾞﾘｺｰﾙ	7
4	ﾊﾟﾗｵｷｼ安息香酸ﾒﾁﾙ	0.2
5	ｾﾄｽﾃｱﾘﾙｱﾙｺｰﾙ	1.5
6	ﾍﾞﾍﾆﾙｱﾙｺｰﾙ	1.5
7	ﾍｷｻ(ﾋﾄﾞﾛｷｼｽﾃｱﾘﾝ酸/ｽﾃｱﾘﾝ酸/ﾛｼﾞﾝ酸)ｼﾞﾍﾟﾝﾀｴﾘｽﾘﾁﾙ	2
8	ｱｽﾀｷｻﾝﾁﾝ	0.05
9	ﾊﾟﾙﾐﾁﾝ酸ﾚﾁﾉｰﾙ	0.25
10	精製水	残分
11	ｶﾙﾎﾞｷｼﾋﾞﾆﾙﾎﾟﾘﾏｰ	0.18
12	ｷｻﾝﾀﾝｶﾞﾑ	0.02
13	精製水	20
14	水酸化ナトリウム	0.054
15	精製水	5.346

【０１０４】

製法

１．Ｎｏ．１～Ｎｏ．６を７５℃に加温し均一に混合する。

２．Ｎｏ．７～Ｎｏ．９を７５℃に加温し均一に混合する。

３．７５℃にてアジディスパーにて３０００ｒｐｍで攪拌しながら１に２を徐注入し５ｍｉｎ混合する。

４．７５℃にてアジディスパーにて３０００ｒｐｍで攪拌しながら３に７５℃まで加温したＮｏ．１０を徐注入し５ｍｉｎ混合する。

５．４を４０℃まで冷却する。

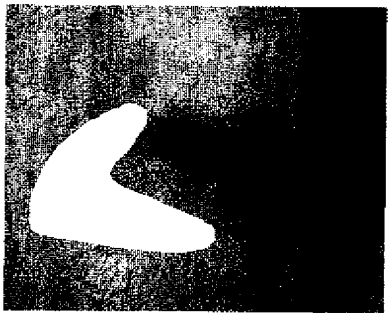
６．アジディスパーにて１５００ｒｐｍで攪拌しながら５にＮｏ．１１～Ｎｏ．１３を混合する。

７．アジディスパーにて１５００ｒｐｍで攪拌しながら６にＮｏ．１４及びＮｏ．１５を混合する。

【０１０５】

実施例２４のアイクリームを目じりに塗布後、皮膚貼付用シートを貼付し、就寝した。翌日目じりを観察したところ、小じわの低減が見られ、角質層の乾燥状態、キメを改善が確認できた。２週間連続使用後の皺改善度は０．５であった。

【図１】



フロントページの続き

(51)Int.Cl.	F I	テーマコード（参考）
A61Q 19/00 (2006.01)	A61Q 19/00	

(74)代理人 100120086
弁理士 ▲高▼津 一也
(74)代理人 100131093
弁理士 堀内 真
(72)発明者 福島 祐子
東京都北区栄町４８番１８号 株式会社コーセー研究所内
(72)発明者 一色 隆
東京都北区栄町４８番１８号 株式会社コーセー研究所内
(72)発明者 中山 純子
東京都北区栄町４８番１８号 株式会社コーセー研究所内
(72)発明者 高橋 尚則
大阪府茨木市下穂積１丁目１番２号 日東電工株式会社内
(72)発明者 今野 真之
大阪府茨木市下穂積１丁目１番２号 日東電工株式会社内
(72)発明者 鈴木 清志
大阪府茨木市下穂積１丁目１番２号 日東電工株式会社内

Ｆターム(参考) 4C083 AA082 AB032 AB332 AC012 AC022 AC071 AC122 AC171 AC352 AC392
AC402 AC421 AC422 AC442 AC482 AC662 AD071 AD092 AD152 AD162
AD352 AD492 AD572 AD622 BB11 CC03 CC14 DD12 DD31 DD32
DD33 EE12

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 759 572 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
30.07.2014 Bulletin 2014/31

(51) Int Cl.:
C08L 53/02 *(2006.01)* ***C08K 5/00*** *(2006.01)*
C08L 3/02 *(2006.01)*

(21) Application number: **13152325.0**

(22) Date of filing: **23.01.2013**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(71) Applicants:
- **Teknor Apex Company**
  Pawtucket, RI 02861 (US)
- **Cerestech, Inc.**
  Montréal, Québec H3T 2B1 (CA)

(72) Inventors:
- **Cai, Kevin**
  Cumberland, RI Rhode Island 02864 (US)
- **Wang, Yundong**
  Lancaster, MA Massachusetts 01523 (US)
- **Brzoskowski, Ryszard**
  Village of Nagog Woods, MA Massachusetts 01718 (US)
- **Bhadane, Prashant A.**
  Montreal, Québec H4M 2K4 (CA)
- **Favis, Basil D.**
  Kirkland, Québec H9J 3B9 (CA)
- **Perreault, Alain**
  Outremont, Québec H2V 3G4 (CA)

(74) Representative: **Renkema, Jaap**
IPecunia Patents B.V.
P.O. Box 593
6160 AN Geleen (NL)

(54) Thermoplastic elastomer compositions having biorenewable content

(57) Thermoplastic elastomer compositions, in particular derived from one or more styrenic block copolymers, a plurality of biorenewable materials, preferably a softener and one or more synergistic additives such as a polar polymer; a synergistic block copolymer such as a relatively high molecular weight styrenic block copolymer; and/or filler. In one preferred embodiment, the styrenic block copolymer comprises a controlled distribution copolymer block including a conjugated diene and a mono alkenyl arene. Numerous desirable articles can be formed from the compositions. Processes for preparing the compositions and articles are disclosed.

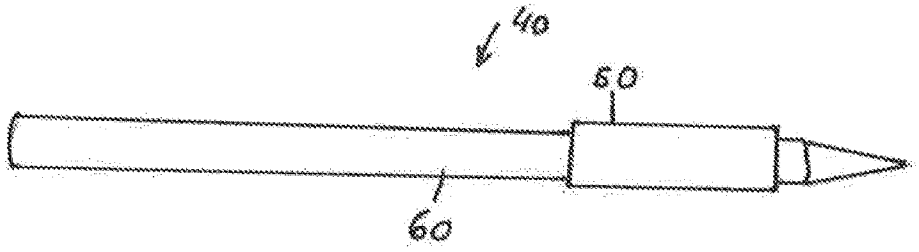


FIG. 2

EP 2 759 572 A1

Description

FIELD OF THE INVENTION

[0001] The present invention relates to thermoplastic elastomer compositions, in particular derived from one or more styrenic block copolymers, a plurality of biorenewable materials, preferably a softener and one or more synergistic additives such as a polar polymer; a synergistic block copolymer such as a relatively high molecular weight styrenic block copolymer; and/or filler. In one preferred embodiment, the styrenic block copolymer comprises a controlled distribution copolymer block including a conjugated diene and a mono alkenyl arene. Numerous desirable articles can be formed from the compositions. Processes for preparing the compositions and articles are disclosed.

BACKGROUND OF THE INVENTION

[0002] Thermoplastic elastomer compositions are versatile as they exhibit beneficial elastomeric properties and yet may be processed using standard thermoplastic processing equipment. Numerous different thermoplastic elastomer compositions, some with biorenewable components, have been proposed.

[0003] U.S. Patent Application Publication No. 2011/0184082 relates to a composition that includes a hydrogenated styrenic block copolymer that has at least one block A and at least one block B, and about 10 to about 90 percent by weight of an styrene-isobutylene-styrene block copolymer. Each A is an monoalkenyl arene and each B block is a controlled distribution copolymer of at least one mono alkenyl arene and at least one conjugated diene, having the general formula A-EB/A-A and (A-EB/A)nX. Each B block comprises terminal regions adjacent to the A blocks that are rich in conjugated diene units and one or more regions not adjacent to the A blocks that are rich in mono alkenyl arene units. Oil-free compositions that reportedly result in the combination of low gaseous permeability, low thermal conductivity, strong vibration and sound attenuation, and optionally high levels of light transmission with relatively low haze values while maintaining melt flow rates suitable for easy processibility are preferred.

[0004] U.S. Patent Application Publication No. 2010/00630008 relates to gelatinous elastomer compositions. In certain embodiments, a gelatinous elastomer composition is disclosed comprising about 1.0% to 50.0% block copolymer, about 0% to 98% mineral and/or synthetic oil, and about 0.0% to 98% triglyceride oil, about 0-15.0% free fatty acids, about 0-30% of a tack modification agent, about 0-20.0% of a biologically active agent and, optionally a phytosterol, ceramide and/or bisabolol. The gelatinous elastomer compositions are reportedly useful for applying a biologically active agent to a mammal. In certain embodiments, the gelatinous elastomer composition is formed into a molded article.

[0005] U.S. Patent Application Publication No. 2008/0171007 relates to a method of making up keratinous substrates involving applying onto the keratinous substrates a composition containing a) a block copolymer, b) a tackifier, c) a wax, d) a liquid fatty phase, e) a high viscosity ester, and f) optionally, a colorant.

[0006] U.S. Patent Application Publication No. 2008/0171006 relates to a method of making up keratinous substrates involving applying onto the keratinous substrate a composition containing a) a block copolymer, b) a tackifier, c) an alkyl silsesquioxane wax, d) a liquid fatty phase, and e) optionally, a colorant.

[0007] U.S. Patent Application Publication No. 2006/0121170 relates to a nonflowable gel composition including a vegetable oil and a thermoplastic elastomer. The nonflowable gel composition is characterized by its inability to flow when subjected to pressure. In another embodiment, the invention is a resilient gel composition includes a vegetable oil and a thermoplastic elastomer. The resilient gel composition is characterized by its ability to recover its size and form following deformation. In another embodiment, a support surface for supporting the human body is disclosed, including the composition and a holding structure for holding the composition.

[0008] U.S. Patent No. 7,884,158 relates to a cosmetic composition containing at least one block copolymer having a hard segment and a soft segment, at least one tackifier component, at least one phenylated silicone, at least one solvent, and optionally, at least one colorant.

[0009] U.S. Patent No. 7,625,967 relates to oil gel compositions that include at least one non-aromatic ester oil and an anionic block copolymer of a mono alkenyl arene and a conjugated diene. The block copolymer is selectively hydrogenated and has mono alkenyl arene end blocks and a controlled distribution block of a mono alkenyl arene and a conjugated diene midblock. The ester oil is a non-aromatic, ester compound such as soybean oil, rapeseed oil, and other like compounds.

[0010] U.S. Patent No. 7,267,855 relates to articles prepared from anionic block copolymers of mono alkenyl arenes and conjugated dienes, and to blends of such block copolymers with other polymers. The block copolymers are selectively hydrogenated and have mono alkenyl arene end blocks and controlled distribution blocks of mono alkenyl arenes and conjugated dienes. The block copolymer may be blended with at least one other polymer selected from the group consisting of olefin polymers, styrene polymers, amorphous resins and engineering thermoplastic resins.

[0011] U.S. Patent No. 7,169,848 relates to a block copolymer containing a controlled distribution copolymer block of a conjugated diene and a mono alkenyl arene, where the controlled distribution copolymer block has terminal regions

that are rich in conjugated diene units and a center region that is rich in mono alkenyl arene units. Also disclosed is a method for manufacture of the block copolymer.

[0012] U.S. Patent No. 6,984,688 relates to a plasticized HSBC blended with polypropylene and free of a filler material which adversely affects clarity, provides an injection-moldable composition for an article required to have specific properties, namely, tensile strength in the range from about 4.13 to 8.96 MPa (600 to 1300 psi); tear strength in the range from about 21 to 52.6 N/mm (120 to 300 lbs/in); softness in the range from about 45 but less than 65 Shore A; and haze less than 20%, measured by ASTM D1003 using a BYK Gardner Micro Tri-gloss 4525 meter; and it is essential that all of these properties, along with the physical dimensions of the molded article, remain substantially unchanged after immersion of the article in boiling water for 1 hour. Such a composition reportedly may be injection molded to form a nipple for feeding an infant, or a teething ring, or goggles for a diver, and the articles are reportedly sterilizable and recyclable.

[0013] U.S. Patent No. 6,673,857 relates to a thermoplastic elastomer composition comprising a) from 5 to 99% by weight of a block copolymer which is composed of hard blocks S made from vinyl aromatic monomers and of one or more random soft blocks B/S made from dienes and from vinyl aromatic monomers, b) from 1 to 95% by weight of a plasticizer with a higher polarity than white oil and with a lower polarity than diisooctyl phthalate, c) from 0 to 50% by weight of a polyolefin, and d) from 0 to 60% by weight of additives, where the total of a) to d) is 100% by weight. The use of the molding compositions to produce flexible or elastic moldings is described, as are the resultant moldings.

[0014] U.S. Patent No. 6,031,053 relates to an elastomeric block copolymer comprising at least one block A having polymerized units of a vinylaromatic monomer and forming a rigid phase and at least one elastomeric block B/A having polymerized units of both vinylaromatic monomers and of a diene and forming a flexible phase, and glass transition temperature Tg of the block A being above 25°C. and that of the block B/A being below 25°C. and the phase volume ratio of block A to block B/A being chosen so that the amount of the rigid phase in the total block copolymer is 1 to 40% by volume and the amount of the diene is less than 50% by weight.

[0015] WO 2009/152870 relates to a group of thermoplastic elastomers reportedly with high environmental compatibility and biodegradability. The compositions include styrenic block copolymers, vegetaloils, solid vegetaloil products and at least one styrenic block copolymer modified with maleic anhydride, see claim 1.

[0016] WO 2008/087675 relates to a plastification process of thermoplastic elastomers derived from styrenic block copolymers, in which vegetal oils are used as plastifying substances, and thermoplastic elastomers obtained with the said process.

[0017] In view of the above it would be desirable to provide a high performance thermoplastic elastomer composition having biorenewable components, in particular at least a softener and/or at least one additional synergistic additive, preferably in a relatively high percentage by total weight in order to improve oil stability, and achieve desirable properties including low gloss, high physical strength, improved melt strength, and suitable melt viscosity range for both molding and extrusion. In reality, the solution is not simple as numerous issues exist that must be addressed, including, but not limited to, providing a relatively low hardness material without sacrificing tensile strength, recoverable high elongations, component compatibility, processibility, heat stability, weatherability, and substantially low or no softener or plasticizer bleed-out. Desirably, the properties should be met not only at the room temperature but from -30°C to 135°C, more typically from -10°C to 70°C, for about 168hrs (1 week) for most of the applications. In spite of many disclosures reporting thermoplastic elastomer compositions including biorenewable content, the applicants have discovered oil bleed-out problems with many proposed formulations at various temperatures, which limit the commercialization and application of the bio based thermoplastic elastomer compositions containing vegetable oils and the like.

SUMMARY OF THE INVENTION

[0018] In view of the above, it would be desirable to provide a thermoplastic elastomer composition having relatively high biorenewable content yet additionally exhibits sought-after properties, especially excellent elasticity, high physical strength and desirable oil stability, that is, little or no oil bleed-out at various temperatures, depending on article requirements.

[0019] Therefore, it is an object of the present invention to provide a composition comprising at least one styrenic block copolymer, in a preferred embodiment having a controlled distribution block of a conjugated diene and a mono alkenyl arene, and further one or more and preferably a plurality of biorenewable components comprising a softener, for example an ester group-containing oil, generally a triglyceride; a wax; an ester; an alcohol; an amine, a starch, a thermoplastic starch, and a polar polymer such as polylactic acid (PLA), polyhydroxyalkanoates (PHAs), polyhydroxybutyrate (PHB), ethylene vinyl acetate (EVA) copolymer, polyether-block-amide (PEBA) etc. When starch is included, the mixture may also contain a plasticizer or dispersion aid dedicated for the starch phase for its effective gelatinization and dispersion. The effective plasticizer or dispersion aid can be from a family of polyols, polyglycols, carboxylic acid derivatives, or polyesters.

[0020] Yet another object of the present invention is to provide, when present, the controlled distribution block with

terminal regions that are rich in conjugated diene units and one or more regions that are rich in mono alkenyl arene units, wherein said block surprisingly provides high compatibility and low oil bleeding or leaching with both a biorenewable ester, preferably glyceride-containing component and a biorenewable additive.

[0021] Still another object of the present invention is to provide the composition with a fatty - triglyceride, wax, an ester, alcohol, or amine, or a mixture thereof-containing component derived from a vegetable product, wherein vegetable oils or their derivatives, such as partially or fully hydrogenated vegetable oil, are particularly preferred in some embodiments, for example when a styrenic block copolymer having a controlled distribution block is utilized, wherein esters and alcohols are more preferred than triglycerides for some styrenic block copolymer such as SEEPS, these products with saturation and branching are preferred; and a synergistic biorenewable additive comprising one or more of a starch, thermoplastic starch, and polar polymer.

[0022] A further object of the present invention is to provide the composition with biorenewable components comprising triglycerides of saturated and unsaturated fatty acids.

[0023] An additional object of the present invention is to provide the compositions with relatively low hardness without sacrificing tensile strength low modulus and desirable elongation.

[0024] Yet another object of the present invention is to provide a thermoplastic elastomer composition with enhanced biodegradability, due at least in part to the presence of a plurality of biorenewable components. When a composition includes one or more of an ester and a starch, their hydrophilic natures are keys to biodegradability.

[0025] Still another object of the present invention is to provide compositions with a relatively high biorenewable component content that can be formed into articles having a soft-grip feel, have a smooth appearance, are dry, and are substantially free of oil leaching.

[0026] A further object of the present invention is to provide a thermoplastic elastomer composition that can be processed utilizing standard processing equipment, such as injection molders and extruders.

[0027] Another object of the present invention is to provide a thermoplastic elastomer composition including a styrenic block copolymer having a controlled distribution mid block including a mono alkenyl arene and a conjugated diene, wherein the mono alkenyl arene is present in an amount of less than 30% by weight based on the total weight of the block.

[0028] An additional object of the present invention includes providing the thermoplastic elastomer composition having the styrenic block copolymer with a controlled distribution polymer block and biorenewable components with other compounds that enhance the properties of the composition, for example, a softener such as mineral oil, a polyolefin, other styrenic block copolymer or a polar polymer such as EVA.

[0029] Yet another object of the invention is to provide a thermoplastic elastomer composition including a styrenic block copolymer having a controlled distribution polymer block, a softener, preferably an ester group-containing oil, a functional group containing styrenic block copolymer, one or more of starch and a thermoplastic starch, and glycerin or a glycerin-like component.

[0030] Still another object of the invention is to provide a thermoplastic elastomer composition including a styrenic block copolymer having a controlled distribution polymer block, a softener, preferably an ester group-containing oil, and a polar polymer comprising one or more of polylactic acid (PLA), polyhydroxyalkanoates (PHAs), polyhydroxybutyrate (PHB), ethylene vinyl acetate copolymer, polyether-block-amide (PEBA) etc.

[0031] Yet another object of the invention is to provide a thermoplastic elastomer composition including a styrenic block copolymer having a controlled distribution polymer block, a softener, preferably an ester group-containing oil, and a relatively high molecular weight styrenic block copolymer such as ultra-high molecular weight SEBS.

[0032] Still another object of the invention is to provide a thermoplastic elastomer composition including a styrenic block copolymer having a controlled distribution polymer block, a softener, preferably an ester group-containing oil, a polyolefin, such as polypropylene, and a polar polymer such as described herein.

[0033] Still another object of the present invention is to provide a composition including a styrenic block copolymer, and one or more of a starch and a thermoplastic starch with glycerin or a glycerin like component, a natural wax, a fatty ester, a fatty alcohol, a fatty amine, and a polar polymer.

[0034] Accordingly, in one aspect, a thermoplastic elastomer composition is disclosed, comprising: an elastomer comprising a styrenic block copolymer; a biorenewable softener comprising one or more of a natural, fatty ester; a natural, fatty ether; a natural, fatty alcohol; and a natural, fatty amine in an amount from 1 to 90% by weight; a thermoplastic polymer or copolymer in an amount from 0 to 30% by weight; a bio-based thermoplastic comprising one or more of starch, polylactic acid, and PHA in an amount from 0 to 50% by weight; glycerol in an amount from 0 to 25% by weight; a mineral oil in an amount from 0 to 50% by weight; a maleated copolymer in an amount from 0 to 20% by weight; a filler in an amount from 0 to 70% by weight; optionally, other processing aids selected from one or more of antioxidants, lubricants, flame retardants, and UV stabilizers; and wherein all said percentages are based on 100% by weight of the composition.

[0035] In a further embodiment, the composition also includes a functionalized styrenic block copolymer, a polyolefin, starch and/or thermoplastic starch, and glycerol.

[0036] In a further embodiment, the natural, fatty ester is present and comprises one or more of a wax and an oil.

[0037] In an additional embodiment, the composition further includes a functionalized styrenic block copolymer, a polyolefin, and starch and/or thermoplastic starch; and wherein a natural, fatty alcohol and/or antural, fatty ester are present.

[0038] In a further embodiment, the composition also includes a functionalized styrenic block copolymer, a polyolefin, and starch and/or thermoplastic starch; and wherein a natural, fatty amine is present.

[0039] In a further embodiment, the natural, fatty ester comprises an oil, wherein a polar polymer, more specifically one or more of polylactic acid and PHA, is present and wherein the mineral oil is present.

[0040] In an additional embodiment, the styrenic block copolymer comprises at least one controlled distribution copolymer block having a conjugated diene and a monoalkenyl arene, wherein the the biorenewable softener comprises the natural, fatty ester, and wherein the composition includes at least one synergistic additive comprising one or more of starch, thermoplastic starch, a biorenewable polar polymer, a high molecular weight styrenic block copolymer, and ethylene vinyl acetate.

[0041] In a further embodiment, the styrenic block copolymer having a controlled distribution copolymer block is present in an amount from 5% to 90% by weight; wherein the biorenewable softener comprises the natural, fatty ester that is an ester-containing oil which is present in an amount from 1% to 85% by weight of the composition; and wherein the composition further includes a polyolefin.

[0042] In a further embodiment, the composition includes the biorenewable polar polymer in an amount from about 2% to 60% by weight, and wherein the composition is free of a mineral oil.

[0043] In an additional embodiment, the composition includes a functionalized styrenic block copolymer, and a polyolefin; and wherein the composition further includes one or more of starch and thermoplastic starch that is present in an amount from 2% to 80% by weight of the composition.

[0044] In a further embodiment, the composition comprises the biorenewable polar polymer in an amount from 2% to 60% by weight of the composition, wherein the biorenewable softener comprises the natural, fatty ester that is an ester-containing oil which is present in an amount from 10% to 65% by weight of the composition, and wherein the composition is free of a mineral oil.

[0045] In a further embodiment, the composition also includes a high molecular weight styrenic block copolymer in an amount from 1% to 30% by weight of the composition.

[0046] In a further embodiment, the composition also includes a polyolefin.

BRIEF DESCRIPTION OF THE DRAWINGS

[0047] FIG.1 illustrates a cross-sectional side view of one embodiment of a composite of the present invention including a layer comprising a thermoplastic elastomer composition having biorenewable content;

[0048] FIG. 2 illustrates one embodiment of an article, in particular a grip, of a thermoplastic elastomer composition having biorenewable content connected to a substrate, in particular a writing utensil.

DETAILED DESCRIPTION OF THE INVENTION

[0049] The thermoplastic elastomer compositions of the present invention include a styrenic block copolymer, in some preferred embodiments having a controlled distribution copolymer block having a conjugated diene and a mono alkenyl arene, wherein said block comprises terminal regions adjacent relatively harder blocks, with the controlled distribution block being rich in conjugated dienes adjacent to the relatively hard blocks and one or more regions not adjacent to the relatively hard blocks that are rich in mono alkenyl arene units, and biorenewable components comprising a softener and an additive. Surprisingly, the inventive compositions exhibit lower hardness without sacrificing much tensile strength when compared to combining the styrenic block copolymer having the controlled distribution copolymer block with a mineral oil. Polar components such as starch, PLAs, etc. have also found to help better retain the softener in various formulations. The compositions of the present invention can also include other compounds, for example as described herein.

[0050] General Styrenic Block Copolymers

[0051] In various embodiments, the compositions of the present invention include one or more styrenic block copolymers. In a preferred embodiment, the styrenic block copolymers have a hard block (A) including aromatic vinyl repeat units and at least one soft polymer block (B) containing two or more repeat units, that are the same or different, and independently derived from olefin monomers. The styrenic block copolymer can be, for example, a triblock copolymer (A-B-A); or a tetrablock or higher multiblock copolymer. In a preferred embodiment, the styrenic block copolymer is a triblock copolymer (A-B-A) having two hard blocks.

[0052] Each hard polymer block (A) can have two or more same or different aromatic vinyl repeat units. For example, the block copolymer may contain (A) blocks which are styrene/alpha-methylstyrene copolymer blocks or styrene/butadiene random or tapered copolymer blocks so long as a majority of the repeat units of each hard block are aromatic

vinyl repeat units. The (A) blocks are aromatic vinyl compound homopolymer blocks in one embodiment. The term "aromatic vinyl" is to include those of the benzene series, such as styrene and its analogs and homologs including o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 1,3-dimethylstyrene, alpha-methylstyrene and other ring alkylated styrenes, particularly ring-methylated styrenes, and other monoalkenyl polycyclic aromatic compounds such as vinyl naphthalene, vinyl anthracene and the like. The preferred aromatic vinyl compounds are monovinyl monocyclic aromatics, such as styrene and alpha-methylstyrene, with styrene being most preferred. When three or more different repeat units are present in hard polymer block (A), the units can be combined in any form, such as random form, block form and tapered form.

[0053] Optionally, the hard polymer block (A) can comprise small amounts of structural units derived from other copolymerizable monomers in addition to the structural units derived from the aromatic vinyl compounds. The proportion of the structural units derived from other copolymerizable monomers is desirably 30% by weight or less and preferably 10% by weight or less based on the total weight of the hard polymer block (A). Examples of other copolymerizable monomers include, but are not limited to, 1-butene, pentene, hexene, conjugated dienes such as butadiene or isoprene, methyl vinyl ether, and other monomers.

[0054] The soft polymer block (B) of the styrenic block copolymer includes two or more same or different structural units. Soft polymer block (B) can be derived from olefin monomers generally having from 2 to about 12 carbon atoms and can include, for example, ethylene, propylene, butylene, isobutylene, etc. When the soft polymer block (B) has structural units derived from three or more repeat units, the structural units may be combined in any form such as random, tapered, block or any combination thereof. In one embodiment, the soft polymer block does not contain any unsaturated bonds.

[0055] In additional embodiments of the present invention, the styrenic block copolymer can have at least one soft polymer block (B) including two or more repeat units that are the same or different, independently derived from one or more of an olefin monomer and a diene monomer. When the diene monomer is present, the styrenic block copolymer is preferably hydrogenated or substantially hydrogenated. The conjugated diene monomers preferably contain from 4 to about 8 carbon atoms with examples including, but not limited to, 1,3-butadiene (butadiene), 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene (piperylene), 1,3-hexadiene, and the like. Therefore, in one embodiment, the soft polymer block (B) can have structural units derived from one or more of an olefin monomer(s) and diene monomer(s). As indicated hereinabove, when the soft polymer block (B) has structural units derived from three or more repeat units, the structural units may be combined in any form.

[0056] The styrenic block copolymers may be prepared utilizing bulk, solution or emulsion or other techniques as known in the art.

[0057] Optionally, the soft polymer block (B) can include small amounts of structural units derived from other copolymerizable monomers in addition to the structural units described. In this case, the proportion of the other copolymerizable monomers is generally 30% by weight or less, and preferably 10% by weight or less based on the total weight of the soft polymer block (B) of the styrenic block copolymer. Examples of other copolymerizable monomers include, for example, styrene, p-methylstyrene, α-methylstyrene, and other monomers that can undergo ionic polymerization.

[0058] Optionally, the styrenic block copolymer can be a functionalized styrenic block copolymer such as an acid or anhydride functionalized block copolymer, such as prepared by graft reacting an acid moiety or its derivative into the styrenic block copolymer via a free radically initiated reaction. Examples of suitable monomers which may be grafted include unsaturated mono and polycarboxylic acids and anhydrides containing from about 3 to about 10 carbon atoms. Examples of such monomers are fumaric acid, itaconic acid, citraconic acid, acrylic acid, maleic anhydride, itaconic anhydride, and citraconic anhydride, or the like. Suitable functionalized styrenic block copolymers generally contain from about 0.1 to about 10 percent by weight, preferably from about 0.2 to about 5 percent by weight of the grafted monomer, based on the total weight of the styrenic block copolymer. Grafting reactions can be carried out in solution or by melt mixing the base block copolymer and the acid/anhydride monomer in the presence of a free radial initiator, such as known in the art, see for example U.S. Patent No. 6,653,408, herein fully incorporated by reference. Suitable functionalized block copolymers are available from KRATON Polymers, Kuraray, Asahi-Kasei, BASF and the like.

[0059] In various embodiments, the styrenic block copolymers include, but are not limited to, styrene-butadiene-styrene (SBS), styrene-butadiene/butylene-styrene (SBBS), styrene-isoprene-styrene (SIS), styrene-ethylene/propylene-styrene (SEPS), styrene-ethylene/propylene (SEP), styrene-ethylene/butylene-styrene (SEBS), styrene-ethylene/ethylene/propylene-styrene (SEEPS) and styrene-isobutylene-styrene (SIBS).

[0060] Styrenic block copolymers are available in the art from sources such as Kraton Polymers of Houston, Texas, as Kraton; Kuraray Co., Ltd. of Tokyo, Japan as SEPTON™ styrenic block copolymers, LCY Chemical Industry Corp, as Globalprene®, and TSRC Corporation of Taiwan as Taipol.

[0061] When present, the amount of the one or more styrenic block copolymers utilized in the compositions of the present invention ranges generally from about 1 to about 40 or 45 parts, desirably from about 10 to about 35 parts and preferably from about 1 or 15 to about 30 parts based on 100 parts by weight of the composition.

[0062] Controlled distribution copolymer block-containing styrenic block copolymers

[0063] The controlled distribution block-containing styrenic block copolymers utilized in the invention have at least a first block of a mono alkenyl arene, such as styrene, and a second block of a controlled distribution copolymer of diene and mono alkenyl arene. Thus, the block copolymers can be any di-or higher block copolymers. In the case of a di-block copolymer composition copolymer, one block is an alkenyl arene-based block and polymerized therewith is a second block of the controlled distribution copolymer comprising diene and alkenyl arene. Tri-block or higher multi-block copolymers include at least one alkenyl arene-based block and at least one controlled distribution copolymer block comprising diene and alkenyl arene. In one preferred embodiment, the triblock-composition comprises, as end blocks, alkenyl arene-based blocks and a mid block of a controlled distribution copolymer comprising diene and alkenyl arene. Where a tri-block copolymer composition is prepared, the controlled distribution copolymer block can be designated as "B" and the alkenyl arene-based block designated as "A". The A-B-A tri-block compositions can be made by either sequential polymerization or coupling. In one embodiment, in the sequential solution polymerization technique, the mono alkenyl arene is first introduced to produce a relatively hard aromatic-containing block, followed by introduction of the controlled distribution diene and alkenyl arene-containing mixture to form the mid block, and then followed by introduction of the mono alkenyl arene to form the terminal block.

[0064] In one embodiment, a method for making a controlled distribution copolymer block-containing styrenic block copolymer is set forth in U.S. Patent No. 7,169,848 herein incorporated by reference. As utilized herein, "controlled distribution" is defined as referring to a molecular structure having the following attributes: (1) terminal regions adjacent to the mono alkenyl arene homopolymer ("A") blocks that are rich in (i.e., having a greater than average amount of) conjugated diene units; (2) one or more regions not adjacent to the A blocks that are rich in (i.e., having a greater than average amount of) mono alkenyl arene units; and (3) an overall structure having relatively low blockiness. For the purposes hereof, "rich in" is defined as greater than the average amount, preferably greater than 5% the average amount.Prior to hydrogenation the styrene in the rubber block portion is copolymerized and incorporated in a controlled distribution having terminal regions that are rich in diene units (e.g. butadiene, isoprene, or a mixture thereof) and a center region that is rich in styrene units. Such polymers were hydrogenated under standard conditions such that greater than 95% of the diene double bonds in the rubbery block have been reduced. The process for producing a selectively hydrogenated styrene block copolymer is described in U.S. Pat. No. 7,169,848 to Bening et al.

[0065] The styrene blockiness is simply the percentage of blocky styrene to total styrene units:

$$\text{Blocky \%} = 100 \text{ times (Blocky Styrene Units/Total Styrene Units)}$$

[0066] Expressed thus, Polymer-Bd-S-(S)n-S-Bd-Polymer, where n is greater than zero is defined to be blocky styrene. For example, if n equals 8 in the example above, then the blockiness index would be 80%. It is preferred that the blockiness index be less than about 40. For some polymers, having styrene contents of ten weight percent to forty weight percent, it is preferred that the blockiness index be less than about 10. In a preferred embodiment of the present invention, the subject controlled distribution copolymer block has two distinct types of regions-conjugated diene rich regions on the end of the block and a mono alkenyl arene rich region near the middle or center of the block. What is desired is a mono alkenyl arene-conjugated diene controlled distribution copolymer block, wherein the proportion of mono alkenyl arene units increases gradually to a maximum near the middle or center of the block and then decreases gradually until the polymer block is fully polymerized.

[0067] The alkenyl arene can be styrene, alpha-methylstryene, para-methylstyrene, vinyl toluene, vinylnaphthalene, or para-butyl styrene or mixtures thereof. Of these, styrene is most preferred and is commercially available, and relatively inexpensive, from a variety of manufacturers. The conjugated dienes for use herein comprise 1,3-butadiene and substituted butadienes such as isoprene, piperylene, 2,3-dimethyl-1,3-butadiene, and 1-phenyl-1,3-butadiene, or mixtures thereof. Of these, 1,3-butadiene is most preferred.

[0068] For the controlled distribution or B block the weight percent of mono alkenyl arene in each B block is between about 10 weight percent and about 75 weight percent, preferably between about 25 weight percent and about 50 weight percent for selectively hydrogenated polymers.

[0069] It is preferred that, to ensure significantly elastomeric performance while maintaining desirably high Tg and strength properties, as well as desirable transparency, the tri-block and multi-block polymer's alkenyl arene content is greater than about 20% weight, preferably from about 20% to about 80% weight. This means that essentially all of the remaining content, which is part of the diene/alkenyl arene block, is diene. It is also important to control the molecular weight of the various blocks. For an AB diblock, desired block weights are 3,000 to about 60,000 for the monoalkenyl arene A block, and 30,000 to about 300,000 for the controlled distribution conjugated diene/mono alkenyl arene B block. Preferred ranges are 5,000 to 45,000 for the A block and 50,000 to about 250,000 for the B block. For the triblock, which may be a sequential ABA or coupled $(AB)_2X$ block copolymer, the A blocks should be 3,000 to about 60,000 preferably 5,000 to about 45,000, while the B block for the sequential block should be about 30,000 to about 300,000 and the B

blocks (two) for the coupled polymer half that amount. The total average molecular weight for the triblock copolymer should be from about 40,000 to about 400,000 and for the radial copolymer from about 60,000 to about 600,000. For the tetrablock copolymer ABAB the block size for the terminal B block should be about 2,000 to about 40,000, and the other blocks may be similar to that of the sequential triblock copolymer. These molecular weights are most accurately determined by light scattering measurements, and are expressed as number average molecular weight.

[0070] The controlled distribution block copolymer can be hydrogenated in various embodiments. One preferred hydrogenation is selective hydrogenation of the diene portions of the final block copolymer alternatively both the "B" blocks and the "A" blocks may be hydrogenated, or merely a portion of the "B" blocks may be hydrogenated.

[0071] Hydrogenation can be carried out via any of the several hydrogenation or selective hydrogenation processes known in the prior art. For example, such hydrogenation has been accomplished using methods such as those taught in, for example, U.S. Pat. Nos. 3,595,942; 3,634,549; 3,670,054; 3,700,633; and Re. No. 27,145, the disclosures of which are incorporated herein by reference. These methods operate to hydrogenate polymers containing aromatic or ethylenic unsaturation and are based upon operation of a suitable catalyst. Such catalyst, or catalyst precursor, preferably comprises a Group VIII metal such as nickel or cobalt which is combined with a suitable reducing agent such as an aluminum alkyl or hydride of a metal selected from Groups I-A, II-A, AND III-B of the Periodic Table of the Elements, particularly lithium, magnesium or aluminum. This preparation can be accomplished in a suitable solvent or diluent at a temperature from about 20 °C. to about 80°C. Other catalysts that are useful include titanium based catalyst systems. Hydrogenation can be carried out under such conditions that at least about 90 percent of the conjugated diene double bonds have been reduced, and between zero and 10 percent of the arene double bonds have been reduced. Preferred ranges are at least about 95 percent of the conjugated diene double bonds reduced, and more preferably about 98 percent of the conjugated diene double bonds are reduced. Alternatively, it is possible to hydrogenate the polymer such that aromatic unsaturation is also reduced beyond the 10 percent level mentioned above. Such exhaustive hydrogenation is usually achieved at higher temperatures. In that case, the double bonds of both the conjugated diene and arene may be reduced by 90 percent or more.

[0072] In an alternative, the block copolymer of the present invention may be functionalized in a number of ways. One way is by treatment with an unsaturated monomer having one or more functional groups or their derivatives, such as carboxylic acid groups and their salts, anhydrides, esters, imide groups, amide groups, and acid chlorides. The preferred monomers to be grafted onto the block copolymers are maleic anhydride, maleic acid, fumaric acid, and their derivatives. A further description of functionalizing such block copolymers can be found in Gergen et al, U.S. Pat. No. 4,578,429 and in U.S. Pat. No. 5,506,299. In another manner, the selectively hydrogenated block copolymer of the present invention may be functionalized by grafting silicon or boron containing compounds to the polymer as taught in U.S. Pat. No. 4,882,384. In still another manner, the block copolymer of the present invention may be contacted with an alkoxy-silane compound to form silane-modified block copolymer. In yet another manner, the block copolymer of the present invention may be functionalized by grafting at least one ethylene oxide molecule to the polymer as taught in U.S. Pat. No. 4,898, 914, or by reacting the polymer with carbon dioxide as taught in U.S. Pat. No. 4,970,265. Still further, the block copolymers of the present invention may be metallated as taught in U.S. Pat. Nos. 5,206,300 and 5,276,101, wherein the polymer is contacted with an alkali metal alkyl, such as a lithium alkyl. And still further, the block copolymers of the present invention may be functionalized by grafting sulfonic groups to the polymer as taught in U.S. Pat. No. 5,516,831. All of the patents mentioned in this paragraph are incorporated by reference into this application.

[0073] In various embodiments of the invention, the mono alkenyl arene is present in a total weight in an amount of greater than 20% and preferably greater than 35% based on the total weight of the controlled distribution block copolymer. In various embodiments the soft or B block of the controlled distribution copolymer block has a mono alkenyl arene content of less than 30%, desirably less than 29% by weight. The controlled distribution block copolymer of the present invention may include the copolymers sold under the trade name Kraton A ® by Kraton Polymers, Kraton A1536 and A1535 are examples.

[0074] In various embodiments of the invention, when present, the controlled distribution block-containing styrenic block copolymers are utilized in compositions of the present inventon in an amount from about 5 to about 90 parts, desirably from about 10 or about 15 to about 70 or 80 parts, and preferably from about 20 to about 30 or 35 parts based on 100 parts by weight of the composition.

[0075] High Molecular weight Styrenic Block Copolymers.

[0076] In some embodiments of the present invention, the compositions include one or more relatively high molecular weight styrenic block copolymers. High molecular weight as utilized herein refers to those block copolymers having a number average molecular weight generally greater than 300,000 g/mol. The high molecular weight styrenic block copolymers have been found to reduce gloss, improve physical strength and elasticity, increase melt strength, improve processibility, especially in extrusion applications, and to reduce softener or vegetable oil bleeding in various compositions of the present invention including biorenewable content.

[0077] In one embodiment tri-block styrenic block copolymers are preferred with the copolymers having styrene end blocks with average block length greater than 50,000 and a butadiene mid-block greater than 200,000. Such copolymers

can be made from sequential anionic living polymerization. In one embodiment, the high molecular weight styrenic block copolymers are substantially fully hydrogenated. High molecular weight styrenic block copolymers are available from Kraton as Kraton 1633, Kuraray as Septon 4099 and TSRC as Taipol 6159.

[0078] When present in a composition of the present invention, the high molecular weight styrenic block copolymer is utilized in an amount generally from about 1 to about 30, desirably from about 2 to about 20 and preferably from about 3 to about 15 parts by weight based on 100 total parts by weight of the composition.

[0079] Biorenewable components

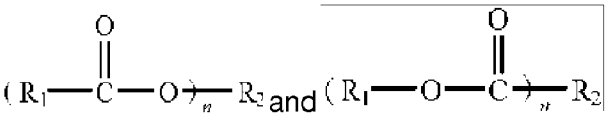
[0080] The composition of the present invention includes at least one or at least two biorenewable components, preferably at least one biorenewable softener and at least one biorenewable additive in various embodiments.

[0081] A)Softener

[0082] As indicated hereinabove, one of the biorenewable components is a softener preferably an oil, such as an ester group-containing oil, such as a monoester, diester, or triester. As defined in the art, an ester comprises the formula R-COO-R^1, wherein R is hydrogen or a hydrocarbyl and R^1 is a hydrocarbyl, e.g. an alkyl, aryl, or alkyl aryl, each optionally substituted.

[0083] In one preferred embodiment, the biorenewable softener component comprises a glyceride or acylglycerol, i.e. a monoglyceride, diglyceride, triglyceride, or combination thereof. Many naturally occurring fats and oils are the fatty acid esters of glycerol. Triglycerides are preferred in one embodiment. The glycerides can be saturated or unsaturated or a combination thereof.The styrenic block copolymers having a controlled distribution copolymer block including a conjugated diene and a mono alkenyl arene are less polar than a styrenic block copolymer containing a random conjugated diene and mono alkenyl arene block. Thus, it is expected that such block copolymers are miscible with standard mineral or white oil. However, it was surprisingly discovered that such controlled distribution copolymer block-containing styrenic block copolymers can be formulated with relatively high amounts of biorenewable softeners.

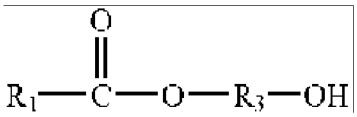
[0084] One or more esters can be employed in the present invention. In a preferred embodiment at least one ester utilized is biorenewable. Suitable esters that can be employed in the present invention include those of the following formulas:



[0085] where n has any value from 1 to about 8, and R_1 and R_2 are the same or different and are hydrogen or a hydrocarbyl (including substituted hydrocarbyls) provided the ester is compatible in the compositions of the invention. It is noted that a suitable group for R_2 depends on the value of n.

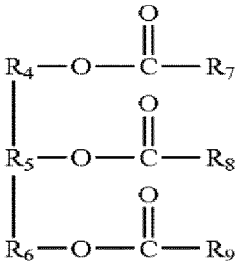
[0086] In one embodiment of the present invention, n is 1, and the ester has the formula $R_1C(O)OR_2$where R_1 is a C_{10}-C_{22}, preferably a C_{15}-C_{22}, alkyl, and R_2 is a lower alkyl radical containing from 1 to 22 carbon atoms. R_1 is preferably C_{13} or more when SEEPS is present in a composition.

[0087] Another class of suitable esters that may be employed in the present invention is represented by the following formula:



where R_1 is defined above and R_3 includes alkylene or substituted alkylene.

[0088] Still another class of suitable esters that may be employed in the present invention is represented by the following formula:



where R_4, R_5, and R_6 individually include alkylene or substituted alkylene; and R_7, R_8, and R_9 individually include hydrogen or a hydrocarbyl.

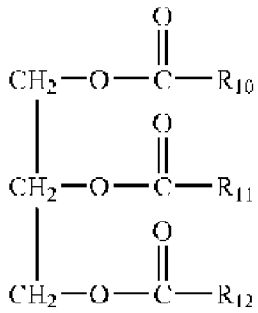
[0089] Suitable esters of the type mentioned above are eicosyl erucate ester or a C_{12-15} alkyl octanoate. Examples of other suitable esters include, but are not limited to: acetylline methylsilanol mannuronate; acetaminosalol; acetylated cetyl hydroxyprolinate; acetylated glycol stearate; acetylated sucrose distearate; acetylmethionyl methylsilanol elastinate; acetyl tributyl citrate; acetyl triethyl citrate; acetyl trihexyl citrate; aleurites moluccana ethyl ester; allethrins; allyl caproate; amyl acetate; arachidyl behenate; arachidyl glycol isostearate; arachidyl propionate; ascorbyl dipalmitate; ascorbyl palmitate; ascorbyl stearate; aspartame; batyl isostearate; batyl stearate; bean palmitate; behenyl beeswax; behenyl behenate; behenyl erucate; behenyl isostearate; behenyl/isostearyl beeswax; borago officinalis ethyl ester; butoxyethyl acetate; butoxyethyl nicotinate; butoxyethyl stearate; butyl acetate; butyl acetyl ricinoleate; 2-t-butylcyclohexyl acetate; butylene glycol dicaprylate/dicaprate; butylene glycol montanate; butyl ester of ethylene/MA copolymer; butyl ester of PVNI copolymer; butylglucoside caprate; butyl isostearate; butyl lactate; butyl methacrylate; butyl myristate; butyloctyl beeswax; butyloctyl candelillate; butyloctyl oleate; butyl oleate; butyl PABA; butylparaben; butyl stearate; butyl thioglycolate; butyroyl trihexyl citrate; C_{18-36} acid glycol ester; C_{12-20} acid PEG-8 ester; calcium stearoyl lactylate; C_{18-28} alkyl acetate; C_{18-38} alkyl beeswax; C_{30-50} alkyl beeswax; C_{20-40} alkyl behenate; C_{18-38} alkyl C_{24-54} acid ester; C_8 alkyl ethyl phosphate; C_{18-38} alkyl hydroxystearoyl stearate; C_{12-13}alkyl lactate; C_{12-15} alkyl lactate; C_{12-13} alkyl octanoate; C_{12-15} alkyl octanoate; C_{18-36} alkyl stearate; C_{20-40} alkyl stearate; C_{30-50} alkylstearate; C_{40-60} alkyl stearate; caproyl ethyl glucoside; caprylyl butyrate; C_{10-30} cholesterol/lanoster-ol esters; cellulose acetate; cellulose acetate butyrate; cellulose acetate propionate; cellulose acetate propionate carboxylate; Ceteareth-7 stearate; cetearyl behenate; cetearyl candelillate; cetearyl isononanoate; cetearyl octanoate; cetearyl palmitate; cetearyl stearate; cetyl acetate; acetyl ricinoleate; cetyl caprylate; cetyl C_{12-15}Parath-9 carboxylate; cetyl glycol isostearate; cetyl isononanoate; cetyl lactate; cetyl laurate; cetyl myristate; cetyl octanoate; cetyl oleate; cetyl palmitalte; cetyl PCA; cetyl PPG-2 Isodeceth-7 carboxylate; cetyl ricinoleate; cetyl stearate; C_{16-20} glycol isostearate; C_{20-30} glycol isostearate; C_{14-16} glycol palmitate; chimyl isostearate; chimyl stearate; cholesteryl acetate; cholesteryl/behenyl/octyldodecyl lauroyl glutamate; cholesteryl butyrate; cinoxate; citronellyl acetate; coco-caprylate/caprate; coco rapeseedate; cocoyl ethyl glucoside; corylus avellanna ethyl ester; C_{12-15} Pareth-9 hydrogenated tallowate; C_{11-15} Pareth-3 oleate; C_{12-15} Pareth-12 oleate; C_{11-15} Pareth-3 stearate; C_{11-15} Pareth-12 stearate; decyl isostearate; decyl myristate; decyl oleate; decyl succinate; DEDM hydantoin dilaurate; dextrin behenate; dextrin laurate; dextrin myristate; dextrin palmitate; dextrin stearate; diacetin; dibutyl adipate; dibutyl oxalate; dibutyl sebacate; di-C_{12-15} alkyl adipate; di-C_{12-15} alkyl fumarate; di-C_{12-13} alkyl malate; di-C_{12-13} alkyl tartrate; di-C_{14-15} alkyl tartrate; dicapryl adipate; dicaprylyl maleate; dicetearyl dimer dilinoleate; dicetyl adipate; dicetyl thiodipropionate; dicocoyl pentaerythrilyl distearyl citrate; diethoxyethyl succinate; diethyl acetyl aspartate; diethylaminoethyl cocoate; diethylaminoethyl PEG-5 cocoate; diethylaminoethyl PEG-5 laurate; diethylaminoethyl stearate; diethyl aspartate; diethylene glycol diisononanoate; diethylene glycol dioctanoate; diethylene glycol dioctanoate/diisononanoate; diethyl glutamate; diethyl oxalate; diethyl palmitoyl aspartate; diethyl sebacate; diethyl succinate; digalloyl trioleate; diglyceryl stearate malate; dihexyl adipate; dihexyldecyl lauroyl glutamate; dihydroabietyl behenate; dihydroabietyl methacrylate; dihydrocholesteryl butyrate; dihydrocholesteryl isostearate; dihydrocholesteryl macadamiate; dihydrocholesteryl nonanoate; dihydrocholesteryl octyldecanoate; dihydrocholesteryl oleate; dihydrophytosteryl octyldecanoate; dihydroxyethylamino hydroxypropyl oleate; dihydroxyethyl soyamine dioleate; diisobutyl adipate; diisobutyl oxalate; diisocetyl adipate; diisodecyl adipate; diisopropyl adipate; diisopropyl dimer dilinoleate; diisopropyl oxalate; diisopropyl sebacate; diisostearamidopropyl epoxypropylmonium chloride; diisostearyl adipate; diisostearyl dimer dilinoleate; diisostearyl fumarate; diisostearyl glutarate; diisostearyl malte; dilaureth-7 citrate; dilauryl thiodipropionate; dimethicone copolyol acetate; dimethicone copolyol adipate; dimethicone copolyol almondate; dimethicone copolyol beeswax; dimethicone copolyol behenate; dimethicone copolyol borageate; dimethicone copolyol cocoa butterate; dimethicone copolyol dhupa butterate; dimethicone copolyol hydroxystearate; dimethicone copolyol isostearate; dimethicone copolyol kokum butterate; dimethicone copolyol lactate; dimethicone copolyol laurate; dimethicone copolyol mango butterate; dimethicone copolyol meadowfoamate; dimethicone copolyol mohwa butterate; dimethicone copolyol octyldodecyl citrate; dimethicone copolyol olivate; dimethicone copolyol sal butterate; dimethicone copolyol shea butterate; dimethicone copolyol stearate;

dimethicone copoly undecylenate; dimethiconol beeswax; dimethiconol behenate; dimethiconol borageate; dimethiconol dhupa butterate; dimethiconol fluoroalcohol dillnoleic acid; dimethiconol hydroxystearate; dimethiconol illipe butterate; dimethiconol isostearate; dimethiconol kokum butterate; dimethiconol lactate; di methiconol mohwa butterate; dimethiconol sal butterate; dimethiconol stearate; dimethyl adipate; dimethylaminoethyl methacrylate; dimethyl brassylate; dimethyl cystinate; dimethyl glutarate; dimethyl maleate; dimethyl oxalate; dimethyl succinate; dimyristyl tartrate; dimyristyl thiodipropionate; dinonoxynol-9 citrate; dioctyl adipate; dioctyl butamido triazone; dioctyl dimer dilinoleate; dioctyldodeceth-2 lauroyl glutamate; dioctyldodecyl adipate; dioctyldodecyl dimer dilinoleate; dioctyldodecyl dodecanedioate; dioctyldodecyl fluoroheptyl citrate; dioctyldodecyl lauroyl glutamate; dioctyldodecyl stearoyl dimer dilinoleate; dioctydodecyl stearoyl glutamate; diocty fumarate; dioctyl malate; dioctyl maleate; dioctyl sebacate; dioctyl succinate; dioleoyl edetolmonium methosulfate; dipalmitoyl hydroxyproline; dipentaerythrityl hexacaprylate/hexacaprate; dipentaerythrityl hexaheptanoate/hexacaprylate/hexacaprate; dipentaerythrityl hexahydroxystearate; dipentaerythrityl hexahydroxystearate/stearate/rosinate; dipentaerythrityl hexaoctanoate/behenate; dipentaerythrityl pentahydroxystearate/isostearat-e; dipropyl adipate; dipropylene glycol caprylate; dipropylene dipropyl oxalate; disodium laureth-7 citrate; disodium PEG-5 laurylcitrate sulfosuccinate; disodium PEG-8 ricinosuccinate; disodium succinoyl glycyrrhetinate; disodium 2-sulfolaurate; distearеth-2 lauroyl glutamate; distearеth-5 lauroyl glutamate; distearyl thiodipropionate; ditallowoylethyl hydroxyethylmonium methosulfate; ditridecyl adipate; ditridecyl dimer dilinoleate; ditridecyl thiodipropionate; dodecyl gallate; erucyl arachidate; erucyl erucate; erucyl oleate; ethiodized oil; ethoxydiglycol acetate; ethoxyethanol acetate; ethyl almondate; ethyl apricot kemelate; ethyl arachidonate; ethyl aspartate; ethyl avocadate; ethyl biotinate; ethyl butylacetylaminopropionate; ethyl cyanoacrylate; ethyl cycolhexyl propionate; ethyl digydroxypropyl paba; ethylene brassylate; ethylene carbonate; ethy ester of hydrolyzed animal protein; ethyl ester of hydrolyzed keratin; ethyl ester of hydrolyzed silk; ethyl ester of pvm/ma copolymer; ethyl ferulate; ethyl glutamate; ethyl isostearate; ethyl lactate; ethyl laurate; ethyl linoleate; ethyl linolenate; ethyl niethacrylate; ethyl methylphenylglycidate; ethyl minkate; ethyl morrhuate; ethyl myristate; ethyl nicotinate; ethyl oleate; ethyl olivate; ethyl paba ethyl palmitate; ethylparaben; ethyl pelargonate; ethyl persate; ethyl phenylacetate; ethyl ricinoleate; ethyl serinate; ethyl stearate; ethyl thioglycolate; ethyl urocanate; ethyl wheat germate; ethyl ximenynate; ltocrylene; famesyl acetate; galactonolactone; galbanum (ferula galbaniflua) oil; gamrnma-nonalacione; geranyl acetate; glucarolactone; glucose glutamate; glucose pentaacetate; glucuronolactone; glycereth-7 diisononanoate; glycereth-8 hydroxystearate; glycereth-5 lactate; glycereth-25 PCA isostearate; glycereth-7 triacetate; glyceryl triacetyl hydroxystearate; glyceryl triacetyl ricinoleate; glycolamide stearate; glycol/butylene glycol montanate; glycol catearate; glycol dibehenate; glycol dilaurate; glycol dioctanoate; glycol dioleate; glycol distearate; glycol ditallowate; glycol hydroxystearate; glycol montanate; glycol octanoate; glycol oleate; glycol palmitate; glycol ricinoleate; glycol stearate; glycol stearate SE; glycyrrhetinyl stearate; hexacosyl glycol isostearate; hexanediol beeswax; hexanediol distearate; hexanetriol beeswax; hexyldecyl ester of hydrolyzed collagen; hexyldecyl isostearate; hexyldecyl laurate; hexyldecyl octanoate; hexyldecyl oleate; hexyldecyl palmitate; hexyldecyl stearate; hexyl isostearate; hexyl laurate; hexyl nicotinate; homosalate; hydrogenated castor oil hydroxystearate; hydrogenated castor oil isostearate; hydrogenated castor oil lauirate; hydrogenated castor oil stearate; hydrogenated castor oil triisostearate; hydrogenated methyl abietate; hydrogenated rosin; hydroquinone pca; hydroxycetyl isostearate; hydroxyoctacosanyl hydroxystearate; inositol hexa-pca; iodopropynyl butylcarbamate; isoamyl acetate; isoamyl laurate; isobutylated lanolin oil; isobutyl myristate; isobutyl palmitate; isobutylparaben; isobutyl pelargonate; isobutyl stearate; isobutyl tallowate; isocetearеth-8 stearate; isoceteth-10 stearate; isocetyl behenate; isocetyl isodecanoate; isocetyl isostearate; isocetyl laurate; isocetyl linoleoyl stearate; isocetyl myristate:, isocetyl octanoate; isocetyl palmitate; isocetyl stearate; isocetyl stearoyl stearate; isodeceth-2 cocoate; isodecyl citrate; isodecyl cocoate; isodecyl hydroxystearate; isodecyl isononanoale; isodecyl laurate; isodecyl myristate; isodecyl neopentanoate; isodecyl octanoate; isodecyl oleate; isodecyl palmitate; isodecylparaben; isodecyl stearate; isohexyl laurate; isohexyl neopentanoate; isohexyl palmitate; isolauryl behenate; isomerized jojoba oil; isononyl ferulate; isooctyl thioglycolate; isopropyl arachidate; isopropyl avocadate; isopropyl behenate; isopropyl citrate; isopropyl C_{12-15}-pareth-9 carboxylate; isopropyl hydroxystearate; isopropyl isostearate; isopropyl jojobate; isopropyl lanolate; isopropyl laurate; isopropyl linoleate; isopropyl myristate; isopropyl oleate; isopropylparaben; isopropyl PPG-2-isodeceth-7 carboxylate; isopropyl ricinoleate; isopropyl sorbate; isopropyl stearate; isopropyl tallowate; isopropyl thioglycolate; isosorbide laurate; isostearеth-10 stearate; isostearyl avocadate; isostearyl behenate; isostearyl erucate; isostearyl isononanoate; iscstearyl isostearate; isostearyl isostearoyl stearate; isostearyl lactate; isostearyl laurate; isostearyl myristate; isostearyl neopentanoate; isostearyl octanoate; isostearyl palmitate; isostearyl stearoyl stearate; isotridecyl isononanoate; isotridecyl laurate; isotridecyl myristate; jojoba (buxus chinensis) oil; jojoba esters; kojic dipalmitate; laneth-9 acetate; laneth-10 acetate; laneth-4 phosphate; lanolin linoleate; lanolin ricinoleate; laureth-2 acetate; laureth-6 citrate; laureth-7 citrate; laureth-2 octanoate; laureth-7 tartrate; lauroyl ethyl glucoside; lauroyl lactylic acid; lauryl behenate; lauryl cocoate; lauryl isostearate; lauryl lactate; lauryl methacrylate; lauryl myristate; lauryl octanoate; lauryl oleate; lauryl palmitate; lauryl stearate; linalyl acetate; linoleyl lactate; madecassicoside; mannitan laurate; mannitan oleate; menthyl acetate; menthyl anthranilate; menthyl lactate; menthyl pca; methoxyisopropyl acetate; methoxy-PEG-7 rutinyl succinate; methyl acetyl ricinoleate; methyl anthranilate; methyl behenate; methyl caproate; methyl caprylate; methyl caprylate/caprate; methyl cocoate; 6-methyl coumarin; methyl dehydroabietate; methyl dihydroabietate; methyl-

dihydrojasmonate; methyl glucose dioleate; methyl glucose isostearate; methyl glucose laurale; methyl glucose sesquicaprylate/sesquicaprate; methyl glucose sesquicocoate; methyl glucose sesquiisostearate; methyl glucose sesquilaurate; methyl glucose sesquioleate; methyl glucose sesquistearate; methyl glycyrrhizate; methyl hydrogenated rosinate; methyl hydroxystearate; methyl isostearate; methyl laurate; methyl linoleate; methyl 3-methylresorcylate; methyl myristate; methyl nicotinate; methyl oleate; methyl palmate; methyl palmitate; methylparaben; methyl pelargonate; methyl ricinoleate; methyl rosinate; methylsilanol acetylmethionate; methylsilaiaol carboxymethyl theophylline; methylsilanol carboxymethyl theophylline alginate; methylsilanol hydroxyproline; methylsilanol hydroxyproline aspartate; methylsilanol mannuronate; methylsilanol pca; methyl soyate; methyl stearate; methyl thioglycolate; monosaccharide lactate condensata; myreth-3 caprate; myreth-3 laurate; myreth-2 myristate; myreth-3 myristate; myreth-3 octanoate; myreth-3 palmitate; myristoyl ethyl glucoside; myristoyl lactylic acid; myristyl isostearate; myristyl lactate; myristyl lignocerate; myristyl myristate; myristyl octanoate; myristyl propionate; myristyl stearate; neopentyl glycol dicaprate; neopentyl glycol dicaprylate/dicaprate; neopentyl glycol dicaprylate/dipelargonate/dicaprate; neopentyl glycol diheptanoate; neopentyl glycol diisostearate; neopentyl glycol dilaurate; neopentyl glycol dioctanoate; nonyl acetate; nopyl acetate; octacosanyl glycol isostearate; octocrylene; octyl acetoxystearate; octyl caprylate/caprate; octyl cocoate; octyldecyl oleate; octyldodecyl behenate; octyldodecyl erucate; octyldodecyl hydroxystearate; octyldodecyl isostearate; octyldodecyl lactate; octyldodecyl lanolate; octyldodecyl meadowfoamate; octyldodecyl myristate; octyldodecyl neodecanoate; octyldodecyl neopentanoate; octyldodecyl octanoate; octyldodecyl octyldodecanoate; octyldodecyl oleate; octyldodecyl olivate; octyldodecyl ricinoleate; octyldodecyl stearate; octyldodecyl steroyl stearate; octyl gallate; octyl hydroxystearate; octyl isononanoate; octyl isopalmitate; octyl isostearate; octyl laurate; octyl linoleayl stearate; octyl myristate; octyl neopentanoate; octyl octanoate; octyl oleate; octyl palmitate; octyl PCA; octyl pelagonate; octyl stearate; oleoyl ethyl glucoside; oleyl acetate; oleyl arachidate; oleyl erucate; oleyl ethyl phosphate; oleyl lactate; oleyl lanolate; oleyl linoleate; oleyl myristate; oleyl oleate; oleyl phosphate; oleyl stearate; oryzanol; ozonized jojoba oil; palmitoyl carniline; palmitoyl inulin; palmitoyl myristyl serinate; pantethine; panthenyl ethyl ester acetate; panthenyl triacetate; pca glyceryl oleate; pea palmitate; PEG-18 castor oil dioleate; PEG-5 DMDM hydantoin oleate; PEG-15 dmdm hydantoin stearate; PEG-30 dipolyhydroxystearate; PEG-20 hydrogenated castor oil isostearate; PEG-50 hydrogenated castor oil isostearate; PEG-20 hydrogenated castor oil triisostearate; PEG-20 mannitan laurate; PEG-20 methyl glucose distearate; PEG-80 methyl glucose laurate; PEG-20 methyl glucose sesquicaprylate/sescquicaprate; PEG-20 methyl glucose sesquilaurate; PEG-5 oleamide dioleate; PEG-150 pentaerythrityl tetrastearate; PEG-3/PPG-2 glyceryl/sorbitol hydroxystearate/isostearate; PEG-4 proline linoleate; PEG-4 proline linolenate; PEG-8 propylene glycol cocoate; PEG-55 propylene glycol oleate; PEG-25 propylene glycol stearate; PEG-75 propylene glycol stearate; PEG-120 propylene glycol stearate; PEG40 sorbitol hexaoleate; PEG-50 sorbitol hexaoleate; PEG-30 sorbitol tetraoleate laurate; PEG-60 sorbitol tetrastearate; PEG-5 tricapryl citrate; PEG-5 tricetyl citrate; PEG-5 trilauryl citrate; PEG-5 trimethylolpropane trimyristate; PEG-5 trimyristyl citrate; PEG-5 tristeaiyl citrate; PEG-6 undecylenate; pentadecalacione; pentaerythrityl dioleate; pentaerythrityl distearate; pentaerythrityl hydrogenated rosinate; pentaerythrityl isostearate/caprate/caprylate/adipate; pentaerythrityl rosinate; pentaerythrityl stearate; pentaerythrityl stearate/caprate/caprylate/adipate; pentaerythrityl stearate/Isostearate/adipate/hydroxystearate; pentaerythrityl tetraabietate; pentaerythrityl tetraacetate; pentaerityl tetrabehenate; petaerythrityl tetracaprylate/tetracaprate;; pentaerythrityl tetracocoate; pentaerythrityl tetraisononanoate; pentaerythrityl tetralaurate; pentaerythrityl tetramyristate; pentaerythrityl tetraoctanoate; pentaerythrityl tetraoleate; pentaerythrityl tetrapelargonate; petaerythrityl tetrastearate; pentaerythrityl trioleate; phenoxyethylparaben; phylosteryl macadamiate; potassium butylparaben; potassium deceth-4 phosphate; potassium ethylparaben; potassiuim methylparaben; potassium propylparaben; PPG-2 isoceleth-20 acetate; PPG-14 laureth-60 alkyl dicarbamate; PPG-20 methyl glucose ether acetate; PPG-20 methyl glucose ether distearate; PPG-2 myristyl ether propionate; PPG-14 palmeth-60 alkyl dicarbamate; pregnenolone acetate; propylene glycol alginate; propylene glycol behenate; propylene glycol caprylate; propylene glycol Ceteth-3 acetate; propylene glycol Ceteth-3 propionate; propylene glycol citrate; propylene glycol cocoate; propylene glycol dicaprate; propylene glycol dicaproate; propylene glycol dicaprylate; propylene glycol dicocoate; propylene glycol diisononanoate; propylene glycol diisostearate; propylene glycol dilaurate; propylene glycol dioctanoate; propylene glycol dioleate; propylene glycol dipelargonate; propylene glycol distearate; propylene glycol diundecanoate; propylene glycol hydroxystearate; propylene glycolisoceteth-3 acetate; propylene glycol isostearate; propylene glycol laurate; propylene glycol linoleate; propylene glycol linolenate; propylene glycol myristate; propylene glycol myristyl ether acetate; propylene glycol oleate; propylene glycol oleate se; propylene glycol ricinoleate; propylene glycol soyate; propylene glycol stearate; propylene glycol stearate se; propyl gallate; propylparaben; pyricarbate; pyridoxine dicaprylate; pyridoxine dilaurate; pyridoxine dioctenoate; pyridoxine dipalmitate; pyridoxine glycyrrhetinate; pyridoxine tripalmitate; raffmose myristate; raffinose oleate; resorcinol acetate; retinyl acetate; retinyl linoleate; retinyl palmitate; retinyl propionate; riboflavin tetraacetate; ribonolaclone; siloxanetriol phytate; silybum marianum ethyl ester; sodium behenoyl lactylate; sodium butylparaben; sodium caproyl lactylate; sodiumn cocoyl lactylate; sodium dilaureth-7 citrate; sodium ethylparaben; sodium ethyl 2-sulfolaurate; sodium isostearoyl lactylate; sodium laureth-7 tartrate; sodium lauroyl lectylate; sodium methylparaben; sodium methyl 2-sulfolaurate; sodium oleoyl lactylate; sodium panteheine sulfonate; sodium phytate; sodium propylparaben; sodium stearoyl lactylate; sorbeth-2 cocoate; sorbeth-6 hexastearate; sorbeth-3 isostearate; sorbityl acetate;

soybean palmitate; soy sterol acetate; stearamide dea-distearate; stearamide diba-stearate; stearamide mea-stearate; steareth-5 stearate; stearoyl lactylic acid; stearyl acetate; stearyl acetyl glutamate; stearyl beeswax; stearyl behenate; stearyl caprylate; stearyl citrate; stearyl erucate; stearyl glycol isostearate; stearyl glycyrrhetinate; stearyl heptanoate; stearyl lactate; stearyl linoleate; stearyl octanoate; stearyl stearalte; stearyl stearoyl stearate; sucrose cocoate; sucrose dilaurate; sucrose distearate; sucrose laurate; sucrose myristate; sucrose octaacetate; sucrose oleate; sucrose palmitate; sucrose polybehenate; sucrose polycottonseedate; sucrose polylaurate; sucrose polylinoleate; sucrose polypalmate; sucrose polysoyate; sucrose polystearate; sucrose ricinoleate; sucrose stearate; sucrose tetrastearate triacetate; sucrose tribehenate; sucrose tristearate;tallowoyl ethyl glucoside; tannic acid; TEA-lauroyl lactylate; telmesteine; terpineol acetate; tetradecyleicosyl stearate; tetrahexyldecyl ascorbate; tetrahydrofurfuryl ricinoleate; tocophersolan; tocopheryl acetate; tocopheryl linoleate; tocopheryl linoleate/oleate; tocopheryl nicotinate; tocopheryl succinate; tributyl citrate; tri-C_{12-13} alkyl citrate; tri-C_{14-15} alkyl citrate; tricaprylyl citrate; tridecyl behenate; tridecyl cocoate; tridec), erucate; tridecyl isononanoate; tridecyl laurate; tridecyl myristate; tridecyl neopentanoate; tfridecyl octanoate; tridecyl stearate; tridecyl stearoyl stearate; tridecyl trimellitate; triethylene glycol hydrogenated rosinate; trihexyldecyl citrate; triisocetyl citrate; triisopropyl trilinoleate; triisostearyl citrate; triisostearyl trilinoleate; trilactin; trilauryl citrate; trimethylolpropane tricaprylate/tricaprate; trimethylolpropane tricocoate; trimethylolpropane trilaurate; trimethylalpropane trioctanoate; trimethylolpropane tristearate; trimethyl pentanyl diisobutyrate; trioctyl citrate; trioctyldodecyl borate; trictyl trimellitate; trioleyl citrate; tripaba panthenol; tripropylene glycol citrate; tristearyl citrate; tristearyl phosphate; and yeast palmitate.

[0090] In a preferred embodiment, the ester oils are natural product oils that are typically found in animal or plant tissues, including those which have been hydrogenated to eliminate or reduce unsaturation. These natural product oils that can be employed in the present invention include compounds that have the following formula:



where R_{10} R_{11} and R_{12} may be the same or different fatty acid radicals containing from 8 to 22 carbon atoms.

[0091] Suitable natural product oils of the above formula that can be employed in the present invention include, but are not limited to: Kernel Oil; Argania Spinosa Oil; Argemone Mexicana Oil; Avocado (Persea Gratissima) Oil; Babassu (Orbignya Olelfera) Oil; Balm Mint (Melissa Officinalis) Seed Oil; Bitter Almond (Prunus Amygdalus Amara) Oil; Bitter Cherry (Prunus Cerasus) Oil; Black Currant (Ribes Nigrrrm) Oil; Borage (Borago Officinalis) Seed Oil; Brazil (B3ertholletia Excelsa) Nut Oil; Burdock (Arctium Lappa) Seed Oil; Butter; C_{12-18} Acid Triglyceride; Calophyllurn Tacamahaca Oil; Camellia Kissi Oil; Camellia Oleifera Seed Oil; Canola Oil; Caprylic/Capric/Liuric Triglyceride; Caprylic/Capric/Linoleic Triglyceride; Caprylic/Capric/Myristic/Stearic Triglyceride; Caprylic/Capric/Stearic Triglyceride; Caprylic/Capric Triglyceride; Caraway (Canimn Carvi) Seed Oil; Carrot (Daucus Carota Sativa) Oil; Cashew (Anacardium Occidentale) Nut Oil; Castor (Ricinus Communis) Oil; Cephalins; Chaulmoogra (Taraktogenos Kurzii) Oil, Chia (Salvia Hispanica) Oil; Cocoa (Theobrama Cocao) Butter; Coconut (Cocos Nucifera) Oil; Cod Liver Oil; Coffee (Coffea Arabica) Oil; Corn (Zea Mays) Germ Oil; Corn (Zea Mays) Oil; Cottonseed (Gossypium) Oil; C_{10-18} Triglycerides; Cucumber (Cucumis Sativus) Oil; Dog Rose (Rosa Canina) Hips Oil; Egg Oil; Emu Oil; Epoxidized Soybean Oil; Evening Primrose (Oenothera Biennis) Oil; Fish Liver Oil; Gevuina Avellana Oil; Glyceryl Triacetyl Hydroxystearate; Glyceryl Triacetyl Ricinoleate; Glycolipids; Glycosphingolipids; Goat Butter; Grape (Vitis Vinifera) Seed Oil; Hazel (Croylus Americana) Nut Oil; Hazel (Corylus Aveilana) Nut Oil; Human Placental Lipids; Hybrid Safflower (Ceathamus Tinctorius) Oil; Hybrid Sunflower (Helianthus Annuus) Seed Oil; Hydrogenated Canola Oil; Hydrogenated Castor Oil; Hydrogenated Castor Oil Laurate; Hydrogenated Castor Oil Triisostearate; Hydrogenated Coconut Oil; Hydrogenated Cottonseed Oil; Hydrogenated C_{12-18} Triglycerides; Hydrogenated Fish Oil; Hydrogenated Lard; Hydrogenated Menhaden Oil; Hydrogenated Milk Lipids; Hydrogenated Mink Oil; Hydrogenated Olive Oil; Hydrogenated Orange Roughy Oil; Hydrogenated Palm Kernel Oil; Hydrogenated Palm Oil; Hydrogenated Peanut Oil; Hydrogenated Rapeseed Oil; Hydrogenated Shark Liver Oil; Hydrogenated Soybean Oil; Hydrogenated Tallow; Hydrogenated Vegetable Oil; Isatis Tinctoria Oil; Job's Tears (Coix Lacryma-Jobi) Oil; Jojoba Oil; Kiwi (Actinidia Chinensis) Seed Oil; Kukui (Aleurites Moluccana) Nut Oil; Lard; Lauric/Palmitic/Oleic Triglyceride; Linseed (Linum Usitatissiumum) Oil; Lupin (Lupinus Albus) Oil; Macadamia Nut Oil; Macadamia Ternifolia Seed Oil; Macadamia Integrifolia Seed Oil; Maleated Soybean Oil; Mango (Mangifera Indica) Seed Oil; Marmot Oil; Meadowfoam

(Limnanthes fragraAlba) Seed Oil; Menhaden Oil; Milk Lipids; Mink Oil; Moringa Pterygosperma Oil; Mortierella Oil; Musk Rose (Rosa Moschata) Seed Oil; Neatsfoot Oil; Neem (Melia Azadirachta) Seed Oil; Oat (Avena Sativa) Kernel Oil; Oleic/Linoleic Triglyceride; Oleic/Palmitic/Lauric/Myristic/L-inoleic Triglyceride; Oleostearine; Olive (Olea Europaea) Husk Oil; Olive (Olea Europaea) Oil; Omental Lipdis; Orange Roughy Oil; Ostrich Oil; Oxidized Corn Oil; Palm (Elaeis Guineensis) Kernel Oil; Palm (Elaeis Guineensis) Oil; Passionflower (Passiflora Edulis) Oil; Peach (Prunus Persica) Kernel Oil; Peanut (Arachis Hypogaea) Oil; Pecan (Caiya Illinoensis) Oil; Pengawar Djambi (Cibotium Barometz) Oil; Phospholipids; Pistachio (Pistacia Vera) Nut Oil; Placental Lipids; Poppy (Papaver Orientale) Oil; Pumpkin (Cucurbita Pepo) Seed Oil; Quinoa (Chenopodium Quinoa) Oil; Rapeseed (Brassica Campestris) Oil; Rice (Oryza Sativa) Bran Oil; Rice (Oryza Sativa) Germ Oil; Safflower (Carthamus Tinctorius) Oil; Salmon Oil; Sandalwood (Santalum Album) Seed Oil; Seabuchthom (Hippophae Rhamnoides) Oil; Sesame (Sesamum Indicum) Oil; Shark Liver Oil; Shea Butter (Butyrospermum Parkii); Silk Worm Lipids; Skin Lipids; Soybean (Glycine Soja) Oil; Soybean Lipid; Sphingolipids; Sunflower (Helianthus Annuus) Seed Oil; Sweet Almond (Prunus Amygdalus Dulcis) Oil; Sweet Cherry (Prunus Avium) Pit Oil; Tali Oil; Tallow; Tea Tree (Melaleuca Altemifolia) Oil; Telphairia Pedata Oil; Tomato (Solanum Lycopersicum) Oil; Triarachidin; Tiibehenin; Tricaprin; Tricaprylin; Trichodesma Zeylanicum Oil; Trierucin; Triheptanoin; Triheptylundecanoin; Trihydroxymethoxystearin; Trihydroxystearin; Triisononanoin; Triisopalmitin; Triisostearin; Trilaurin; Trilinolein; Trilinolenin; Trimyristin; Trioctanoin; Triolein; Tripalmitin; Tripalmitolein; Triricinolein; Trisebacin; Tristearin; Triundecanoin; Tuna Oil; Vegetable Oil; Walnut (Juglans Regia) Oil; Wheat Bran Lipids; and Wheat (Triticum Vulgare) Germ Oil. In some preferred embodiments, the natural oil product is one or more of soybean oil, coconut oil, rapeseed oil, high oleic acid sunflower oil or olive oil. The oils of the present invention may be partially or fully hydrogenated.

[0092] The amount of softener or ester, preferably biorenewable ester-containing oils, present in the thermoplastic elastomer compositions of the present invention can vary depending upon the types of polymers utilized and end products desired to be formed with the compositions. That said, in one embodiment, the amount of softener, preferably biorenewable, utilized in the thermoplastic elastomer compositions ranges generally from about 5 to about 400 parts, desirably from about 50 to about 250 parts, and preferably from about 75 or 100 to about 200 parts by weight based on 100 total parts by weight of totals styrenic block copolymer. In an embodiment wherein the styrenic block copolymer comprises at least one styrenic block copolymer including a controlled distribution block including a conjugated diene and a monoalkenylarene, the softener or ester, preferably biorenewable, ranges in an amount generally from about 1 to about 85 parts, desirably from about 5 to about 75 parts, and preferably from about 10 to 65 about parts by weight based on 100 total parts by weight of the composition.

[0093] Still additional softeners or extenders include fatty ethers, fatty alcohols and fatty amines. Said components, individually, can be utilized in amounts set forth for the softeners or esters hereinabove.

[0094] Fatty Ethers

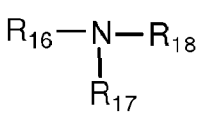
[0095] Fatty ethers are utilized in some compositions of the present invention. Fatty ethers having the general formula R_{13}-O-R_{14}, can be utilized wherein R_{13} contains from about 6 to about 34 carbon atoms and preferably from about 10 to about 22 carbon atoms, and R_{14} contains from about 1 to about 22 carbon atoms and preferably from about 4 to about 22 carbon atoms. The fatty ethers can be linear or branched.

[0096] Fatty Alcohols

[0097] Fatty alcohols are utilized in some compositions of the present invention.Fatty alcohols having the general formula R_{15}-OH, can be utilized wherein R_{15} contains from about 6 to about 34 carbon atoms and preferably from about 13 to about 34 carbon atoms. Examples of fatty alcohols include, but are not limited to1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, 1-undecanol, 1-dodecanol, 1-tridecanol, 1-tetradecanol, 1-pentadecanol, 1-hexadecanol, 1-heptadecanol, 1-octadecanol, 1-nonadecanol, 1-eicosanol, 1-heneicosanol, 1-docosanol, 1-tricosanol, 1-tetracosanol, 1-pentacosanol, 1-hexacosanol, 1-heptacosanol, 1-octasanol, 1-nonacosanol, 1-tricontanol, 1-hentriacontanol, 1-dotriacontanol, 1-tritriacontanol, and 1-tetratriacontanol. In one embodiment, at least one fatty alcohol utilized includes saturation and branching. The fatty alcohols can be linear or branched, for example Guerbet alcohols.

[0098] Fatty Amines

[0099] Fatty amines are utilized in some compositions of the present invention. Fatty amines can be utilized having the general formula:



wherein each R_{16}, R_{17} and R_{18}, independently, is hydrogen, or contains from about 4 to about 34 carbon atoms and preferably from about 10 to about 22 carbon atoms, with the proviso that at least one said R is not hydrogen. Examples of suitable fatty amines include, but are not limited to, amines derived from fatty acids, for example, dimethyl stearamine, stearyl amine, and oleyl amine. In one embodiment at least one fatty amine utilized includes saturation and branching.

The fatty amines can be linear or branched.

[0100] B) Synergistic Additives, Preferably Biorenewable

[0101] As indicated hereinabove in some embodiments, the compositions of the present invention also include a synergistic additive that is believed to create greater stability within the thermoplastic elastomer compositions. Some biorenewable synergistic additives are polar components in various embodiments. The polar synergistic additive can provide one or more of better oil retention at room temperature and at higher temperatures and in some embodiments, greater tensile strength, tensile modulus at various percentages, tensile elongation and tear strength when compared to a corresponding composition without the additive. The thermoplastic elastomer compositions of the present invention can be processed in standard processing equipment such as injection molders and extruders.

[0102] A number of different biorenewable synergistic additives can be utilized in combination with the biorenewable softeners of the present invention. For example, additives include, but are not limited to, starches; thermoplastic starches; and biorenewable polar polymers such as aliphatic polyesters, e.g. polylactic acids and polylactides.

[0103] Starch

[0104] In one embodiment, starches and/or starch-containing components are utilized as a biorenewable synergistic additive. Starch-containing components as utilized herein refers to a composition comprising at least starch and preferably a dispersion aid, for example glycerin. For example, in one embodiment of a dry blend process, if starch is used, a dispersion aid such as glycerin is added to provide desired dispersion of the starch in the blend.

[0105] The term "starch" as utilized herein refers to any starch of natural origin whether processed, chemically modified, or treated. Suitable starches comprise corn starch, potato starch, amaranth starch, arrowroot starch, banana starch, barley starch, cassava starch, millet starch, oat starch, pea starch, rice starch, rye starch, sago starch, sorghum starch, sweet potato starch, tapioca starch, wheat starch, and yam starch.

[0106] The effective plasticizer or dispersion aid helps swell and break the crystalline starch granule, and helps lubricate newly exfoliated, amorphous crystalline starch segments to obtain the thermoplastic starch. Heat and shear further aids in the starch gelatinization process. The plasticizer or dispersion aid can include polyols, such as glycerol, sorbitol etc., adipic acid derivatives, such as tridecyl adipate, benzoic acid derivatives, such as isodecyl benzoate, citric acid derivatives, such as tributyl citrate, glycerol derivatives, phosphoric acid derivatives, such as tributyl phosphate, polyesters, sebacic acid derivatives, dimethyl sebacate, urea. The plasticizer or dispersion aid can also be selected from one or more of glycerine, ethylene glycol, propylene glycol, ethylene diglycol, ethylene triglycol, propylene triglycol, polyethylene glycol, polypropylene glycol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3 -butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,5-hexanediol, 1,2,6-hexanetriol, 1,3,5-hexanetriol, neopentyl glycol, trimethylol propane, pantaerythritol, and the acetate, ethoxylate, and propoxylate derivatives thereof. Moreover, the plasticizer or dispersion aid can be selected from one or more of sorbitol ethoxylate, glycerol ethoxylate, pentaerythritol ethoxylate, sorbitol acetate, and pentaerythritol acetate.

[0107] Starches and starch-containing components provide improved softener stability. In various embodiments with other biorenewable components, for example PLA, compositions having desired hardness ranges can be achieved. Starches and starch-containing components further increase bio-renewable content of the compositions in addition to the biorenewable content of the compositions derived from the softener or plasticizer, without significant deterioration of the mechanical properties of the compositions.

[0108] Starch includes modified starches, such as chemically treated and crosslinked starches, and starches in which the hydroxyl groups have been substituted with organic acids, to provide esters or with organic alcohols to provide ethers, with degrees of substitution in the range 0-3.

[0109] Starch also includes extended starches, such as those extended with proteins; for example with soya protein.

[0110] Thermoplastic starch

[0111] The biorenewable additives of the present invention also include thermoplastic starches. Thermoplastic starches offer the advantages of the capability of flow and are thus suitable for use in polymer processing methods and equipment. Thermoplastic starches are available from various commercial sources in compounded form. In various embodiments, thermoplastic starches are prepared and used simultaneously in a compounding process to form compositions of the present invention. Methods of preparing thermoplastic starch are disclosed in U.S. Patent 6,605,657, herein incorporated by reference. In various embodiments of the present invention a dry blended mixture of elastomer such as styrenic block copolymer, thermoplastic and softener together with other processing additives are fed through an extruder. The mixture is then melt mixed with the thermoplastic starch in the remaining downstream portion of the extruder. There are two extruders involved in this operation. The two are connected in a "T" shape.

[0112] When present in compositions of the present invention, the total starch, one or more of starch and thermoplastic starch, is in an amount from about 2 to about 40 or 80, desirably from about 2 to about 60 and preferably from 2 to about 40 parts by weight based on 100 total parts by weight of the composition. When utilized, the dispersion aid is present in an amount from about 1 to about 80, desirably from about 2 to about 60 and preferably from 2 to about 50 parts by weight based on 100 parts of the starch.

[0113] Polar Polymer

[0114] The biorenewable synergistic additives also include polar polymers such as aliphatic polyesters. Examples of suitable aliphatic polyesters include polylactic acids, and polylactides [PLAs], poly(glycolic acids) and polyglycolides [PGAs], poly (lactic-co-glycolic), and poly(lactide-co-glycolide) [PLGA], polyglyconate, poly(hydroxyalkanoates) [PHAs], polyorthoesters [POEs], polycaprolactones [PCLs], polydioxanone [PDS], polyanhydrides [PANs], polyether-block-amide (PEBA), and their copolymers.

[0115] The polar polymers are provided in amounts which impart desirable properties to the thermoplastic elastomer compositions of the invention, and, when present, generally range in an amount from about 0 to about 80 parts, desirably from about 2 to about 60 parts, and preferably from about 2 or 3 to about 20 or 40 parts based on 100 total parts by weight of the composition of the present invention.

[0116] Polyolefins

[0117] In one embodiment, the compositions of the present invention optionally include one or more polyolefins, which as utilized herein are defined as one or more of a polyolefin polymer and a polyolefin copolymer unless otherwise indicated. Polyolefins suitable for use in the compositions of the present invention comprise amorphous or crystalline homopolymers or copolymers of two or more same or different monomers derived from alpha-monoolefins having from 2 to about 12 carbon atoms, and preferably from 2 to about 8 carbon atoms. Examples of suitable olefins include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 2-methyl-1-propene, 3-methyl-1-pentene, 4-methyl-1-pentene, 5-methyl-1-hexene, and combinations thereof. Polyolefins include, but are not limited to, low-density polyethylene, high-density polyethylene, linear-low-density polyethylene, polypropylene (isotactic and syndiotactic), ethylene/propylene copolymers, and polybutene. Polyolefin copolymers can also include the greater part by weight of one or more olefin monomers and a lesser amount of one or more non-olefin monomers such as vinyl monomers including vinyl acetate, or a diene monomer, etc. Polar polyolefin polymers include ethylene acrylate and ethylene vinyl acetate, for example. In a preferred embodiment, EVA is utilized that has a vinyl acetate content of greater than 5 percent. Generally, a polyolefin copolymer includes less than 40 weight percent of a non-olefin monomer, desirably less than 30 weight percent, and preferably less than about 10 weight percent of a non-olefin monomer.

[0118] In a further embodiment, the polyolefin can include at least one functional group per chain or can be a blend of non-functionalized polyolefins and functionalized polyolefins. Functional groups can be incorporated into the polyolefin by the inclusion of for example, one or more non-olefin monomers during polymerization of the polyolefin. Examples of functional groups include, but are not limited to, anhydride groups such as maleic anhydride, itaconic anhydride and citraconic anhydride; acrylates such as glycidyl methacrylate; acid groups such as fumaric acid, itaconic acid, citraconic acid and acrylic acid; epoxy functional groups; and amine functional groups. Functional group-containing polyolefins and methods for forming the same are well known to those of ordinary skill in the art. Functionalized polyolefins are available commercially from sources such as Uniroyal, Atofina, and DuPont. Epoxy modified polyethylenes are available from Atofina as LOTADER®. Acid modified polyethylenes are available from DuPont as FUSABOND®.

[0119] Polyolefin polymers and copolymers are commercially available from sources including, but not limited to, Chevron, Dow Chemical, DuPont, ExxonMobil, Huntsman Polymers, Ticona and Westlake Polymer under various designations.

[0120] When present, the polyolefins range in an amount generally from about 0.5 to about 60 parts, desirably from about 0.5 or 2 to about 30 or 50 parts, and preferably from about 0.5 to about 20 or 40 parts by weight based on 100 total parts by weight of the total composition.

[0121] Additives

[0122] The compositions of the present invention may include additional additives including, but not limited to lubricants, light stabilizers, antioxidant, flame retardant additives, pigments, peroxides, heat stabilizers, processing aids, mold release agents, flow enhancing agents, nanoparticles, foam agent, platelet fillers and non-platelet fillers. Examples of fillers for use in the compositions include, but are not limited to, one or more of calcium carbonate, talc, clay, zeolite, silica, titanium dioxide, carbon black, barium sulfate, mica, glass fibers, whiskers, carbon fibers, magnesium carbonate, glass powders, metal powders, kaolin, graphite, and molybdenum disulfide. Suitable fillers include bio-based fillers, e.g. various fibers, cellulose, and/or lignin.

[0123] Other Polymers

[0124] In various embodiments, other polymers can be added to the compositions of the present invention in an assortment of amounts provided that such polymers do not interfere with the desired performance of the compositions and constructions formed therewith. Examples of additional polymers include, but are not limited to, polyamide such as nylon, polyesters acrylonitrile-butadiene-styrene copolymers (ABS), halogenated polymers such as polyvinyl chloride, polycarbonates, acrylic polymers, PET, PBT, TPU (including TPU with the bio based polyester block), polyether-block-amide (PEBA).

[0125] The high biorenewable content thermoplastic elastomer compositions of the present invention can be formed by blending the desired components in one or more steps, preferably by mixing. The composition is preferably heated to obtain a melted composition, preferably with mixing, to substantially disperse the components thereof. Melt blending is performed at a temperature generally from about 150°C to about 250°C and preferably from about 170°C to about

210°C. The compositions can be prepared for example in a Banbury, on a two roll mill, in a continuous mixer such as a single screw or twin screw extruder, a kneader, or any other mixing machine as known to those of ordinary skill in the art. The compositions containing thermoplastic starch are prepared in a one step process using combination of single screw extruder connected midway to a twin screw extruder. The process is described in detail in US Patent No. 6,844,380 herein fully incorporated by reference. After preparation of the compositions, they can be pelletized or diced utilizing appropriate equipment, if desired for future further processing. Alternatively, the compositions can be directly molded, or shaped as desired for example using an extruder, injection molder, compression molder, calender, or the like.

[0126] As described herein, desirable compositions can be formed utilizing the teachings of the present invention which exhibit high oil stability; low oil softener or ester leaching; or low oil, etc., bleeding. Oil stability or the like is defined in one embodiment according to the present invention utilizing a loop spew test as defined with the examples section. Desirable compositions according to the present invention have a loop spew rating of 2 or less, desirably 1 or less, and preferably 0, that is no visible evidence of oil on the loop surface.

[0127] The compositions of the present invention can be utilized to form a variety of articles or parts of articles such as, but not limited to, shaving razors, toothbrushes, writing utensils such as pens or pencils, brushes such as paint brushes and hair brushes, hair dryers, tools, for example screwdrivers, hammers, wrenches, pliers and saws, kitchen appliances, for example handles for refrigerators, ovens, microwaves, dishwashers, kitchen utensils, such as spoons, forks, knives, spatulas, can openers, bottle openers, corkscrews, whisks and vegetable peelers, vacuum cleaner handles, brooms, mops, rakes, shovels, scissors, sporting equipment, such as fishing poles, firearms, tennis rackets, and golf clubs, bracelets for example for absorbing sweat, various seals including automotive weather seals, window encapsulation. The thermoplastic elastomer compositions of the invention can also be coated on fabric, such as making wet grip gloves, non-skid fabrics, etc.

[0128] The compositions of the present invention may be formed as a composite with a different substrate for example by connecting the composition of the present invention to the substrate utilizing any desired method, for example overmolding, insert molding, coextrusion, welding or bonding with an adhesive. Overmolding generally involves bonding the thermoplastic elastomer composition to a polymeric substrate utilizing a two-shot or multi-shot injection molding process or a co-injection molding process. Overmolding generally includes providing two or more different materials that are injected into the same mold during the same molding cycle. Insert molding generally comprises inserting pre-molded or pre-formed substrate into a mold and the composition of the present invention is molded directly over or to at least a portion of the insert.

[0129] FIG. 1 illustrates one embodiment of a composite 10 which comprises a layer 20 including a thermoplastic elastomer composition having biorenewable content of the present invention connected to a substrate 30. The substrate can be, for example, one or more of a polymer, rubber or other elastomer, glass, metal or natural substrate, such as wood. FIG. 2 illustrates a writing utensil 40 having a grip 50 formed comprising a composition of the present invention including biorenewable content. Grip 50 is connected to body 60, in particular formed in the shape of a pen.

[0130] Examples

[0131] The examples set forth below are provided to illustrate the high biorenewable content thermoplastic elastomer compositions of the present invention. These examples are not intended to limit the scope of the invention.

[0132] Example Set 1

[0133] **Sample preparation:** All formulations were prepared in a Leistriz 30 mm intermeshing co-rotating twin screw extruder with L/D ratio of 40:1. All ingredients were premixed to a uniform, free-flowing state and then fed to the main feed throat. The extrusion temperature was 170-200°C and the extruder screw speed was 180-350 RPM. Samples from the twin screw extruder were then injection molded at 170-190°C into plaques approximately 2 mm thick, 6.0 cm wide by 8.75 cm long.

Specific Gravity		ASTM D-792
Hardness (Inst./5sec)	Shore A	ASTM D-2240
MFR 190°C, 2.16kg	g/10min	ASTM D-1238
Tensile Strength	psi	ASTM D-412
50% Modulus	psi	ASTM D-412
100% Modulus	psi	ASTM D-412
300% Modulus	psi	ASTM D-412
Tensile Elongation	%	ASTM D-412
Tear Strength	pli	ASTM D-624

(continued)

Specific Gravity		ASTM D-792
Shear Viscosity, 5-5000 1/S, 200 °C	Pa.s	ASTM D3835

[0134] Loop Spew Test: The oil stability in the compounded TPE was tested with a method modified from ASTM D 3291, which was designed for testing plasticizer stability in PVC compound. An approximately 2.54 cm x 8.75 cm specimen was cut from an approximately 2 mm thick molded plaque. The test specimen was conditioned for a minimum of 20 hours at 23°C. A line having a width of about 0.5 mm is drawn in the middle of the specimen along the long direction of the specimen using a ballpoint pen. The conditioned specimen was placed in the loop holder so that a 1.27 cm loop was formed from the edge of the clamp to the inner edge of the loop, with tolerance being +/- 0.159 cm. The clamped specimen was conditioned for 24 hrs at 23°C, or other temperature as specified within a specific example. The specimen was removed from the clamp, examined, and rated as follows:

Loop Spew Rating	Amount of Oil Exudation	Comment
0	None	No visible evidence of oil in the loop surface
1	Very Slight	Very slight sign of oil appears near the crease line, ball-point line stays sharp, and cannot be rubbed off
2	Slight	Slight sign of oil appears uniformly in the loop, line stays sharp but starts to widen
3	Moderate	Moderate oil uniformly appears in the loop. Line further widens and can be rubbed off
4	Severe	Some areas have oil drop, some part of the line starts to disappear
5	Heavy/Dripping	Heavy oil dripping, line has mostly disappeared

[0135] The following raw materials were utilized for the first set of examples.

SBC1	Septon 4055 from Kuraray
SBC2	Kraton A1535H
SBC3	Kraton 1633
Soybean oil	Cargill technical grade soybean oil
PP1	Braskem D115A 12 MI PP
PP2	Braskem F008F .8 MI PP
PLA	Nature Works polylactic acid 4032D
SEBS-MA	Kraton FG1901 GT
Pure TPS	Thermoplastic starch containing 24% glycerin and 76% potato starch was prepared according to U.S. Patent No. 6,605,657
White Mineral Oil	Kristaol 550 from Petra-Canada
CaCO3	Omyacarb 3 from Omya Inc
Potato Starch	MSP Potato Starch from Manitoba Starch Products
Glycerin, technical grade	TR-Glycerine from Twin Rivers Technologies Inc.
EVA	Elvax 460 from DuPont

Table 1

Experiment Number	Comparative #1		Comparative #2	Comparative #3	Example #1
SBC1	37.23%				
SBC2			37.23%	37.23%	25.34%
SBC3					6.98%
PP1	13.96%		13.96%	13.96%	
PP2					10.68%
PLA					4.65%
White Mineral Oil	48.40%		48.40%		
Soybean Oil				48.40%	48.17%
CaCO3					3.72%
Irganox 1010	0.20%		0.20%	0.20%	0.23%
Irgafos 168	0.20%		0.20%	0.20%	0.23%
Total Wt.%	100.00%		100.00%	100.00%	100.00%
Total Bio Content %	0.0%		0.0%	48.4%	52.8%
Loop Spew (Room Temperature, 1.27 cm loop, 24hrs)	Units	0, no oil spew	3, oil spew, line straight, easily rubbed off.	2, oil spew, line straight, easily rubbed off.	1 Very minor oil spew at the crease line. Much improved over other hard grade bio TPE
Specific Gravity		0.884	0.904	0.932	0.939
Stand Hardness (inst.)	A	60.0	58.0	56.0	60.0
Stand Hardness (5 sec)	A	54.0	50.0	50.0	53.0
Tensile Strength	Psi	1362	759	1144	804
Tensile Modulus at 50%	Psi	194	177	199	233
Tensile Modulus at 100%	Psi	230	223	244	297
Tensile Modulus at 300%	Psi	326	369	385	452
Tensile Elongation	%	798	611	793	713
Tear Strength (Die C)	Pli	138	103	136	153

Table 2

Experiment Number		Comparative #4	Example #2	Example #3
SBC2		29.44%	26.76%	26.76%
PP1		8.61%	7.83%	7.83%
SOYBEAN OIL		54.45%	49.50%	49.50%
CaCO3		4.00%	3.64%	3.64%
SEBS-MA		3.00%	2.73%	2.73%
Pure TPS			9.09%	
Potato Starch				7.27%
Glycerin, technical grade				1.82%
Irganox 1010		0.25%	0.23%	0.23%

(continued)

Experiment Number		Comparative #4	Example #2	Example #3
Irgafos 168		0.25%	0.23%	0.23%
Total Wt.%		100.00%	100.00%	100.00%
Total Bio Content %		54.5%	58.6%	58.6%
Loop Spew (Room Temperature, 1,27 cm loop, 24hrs)	Units	2, line may be rubbed off	1, No oil spew, but line may be rubbed off	0 No oil spew
Specific Gravity		0.953	0.979	0.979
Melt Flow Rate (190 °C/2160kg)	g/10min	41.0	78.9	41.5
Stand Hardness (inst.) Stand Hardness (5 sec)	A A	38.0 33.0	38.0 30.0	34.0 31.0
Tensile Strength Tensile Modulus at 50% Tensile Modulus at 100% Tensile Modulus at 300% Tensile Elongation	psi psi psi psi %	420 135 172 265 601	466 105 137 224 747	362 108 139 221 638
Tear Strength (Die C)	pli	91	84	88
Shear Viscosity @ 232 1/s (200 °C, UD=30)	Pa.s	73	81	71

Table 3

Experiment Number		Comparative #5	Example #4	Example #5	Example #6	Example #7
SBC2		24.24%	27.24%	25.34%	25.34%	25.34%
SBC3				6.98%	6.98%	6.98%
PP1		16.48%				
PP2					10.68%	10.68%
Soybean Oil		51.78%	51.78%	48.17%	48.17%	48.17%
CaCO3		4.00%	4.00%	3.72%	3.72%	3.72%
SEBS-MA		3.00%				
PLA			16.48%	15.33%	4.65%	
EVA						4.65%
Irganox 1010		0.25%	0.25%	0.23%	0.23%	0.23%
Irgafos 168		0.25%	0.25%	0.23%	0.23%	0.23%
Total Wt.%		100.00%	100.00%	100.00%	100.00%	100.00%
Total Bio Content		51.8%	68.3%	63.5%	52.8%	48.2%
Loop Spew (Room Temperature, 0.5in loop, 24hrs)	Units	3, oil spew visible	0 No Oil Spew	0 No Oil Spew	1 Very minor oil spew at the crease line. Much improved over other hard grade bio TPE	1 Very minor oil spew at the crease line. Much improved over other hard grade bio TPE
Specific Gravity		0.950	1.003	0.995	0.939	0.933

(continued)

Loop Spew (Room Temperature, 0.5in loop, 24hrs)	Units	3, oil spew visible	0 No Oil Spew	0 No Oil Spew	1 Very minor oil spew at the crease line. Much improved over other hard grade bio TPE	1 Very minor oil spew at the crease line. Much improved over other hard grade bio TPE
Melt Flow Rate (190 °C/2160kg)	g/10min	56.1	65.2	14.0	5.1	4.0
Stand Hardness (inst.)	A	57.0	20.0	18.0	60.0	53.0
Stand Hardness (5 sec delayed)	A	52.0	17.0	17.0	53.0	46.0
Tensile Strength	Psi	552	343	417	804	826
Tensile Modulus at 50%	Psi	222	54	157	233	172
Tensile Modulus at 100%	Psi	269	83	219	297	222
Tensile Modulus at 300%	Psi	390	173	349	452	358
Tensile Elongation	%	575	683	540	713	769
Tear Strength (Die C)	Pli	129	54	122	153	113
Shear Viscosity @ 232 1 /s (200 °C, L/D=30)	Pa.s	59	68	144	171	181

Table 4

Experiment Number	Comparative #6	Example #8	Example #9	Example #10	Example #11	Example #12
SBC2	21.19%	21.45%	24.19%	22.50%	22.50%	22.50%
SBC3		7.59%		6.98%	6.98%	6.98%
PP1	20.71%	15.18%				
PP2					14.61%	14.61%
Soybean Oil	50.60%	51.22%	50.60%	47.07%	47.07%	47.07%
CaCO3	4.00%	4.05%	4.00%	3.72%	3.72%	3.72%
SEBS-MA	3.00%					
PLA			20.71%	19.27%	4.65%	
EVA						4.65%
Irganox 1010	0.25%	0.25%	0.25%	0.23%	0.23%	0.23%
Irpafos 168	0.25%	0.25%	0.25%	0.23%	0.23%	0.23%

(continued)

Experiment Number		Comparative #6	Example #8	Example #9	Example #10	Example #11	Example #12
		100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
Total Bio Content		50.6%	51.2%	71.3%	66.3%	51.7%	47.1%
Loop Spew (Room Temperature, 0.5in loop, 24hrs)	Units	3, oil spew visible	2 Slight oil spew. Line stay sharp	0 No oil spew	0 No oil spew	1 Very minor oil spew at the crease line. Much improved over other hard grade bio TPE	1 Very minor oil spew at the crease line. Much improved over other hard grade bio TPE
Specific Gravity		0.948	0.955	1.013	1.006	0.934	0.930
Melt Flow Rate (190 °C/2160kg)	g/10min	58.3	26.1	94.7	22.4	4.8	4.9
Stand Hardness (inst.)	A	67.0	58.0	19.0	13.0	70.0	63.0
Stand Hardness (5 sec)	A	63.0	52.0	16.0	12.0	62.0	57.0
Tensile Strength	Psi	528	687	215	383	859	873
Tensile Modulus at 50%	psi	283	179	36	209	302	264
Tensile Modulus at 100%	psi	330	220	52	283	368	323
Tensile Modulus at 300%	Psi	443	338	117	379	519	470
Tensile Elongation	%	497	750	625	278	686	653
Tear Strength (Die C)	Pli	140	112	69	111	171	147
Shear Viscosity @ 232 1/s (200 °C, L/D=30)	Pa.s	56	91	49	116	160	175

[0136] As shown in Table 1, Comparative #1 is a general purpose TPE based on regular SBC and white mineral oil, Comparative #2 is based on controlled distribution SEBS and mineral oil, and Comparative #3 on controlled distribution SEBS with vegetable oil, and both comparative #2 and #3 showed noticeable oil spew. With the use of high MW SBC, and some PLA, the oil stability is much improved at equivalent hardness as illustrated in Example #1.

[0137] In Table 2, Comparative #4 showed substantial oil bleeding. Examples #2 and #3 with either TPS or starch/glycerin exhibited greatly improved oil stability.

[0138] In Table 3, Comparative #5 showed substantial oil bleeding. Examples #4 and #5 with PLA improved the oil stability, but reduced hardness/strength. Examples #6 & 7 showed improved oil stability and strength while maintaining hardness with the use of high MW SBC, high MW PP in addition to PLA or EVA.

[0139] In Table 4, Comparative #6 showed substantial oil bleeding. Example #8 showed some oil stability improvement with the use of MW SBC. Examples #9 and # 10 with just PLA improved the oil stability, but reduced hardness/strength. Examples #11 and#12 showed improved oil stability and strength while maintaining hardness with the use of high MW SBC, high MW PP in addition to PLA or EVA.

[0140] Example Set 2

[0141] Two different styrenic-block copolymers, styrene-ethylene-ethylene/propylene-styrene (SEEPS) and styrene-ethylene-butylene-styrene (SEBS) with controlled distribution of styrene in the middle block, were used in this set of examples. All the materials before compounding were dry-blended together and were compounded using a twin-screw extruder. The extrusion temperature was 150-200°C and the extruder screw speed was 150-350 RPM. Samples from the twin screw extruder were then injection molded at 170-200°C into plaques approximately 2 mm thick, 9.0 cm wide by 12.5 cm long.

[0142] In the case of formulations containing thermoplastic starch (TPS), it is obtained in a one-step process by gelatinizing the native starch using water, glycerin, heat, and shear on a twin screw extruder. The further details of the process can be found in US Patents 6,605,657 and 6,844,380. The other ingredients after dry-blending were melt-mixed using a single screw extruder. This melt was introduced half-way to the twin screw extruder used for preparing TPS. The latter half of the twin screw extruder was used to melt mix the melt from the single screw extruder with the TPS phase.

[0143] The following raw materials were utilized for the second set of examples.

SBC 2.1	Septon 4033 from Kuraray
SBC 2.2	Septon 4055 from Kuraray
SBC 2.3	Kraton A1535H
SBC 2.4	Kraton A1536H
PP 2.1	Formolene 4100P
PLA 2.0	Nature Works Ingeo 3001D
SEBS-MA 2.0	Kraton FG1901X
Starch	Potato starch - Penford Pencook10 or Corn starch - Cargill Pearl B1103
Glycerol	Twin Rivers Technologies - Glycerin refined technical grade
COAD 10 MATHE (CaSt)	Norac MATHE NF/FG/Kosher
Silicon oil	Dow Xiameter PMX-200 Fluid 500 CS
Mineral oil	Sonneborn, Teknor 215 Oil
Canola, Peanut, Coconut, Hydrogenated vegetable oil,	Off-the-shelf from grocery store
HEAR Oil	Bunge, RB HEAR Oil
Polystyrene	Atfina 535B
Beeswax	Kosterkeunen Beeswax 262P
Candelilla wax	Kosterkeunen 102P
Carnauba wax	Kosterkeunen 420F
Iso-propyl Palmitate	KLK Oleochemicals, Palmester 1517
Iso-stearyl Iso-Stearate	Lubrizol, Schercemol 1818 ester
Oleyl Oleate	Lubrizol, Schercemol OLO ester
Lauryl Alcohol	Kosterkeunen 546P
Cetyl Alcohol	Kosterkeunen 172P
Behenyl Alcohol	Kosterkeunen 2275

(continued)

Guerbet Alcohol	BASF, Synative AL G 20
Dimethyl Stearamine	Kao, Farmin DM8098
PHA	Telles, Mirel M4100

[0144] The samples for tensile testing were cut across the major flow direction from injection molded plaques. A cutting die of approximately ASTM D-412, die C specification was used for this purpose. The dimension C was 11 cm (instead of 11.5 cm) and dimension L was 2.7 cm (instead of 3.3 cm). Hardness plaques of approximate dimension of 5.0 x 5.0 x 0.6 cm were compression molded.

[0145] Following test protocols were used for testing,

Hardness (Inst./5sec)	Shore A	ASTM D-2240
Tensile Strength	psi	ASTM D-412
50% Modulus	psi	ASTM D-412
100% Modulus	psi	ASTM D-412
300% Modulus	psi	ASTM D-412
Tensile Elongation	%	ASTM D-412
Tension Set	%	ASTM D-412
Compression Set, Time (hrs) @ temperature (°C)	%	ASTM D395

[0146] Oil bleeding performance was determined by the above explained loop spew test.

[0147] It was surprisingly found that the formulations demonstrate a wide range of elastomeric properties despite the high bio-based content. For SEEPS based formulations, an increase in the level of saturation and the backbone fatty carbon chain length in an oil/ester/alcohol/amine is found to significantly reduce the oil (extender/softner) bleeding in these materials. In some embodiments, fatty esters/alcohols/amines show even better retention in the formulation than oils. Depending upon the formulation and bio-based content, the bio-TPEs are translucent to opaque and demonstrate excellent soft, dry touch and feel characteristics. The hardness values can be formulated to range, for example, from 40 Shore A to 40 Shore D. The mechanical properties can be controlled over a wide range with tensile strength from 0.9 to 7 MPa; maximum elongation from 100 to 2000%; tension sets from 2 to 45%; compression sets (at 70°C) from 40 to 90%; and excellent oil retention (no bleeding at 110°C up to only slight bleeding at 135°C) properties.

[0148] Two control formulations containing mineral oil and different amounts of PP (27.5 phr (Comparative # 7) and 55phr (Comparative # 8)) are prepared as reference materials (controls). These reference samples form the baseline for the second set of examples and demonstrate excellent oil retention up to 110°C together with high strengths and elongations.

[0149] **Formulations with SEEPS and vegetable oils:**

[0150] In the new formulations, SEEPS with PP and typical vegetable oils (e.g. hydrogenated vegetable oil (HVO)) demonstrate severe oil bleeding as shown by formulation A1. The formulations prepared using mixtures of peanut oil with mineral oil are found to bleed severely up to a ratio of 75/25, formulation A3. The inclusion of native dry starch or the thermoplastic starch (TPS) brings increased biobased content into the formulation and has no further effect on Canola oil bleeding as shown by formulations B4 and B5. These examples demonstrate the inherent incompatibility of vegetable oils with general class SBC elastomers.

[0151] It is found that mixtures of Coconut oil (formulation A4) or HVO (formulation A5) with mineral oil at 75/25 ratio demonstrate increased compatibility with SEEPS elastomer due to an increased level of saturation. No oil bleeding is observed at room temperature. The formulation with HVO is found to be stable even at the higher temperature of 70°C for 168 hrs. The surface of these formulations, however, is found to be slightly slippery, perhaps due to the migration of minute amounts of oil to the surface. The increase in fatty acid chain length of a triglyceride (oil) is also found to increase the compatibility with the elastomer, e.g. high erucic acid rapeseed (HEAR) oil (formulation A56) demonstrates only a slight bleeding at room temperature. Despite a high bio-based content of 60%, this latter formulation is found to demonstrate highly balanced properties with strengths and elongations similar to the control Comparative # 8. This is an important achievement.

Table 5

Formulation Name		Comparative # 7	Comparative #8	A1	A3	B4	B5	A4	A5	A56
SBC 2.1	wt.%	5.0	4.5		4.6	17.0	17.0	4.6	4.6	
SBC 2.2	wt.%	30.8	28.0	32.8	28.2	17.0	17.0	28.0	28.0	22.8
SEBS-MA2.0	wt.%					5.0	5.0			4.7
PP 2.1	wt.%	9.9	18.0	18.0	18.0			17.9	17.9	12.5
Starch	wt.%					30.5	21.4			22.1
Glycerol	wt.%						9.1			9.5
COAD 10 MATHE (CaSt)	wt.%	0.1	0.1		0.1			0.1	0.1	
Silicon oil	wt.%	0.5	0.5	0.7	0.5			0.5	0.5	
Mineral oil	wt.%	53.7	48.9		12.3			12.2	12.2	
Natural oils	Name			HVO*	Peanut oil	Canola oil	Canola oil	Coconut oil	HVO*	HEAR oil
	wt.%			48.5	36.9	30.5	30.5	36.7	36.7	28.4
Bio-based content	wt.%	0.0	0.0	48.5	36.7	61.0	61.0	36.7	36.7	60.0
Hardness, 5sec	Shore A	38	60			39	43			
Max. Stress	MPa		7.95							6.7
Strain at Break	%		1610							713
Tension Set	%									
Compression Set	%, 22h at 70°C	42	47			97	91			

(continued)

Formulation Name		Comparative # 7	Comparative #8	A1	A3	B4	B5	A4	A5	A56
Loop Spew (Room Temperature, 0.5in loop, 24hrs)	Units	0 No oil spew	0 No oil spew	5 Severe Oil Bleeding	5 Severe Oil Bleeding	5 Severe Oil Bleeding	5 Severe Oil Bleeding	1 Minor oil spew, much improved over previous formulations	1 Minor oil spew, much improved over previous formulations	3 Moderate oil spew, much improved over other liquid oils
HVO stands for Hydrogenated Vegetable Oil.										

[0152] Further optimization of the example formulation A56 demonstrates even improved performance on strength, strain at break, and the oil retention at a higher temperature of 70°C as shown below by the example A62.

Table 6

Formulation Name		Comparative # 7	Comparative # 8	A56	A62
SBC 2.1	wt.%	5.0	4.5		
SBC 2.2	wt.%	30.8	28.0	22.8	22.1
SEBS-MA 2.0	wt.%			4.7	5.7
PP 2.1	wt.%	9.9	18.0	12.5	12.2
Starch	wt.%			22.1	24.3
Glycerol	wt.%			9.5	13.6
COAD 10 MATHE (CaSt)	wt.%	0.1	0.1		
Silicon oil	wt.%	0.5	0.5		
Mineral oil	wt.%	53.7	48.9		
Natural oils	Name			HEAR oil	HEAR oil
	wt.%			28.4	22.1
Bio-based content	wt.%	0.0	0.0	60.0	60.0
Hardness, 5sec	Shore A	38	60		
Max. Stress	MPa		7.95	6.7	7.5
Strain at Break	%		1610	713	1162
Tension Set	%				
Compression Set	%, 22h at 70°C	42	47		
Loop Spew (Room Temperature, 0.5in loop, 24hrs)	Units	0 No oil spew	0 No oil spew	3 Moderate oil spew, much improved over other liquid oils	2 Slight oil spew, much improved over A56

[0153] **High styrenic-SEBS - vegetable oils formulation and mixtures of SEEPS and high styrenic-SEBS:**

[0154] High styrene containing SEBS elastomer on the other hand shows good compatibility with typical vegetable oils (formulation B1 to B3, B7) or in mixtures (75/25) with mineral oil (formulation B6). No oil is found to bleed up to 70°C, 168hrs. These formulations, however, bleed severely at the higher temperatures of 110 and 135°C. Thus, compared to similar formulation with SEEPS (formulations B4 and B5) high styrene containing SEBS formulations demonstrate very high acceptability towards polar vegetable oils due to high, overall styrene content and mid-block butadiene-styrene configuration.

[0155] The formulations containing a 50/50 mixture of SEEPS and high styrenic SEBS (formulation B8) also demonstrate very good compatibility with typical vegetable oils such as Canola oil. The formulation shows no oil bleeding at room temperature and only a slight bleeding at 70°C.

Table 7

Formulation Name		B1	B2	B3	B7	B6	B8
SBC 2.3	wt.%	17.0	17.0	12.8	14.3	10.9	
SBC 2.4	wt.%	17.0	17.0	12.8	14.3	10.9	12.5

(continued)

Formulation Name		B1	B2	B3	B7	B6	B8
SBC 2.2	wt.%						12.5
SEBS-MA 2.0	wt.%	5.0		6.3	5.7	3.6	6.2
PP 2.1	wt.%			7.1		6.0	8.8
Polystyrene (PS) (missing descriptions)	wt.%				5.7		
Starch	wt.%	30.5	21.4	37.9	34.3	24.8	37.5
Glycerol	wt.%		9.2			10.6	
COAD 10 MATHE (CaSt)	wt.%					0.1	
Silicon oil	wt.%					0.3	
Mineral oil	wt.%					8.2	
Natural oils	Name	Canola	Canola	Canola	Canola	HVO	Canola
	wt.%	30.5	30.5	23.1	25.7	24.6	22.5
Bio-based content	wt.%	61.0	61.0	61.0	60.0	60.0	60.0
Hardness, 5sec	Shore A	38	42	62		48	
Max. Stress	MPa	1.9	2.0	2.5			
Strain at Break	%	706	521	437			
Tension Set	%						
Compression Set	%, 22h at 70°C	100	100	100		93	
Loop Spew (Room Temperature, 0.5in loop, 24hrs)	Units				0 No oil spew		0 No oil spew

[0156] Formulations with SEEPS, natural waxes and TPS:

[0157] It is further found that SEEPS bio-TPE formulations containing natural waxes as a replacement for mineral oil, e.g. Bees wax, Candelilla wax, and Carnauba wax (formulation A35, A37, and A38) can be prepared. These formulations demonstrate no bleeding of wax up to 70°C for 168hrs. Candelilla wax based Bio-TPE formulation demonstrates no bleeding at 110°C for 168hrs. These formulations showed very high strengths and very limited elongations along with high hardness values.

Table 8

Formulation Name		A35	A37	A38
SBC 2.1	wt.%	3.1	3.1	3.1
SBC 2.2	wt.%	18.8	18.8	18.8
SEBS-MA 2.0	wt.%	3.5	3.5	3.5
PP 2.1	wt.%	6.0	6.0	6.0
Starch	wt.%	24.8	24.8	24.8
Glycerol	wt.%	10.6	10.6	10.6
COAD 10 MATHE (CaSt)	wt.%	0.1	0.1	0.1
Silicon oil	wt.%	0.3	0.3	0.3

(continued)

Formulation Name		A35	A37	A38
Mineral oil	wt.%	8.2	8.2	8.2
Natural waxes	Name	Beeswax	Candelilla	Carnauba
	wt.%	24.6	24.6	24.6
Bio-based content	wt.%	60.0	60.0	60.0
Hardness, 5sec	Shore A/D	84 (A)	35 (D)	37 (D)
Max. Stress	MPa		6.1	
Strain at Break	%		445	
Tension Set	%			
Compression Set	%, 22h at 70°C	86	91	74
Loop Spew (Room Temperature, 0.5in loop, 24hrs)	Units	0 No oil spew	0 No oil spew	0 No oil spew

[0158] Formulations with SEEPS, esters (mono, fatty, tri-esters etc.), and TPS:

[0159] It is also found that various esters (including mono, wax, fatty, bio-diesel methyl/ethyl esters, branched esters etc.) or their mixtures as a replacement for mineral oil demonstrate improved compatibility with SEEPS elastomer and, thus, can be used to prepare successful Bio-TPE formulations. Only selective examples of Bio-TPE formulations, prepared using iso-propyl palmitate (formulation A47), iso-stearyl iso-stearate (formulation A48), and oleyl oleate (formulation A57), are provided. The formulation based on iso-propyl palmitate demonstrates very low hardness (only 45 Shore A) and no oil bleeding up to 110°C for 72hrs despite high (60%) bio-based content. Only a little bleeding was evident after 168hrs at 110°C and at a very high temperatures of 135°C. Formulations based on iso-stearyl iso-stearate and oleyl oleate demonstrate lower hardness values, higher strengths, and excellent elongation at break values. These formulations are also found to not bleed the ester up to 70°C. Comparing the bleeding performance of ester based formulations, in particular oleyl oleate (A57,) with the formulation containing similar or even lower amount of triglycerides (oils) per hundred parts of rubber (elastomer) shows that esters demonstrate generally less bleeding with SEEPS than triglycerides.

Table 9

Formulation Name		A47	A48	A57
SBC 2.1	wt.%	3.1	3.1	
SBC 2.2	wt.%	18.8	18.8	22.8
SEBS-MA 2.0	wt.%	3.5	3.5	4.7
PP 2.1	wt.%	6.0	6.0	12.5
Starch	wt.%	24.8	24.8	22.1
Glycerol	wt.%	10.6	10.6	9.5
COAD 10 MATHE (CaSt)	wt.%	0.1	0.1	
Silicon oil	wt.%	0.3	0.3	
Mineral oil	wt.%	8.2	8.2	
Natural esters	Name	Iso-propyl Palmitate	Iso-stearyl Iso-stearate	Oleyl Oleate
	wt.%	24.6	24.6	28.4
Bio-based content	wt.%	60.0	60.0	60.0
Hardness, 5sec	Shore A	45	48	

(continued)

Formulation Name		A47	A48	A57
Max. Stress	MPa	1.2	3.0	4.4
Strain at Break	%	566	629	638
Tension Set	%			
Compression Set	%, 22h at 70°C	92	83	
Loop Spew (Room Temperature, 0.5in loop, 24hrs)	Units	0 No oil spew	0 No oil spew	0 No oil spew

[0160] Formulations with SEEPS, alcohols (fatty, branched etc.), and TPS:

[0161] Fatty alcohols as a replacement for mineral oil (including branched fatty alcohols etc.) are also found very useful to prepare Bio-TPE formulations with SEEPS. Bio-TPE formulations containing lauryl alcohol (formulation A41) is found to bleed severely at room temperature perhaps due to its shorter aliphatic carbon backbone. Successful examples include cetyl (formulation A42), behenyl (formulation A36), and guerbet alcohol (formulation A54). The formulation based on behenyl alcohol shows no bleeding up to 110 °C and very little at the high temperature of 135°C for 168 hrs. The Shore A hardness, however, is estimated to be around 86. The formulations A42 and A54 show no bleeding up to 70°C, 168 hrs, and only slight at 110C, 168 hrs. Both of these formulations show good strength and elongation at break values. However, the formulation with Guerbet alcohols also demonstrates lower hardness values than the formulation with cetyl alcohol.

Table 10

Formulation Name		A41	A42	A36	A54
SBC 2.1	wt.%	3.1	3.1	3.1	
SBC 2.2	wt.%	18.8	18.8	18.8	22.1
SEBS-MA 2.0	wt.%	3.5	3.5	3.5	5.7
PP 2.1	wt.%	6.0	6.0	6.0	12.2
Starch	wt.%	24.8	24.8	24.8	26.5
Glycerol	wt.%	10.6	10.6	10.6	11.4
COAD 10 MATHE (CaSt)	wt.%	0.1	0.1	0.1	
Silicon oil	wt.%	0.3	0.3	0.3	
Mineral oil	wt.%	8.2	8.2	8.2	
Natural alcohols	Name	Lauryl Alcohol	Cetyl Alcohol	Behenyl Alcohol	Guerbet Alcohol
	wt.%	24.6	24.6	24.6	22.1
Bio-based content	wt.%	60.0	60.0	60.0	60.0
Hardness, 5sec	Shore A	86	90	95	
Max. Stress	MPa				3.5
Strain at Break	%				725
Tension Set	%				
Compression Set	%, 22h at 70°C				

(continued)

Formulation Name		A41	A42	A36	A54
Loop Spew (Room Temperature, 0.5in loop, 24hrs)	Units	5 Sever oil spew	0 No oil spew	0 No oil spew	0 No oil spew

[0162] Formulations with SEEPS, fatty amines, and TPS:

[0163] It is also found that fatty amines can also be used to prepare SEEPS Bio-TPE formulations. The example includes the formulation (A59) prepared using Dimethyl Stearamine. The formulation demonstrates excellent strength and elongation at break over 700%. It is found to have some bleeding at room temperature and only slight bleeding at 70°C.

Table 11

Formulation Name		A59
SBC 2.1	wt.%	
SBC 2.2	wt.%	22.8
SEBS-MA 2.0	wt.%	4.7
PP 2.1	wt.%	12.5
Starch	wt.%	22.1
Glycerol	wt.%	9.5
COAD 10 MATHE (CaSt)	wt.%	
Silicon oil	wt.%	
Mineral oil	wt.%	
Natural amines	Name	Dimethyl Stearamine
	wt.%	28.4
Bio-based content	wt.%	60.0
Hardness, 5sec	Shore A	
Max. Stress	MPa	3.6
Strain at Break	%	946
Tension Set	%	
Compression Set	%, 22h at 70°C	
Loop Spew (Room Temperature, 0.5in loop, 24hrs)	Units	2 Minor oil spew

[0164] Formulations with SEEPS, vegetable oils, and other bio-thermoplastics such as PLA, PHA :

[0165] In these embodiments, it is shown that SEEPS Bio-TPE formulations can also be prepared using other bio-thermoplastics such as PLA and PHAs. These formulations are prepared using different vegetable oils, however, the same can be prepared using the above mentioned esters/alcohols/amines etc. The formulations A2 and C12 prepared using 100% vegetable oils (HVO and Peanut oil respectively) are found to bleed severely at room temperature. The mixture of 85% vegetable oil/15% mineral oil is also found to bleed severely (formulation C13). The formulations containing 75% vegetable oil/25% mineral oil (formulation C11 with the peanut oil, formulation A6 with the coconut oil, and formulation A7 with HVO), however, do not bleed at room temperature. Formulation C14 contains higher amounts of PLA and do not bleed at room temperature. Formulation (A25) prepared using PHA also demonstrates a good compatibility with HVO, no oil bleeding at the room temperaure and demonstrates a hardness of only 56 Shore A.

Table 12

Formulation Name		**A2**	**C12**	**C13**	**C11**	**C14**	**A6**	**A7**	**A25**
SBC 2.1	wt.%						4.6	4.6	3.3
SBC 2.2	wt.%	32.8	32.8	32.8	32.8	26.8	28.0	28.0	20.6
PP 2.1	wt.%								6.6
PLA 2.0	wt.%	17.9	17.9	17.9	17.9	23.9	17.9	17.9	
PHA	wt.%								33.0
COAD 10 MATHE (CaSt)	wt.%						0.1	0.1	0.1
Silicon oil	wt.%	0.8	0.5	0.5	0.5	0.5	0.5	0.5	0.4
Mineral oil	wt.%			7.0	12.1	12.2	12.2	12.2	9.0
Natural oils	Name	HVO	Peanut-oil	Peanut-oil	Peanut-oil	Peanut-oil	Coconut oil	HVO	HVO
	wt.%	48.5	48.8	41.8	36.7	36.6	36.7	36.7	27.0
Bio-based content	wt.%	66.4	66.7	59.7	54.6	60.5	54.6	54.6	60.0
Hardness, 5sec	Shore A			49	47	64			
Max. Stress	MPa								
Strain at Break	%								
Tension Set	%								
Compression Set	%, 22h at 70°C								79
Loop Spew (Room Temperature, 0.5in loop, 24hrs)	Units	5 Severe oil bleeding	5 Severe oil bleeding	5 Severe oil bleeding	0 No oil bleeding	0 No oil bleeding	0 No oil bleeding	0 No oil bleeding	0 No oil bleeding

[0166] While in accordance with the patent statutes the best mode and preferred embodiment have been set forth, the scope of the invention is not intended to be limited thereto, but only by the scope of the attached claims.

Claims

1. A thermoplastic elastomer composition, comprising:

   an elastomer comprising a styrenic block copolymer;
   a biorenewable softener comprising one or more of a natural, fatty ester; a natural, fatty ether; a natural, fatty alcohol; and a natural, fatty amine in an amount from 1 to 90% by weight;
   a thermoplastic polymer or copolymer in an amount from 0 to 30% by weight;
   a bio-based thermoplastic comprising one or more of starch, polylactic acid,
   and PHA in an amount from 0 to 50% by weight;
   glycerol in an amount from 0 to 25% by weight;
   a mineral oil in an amount from 0 to 50% by weight;
   a maleated copolymer in an amount from 0 to 20% by weight;
   a filler in an amount from 0 to 70% by weight;
   optionally, other processing aids selected from one or more of antioxidants, lubricants, flame retardants, and UV stabilizers; and
   wherein all said percentages are based on 100% by weight of the composition.

2. The composition according to claim 1, wherein the composition further includes a functionalized styrenic block copolymer, a polyolefin, starch and/or thermoplastic starch, and glycerol.

3. The composition according to claim 1 or 2, wherein the natural, fatty ester is present and comprises one or more of a wax and an oil.

4. The composition according to anyone of claims 1-3, wherein the composition further includes a functionalized styrenic block copolymer, a polyolefin, and starch and/or thermoplastic starch; and wherein a natural, fatty alcohol or natural, fatty ester is present.

5. The composition according to anyone of claims 1-4, wherein the composition further includes a functionalized styrenic block copolymer, a polyolefin, and starch and/or thermoplastic starch; and wherein a natural, fatty amine is present.

6. The composition according to anyone of claims 1-5, wherein the natural, fatty ester comprises an oil, wherein a polar polymer, more specifically one or more of polylactic acid and PHA, is present and wherein the mineral oil is present.

7. The composition according to anyone of claims 1-6, wherein the styrenic block copolymer comprises at least one controlled distribution copolymer block having a conjugated diene and a monoalkenyl arene, wherein the biorenewable softener comprises the natural, fatty ester, and wherein the composition includes at least one synergistic additive comprising one or more of starch, thermoplastic starch, a biorenewable polar polymer, a high molecular weight styrenic block copolymer, and ethylene vinyl acetate.

8. The composition according to anyone of claims 1-7, wherein the styrenic block copolymer having a controlled distribution copolymer block is present in an amount from 5% to 90% by weight; wherein the biorenewable softener comprises the natural, fatty ester that is an ester-containing oil which is present in an amount from 1% to 85% by weight of the composition; and wherein the composition further includes a polyolefin.

9. The composition according to anyone of claims 1-8, wherein the composition includes the biorenewable polar polymer in an amount from about 2% to 60% by weight, and wherein the composition is free of a mineral oil.

10. The composition according to anyone of claims 1-9, wherein the composition includes a functionalized styrenic block copolymer, and a polyolefin; and wherein the composition further includes one or more of starch and thermoplastic starch that is present in an amount from 2% to 80% by weight of the composition.

11. The composition according to anyone of claims 1-10, wherein the composition comprises the biorenewable polar

polymer in an amount from 2% to 60% by weight of the composition, wherein the biorenewable softener comprises the natural, fatty ester that is an ester-containing oil which is present in an amount from 10% to 65% by weight of the composition, and wherein the composition is free of a mineral oil.

12. The composition according to anyone of claims 1-11, wherein the composition further includes a high molecular weight styrenic block copolymer in an amount from 1% to 30% by weight of the composition.

13. The composition according to anyone of claims 1-12, wherein the composition further includes a polyolefin.

14. An article comprising a composition according to any of the preceding claims.

15. A process for preparing a thermoplastic elastomer composition, comprising the step of combining the components set forth in any of claims 1-13 utilizing a one-step compounding process.

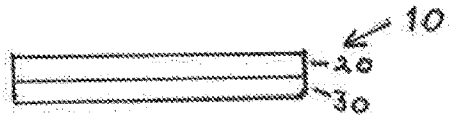


FIG. 1

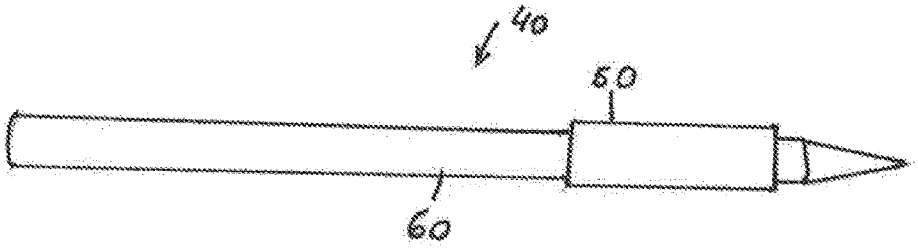


FIG. 2

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 13 15 2325

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2008/085961 A1 (LIN SAMUEL [US] LIN SAMUEL Q [US]) 10 April 2008 (2008-04-10) * claims; examples *	1-15	INV. C08L53/02 C08K5/00
X,D	WO 2009/152870 A1 (TECNOFILM SPA [IT]; CARDINALI BRUNO [IT]) 23 December 2009 (2009-12-23) * claims; examples *	1-15	ADD. C08L3/02
X,D	US 6 673 857 B1 (KNOLL KONRAD [DE] ET AL) 6 January 2004 (2004-01-06) * claims; examples *	1-15	

TECHNICAL FIELDS SEARCHED (IPC)
C08K
C08L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	13 May 2013	Friebe, Lars

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 13 15 2325

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13-05-2013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008085961 A1	10-04-2008	EP 2068820 A1	17-06-2009
		JP 2010506036 A	25-02-2010
		US 2008085961 A1	10-04-2008
		US 2010041754 A1	18-02-2010
		WO 2008045451 A1	17-04-2008
WO 2009152870 A1	23-12-2009	NONE	
US 6673857 B1	06-01-2004	AT 276317 T	15-10-2004
		AU 4558500 A	17-11-2000
		DE 19920257 A1	09-11-2000
		EP 1181333 A1	27-02-2002
		ES 2226830 T3	01-04-2005
		US 6673857 B1	06-01-2004
		WO 0066662 A1	09-11-2000

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 20110184082 A **[0003]**
- US 201000630008 A **[0004]**
- US 20080171007 A **[0005]**
- US 20080171006 A **[0006]**
- US 20060121170 A **[0007]**
- US 7884158 B **[0008]**
- US 7625967 B **[0009]**
- US 7267855 B **[0010]**
- US 7169848 B **[0011] [0064]**
- US 6984688 B **[0012]**
- US 6673857 B **[0013]**
- US 6031053 A **[0014]**
- WO 2009152870 A **[0015]**
- WO 2008087675 A **[0016]**
- US 6653408 B **[0058]**
- US 3595942 A **[0071]**
- US 3634549 A **[0071]**
- US 3670054 A **[0071]**
- US 3700633 A **[0071]**
- US 27145 A **[0071]**
- US 4578429 A, Gerge **[0072]**
- US 5506299 A **[0072]**
- US 4882384 A **[0072]**
- US 4898914 A **[0072]**
- US 4970265 A **[0072]**
- US 5206300 A **[0072]**
- US 5276101 A **[0072]**
- US 5516831 A **[0072]**
- US 6605657 B **[0111] [0135] [0142]**
- US 6844380 B **[0125] [0142]**

Europäisches Patentamt
European Patent Office
Office européen des brevets

Espacenet

JP2018199653A COSMETIC

Applicants: TOSHIKI PIGMENT KK,NEGAMI KOGYO KK

Inventors: SHIGIHARA YASUHIRO,ITO KEIJI,SUZUKI TOSHIHIRO,NISHIDA KEIKO,TAMURA KANAME

Classifications:
IPC ***A61K8/87; A61K8/891; A61Q1/00; A61Q1/02; A61Q1/12;***

Priorities: JP2017105847A 2017-05-29

Application: JP2017105847A·2017-05-29

Publication: JP2018199653A·2018-12-20

Published as: JP2018199653A;**JP6799242B2**

COSMETIC

Abstract

To provide a cosmetic that gives a natural finish feeling, and has high effects of concealing skin blotches and pores.SOLUTION: The present invention provides a powder cosmetic, or makeup cosmetic, containing a composite particle composed of a polyurethane powder encapsulating a silicone resin powder such as a polymethylsilsesquioxane powder. In the total content of the silicone resin powder contained in the composite particle and the polyurethane powder, the content of the silicone resin powder is preferably 2-13 mass%. Preferably, when irradiated with light of blue wavelength (450 nm) and light of red wavelength (700 nm) at the same intensity, the composite particle absorbs more strongly the light of blue wavelength and reflects more strongly the light of red wavelength.SELECTED DRAWING: None

(19)日本国特許庁(JP)　(12)公開特許公報(A)　(11)特許出願公開番号
特開2018-199653
(P2018-199653A)
(43)公開日　平成30年12月20日(2018. 12. 20)

(51) Int.Cl.			F I		テーマコード（参考）
A61K	8/891	(2006.01)	A61K	8/891	4C083
A61Q	1/00	(2006.01)	A61Q	1/00	
A61K	8/87	(2006.01)	A61K	8/87	
A61Q	1/02	(2006.01)	A61Q	1/02	
A61Q	1/12	(2006.01)	A61Q	1/12	

審査請求 未請求　請求項の数 5　ＯＬ　（全 11 頁）

(21)出願番号　特願2017-105847 (P2017-105847)
(22)出願日　平成29年5月29日 (2017. 5. 29)

(71)出願人　595137022
東色ピグメント株式会社
東京都葛飾区立石６－３７－１４
(71)出願人　390028048
根上工業株式会社
石川県能美市道林町ロの２２番地
(74)代理人　100087642
弁理士　古谷　聡
(74)代理人　100098408
弁理士　義経　和昌
(72)発明者　鳴原　靖宏
東京都葛飾区立石６－３７－１４　東色ピグメント株式会社内

最終頁に続く

(54)【発明の名称】化粧料

(57)【要約】　（修正有）
【課題】自然な仕上がり感が得られ、シミや毛穴隠し効果が良い化粧料の提供。
【解決手段】ポリメチルシルセスキオキサン粉末等のシリコーン樹脂粉末を内包するポリウレタン粉末からなる複合粒子を含有している粉体化粧料、又はメイクアップ化粧料。前記複合粒子に含まれているシリコーン樹脂粉末とポリウレタン粉末の合計量中のシリコーン樹脂粉末の含有割合は２～１３質量％であることが好ましい。好ましくは、前記複合粒子が、青い波長の光（４５０ｎｍ）と赤い波長の光（７００ｎｍ）を同一強度で照射したとき、青い光の方をより強く吸収し、赤い光の方をより強く反射できるものである、化粧料。
【選択図】なし

【特許請求の範囲】
【請求項１】
シリコーン樹脂粉末を内包するポリウレタン粉末からなる複合粒子を含有している、化粧料。
【請求項２】
前記複合粒子に含まれている前記シリコーン樹脂粉末がポリメチルシルセスキオキサン粉末を含んでいる、請求項１記載の化粧料。
【請求項３】
前記複合粒子が、シリコーン樹脂粉末とポリウレタン粉末の合計量中のシリコーン樹脂粉末の含有割合が２～１３質量％である、請求項１または２記載の化粧料。
【請求項４】
前記複合粒子が、青い波長の光（450nm）と赤い波長の光（700nm）を同一強度で照射したとき、青い光の方をより強く吸収し、赤い光の方をより強く反射できるものである、請求項１～３のいずれか１項記載の化粧料。
【請求項５】
粉体化粧料またはメイクアップ化粧料である、請求項１～４のいずれか１項記載の化粧料。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は、粉体化粧料、メイクアップ化粧料などとして好適な化粧料に関する。
【背景技術】
【０００２】
従来、球状粉体は化粧料にすべりの良い滑らかな感触を付加する成分として配合されて来たが、遮蔽効果が弱く化粧崩れの原因にもなるため、色々な処理が試みられている（例えば、特許文献１、２参照）。
【０００３】
また、球状粉体の光の屈折や再帰反射により、強い光の下や写真撮影の時に特に白浮きが目立ってしまうという問題があった。しかし、白色粉体を内包することにより遮蔽力と光の屈折や再帰反射を改善する方法が示されている（例えば、特許文献３参照）。
また、特許文献３の課題を解決するものとして、粉体を内包する透明乃至半透明の有機合成球状粉体を含有する化粧料が提案されている（特許文献４）。
【先行技術文献】
【特許文献】
【０００４】
【特許文献１】特開平１－１８０８１１号公報
【特許文献２】特開平９－１６９６２６号公報
【特許文献３】特開２００４－６７６２４号公報
【特許文献４】特開２００８－１６７８号公報
【発明の概要】
【発明が解決しようとする課題】
【０００５】
本発明は、自然な仕上がり感が得られ、シミや毛穴隠し効果の高い化粧料を提供することを課題とする。
【課題を解決するための手段】
【０００６】
本発明は、シリコーン樹脂粉末を内包するポリウレタン粉末からなる複合粒子を含有している、化粧料を提供する。
【発明の効果】
【０００７】

本発明の化粧料は、特に顔のシミや毛穴を目立たなくする効果が優れているため、粉体化粧料、メイクアップ化粧料として好適である。

【図面の簡単な説明】

【０００８】

【図１】製造例２で得られた複合粒子のＳＥＭ写真（３０００倍）。

【図２】製造例２得られた複合粒子の特定波長（青、黄、赤）に対する反射レベルの測定結果を示す図。

【発明を実施するための形態】

【０００９】

＜複合粒子＞

本発明の化粧料で使用する複合粒子は、シリコーン樹脂粉末を内包するポリウレタン粉末からなるものである。

本発明において「内包」とは、ポリウレタン粉末内にシリコーン樹脂粉末が含有されていることを意味する。なお、前記「内包」は、シリコーン樹脂粉末を内包するポリウレタン粉末の製造時を基準とするものであるから、化粧料の製造時などにおいてシリコーン樹脂粉末を内包するポリウレタン粉末同士が擦れることでシリコーン樹脂粉末が露出されるようになった場合であっても、本発明のシリコーン樹脂粉末を内包するポリウレタン粉末に含まれることになる。

【００１０】

ポリウレタンは公知のものであり、例えば、特開２０１０－１６３３８９号公報、特開２０１２－２１９２２１号公報、特開２０１６－１９９５３２号公報に記載されたポリオールとイソシアネート化合物を反応させて得ることができる。

【００１１】

シリコーン樹脂粉末は、化粧料成分として公知のものを使用することができる。

化粧料成分として公知のシリコーン樹脂粉末としては、例えば、特開２０１３－６３９５４号公報に記載されている「（ｂ）シリコーン骨格粉末」、特開２０１２－２４０９９４号公報に記載されている「（Ｂ）架橋型オルガノポリシロキサン重合物」、特開２０１３－２２７３０６号公報において「（Ｃ）油溶性樹脂」の内のシリコーン系樹脂などを使用することができるが、これらの中でもポリメチルシルセスキオキサン粉末が好ましい。

ポリメチルシルセスキオキサン粉末は、シリコーンＫＭＰ－５９０（信越化学社製；粒子径１～３μｍ）、トスパール１２０Ａ、トスパール１４５Ａ、トスパール２０００Ｂ（以上、モメンティブ・パフォーマンス・マテリアルズ・ジャパン社製）などの市販品を使用することができる。

【００１２】

複合粒子中のシリコーン樹脂粉末とポリウレタン粉末の合計１００質量％中のシリコーン樹脂粉末の含有割合は、２～１３質量％が好ましく、４～１０質量％がより好ましく、残部割合がポリウレタン粉末である。

【００１３】

複合粒子の平均粒径（ｄ５０；レーザー回折・散乱法）は、５～８０μｍが好ましく、１０～５０μｍがより好ましい。

複合粒子に内包されているシリコーン樹脂粉末の粒径は、０．１～１．０μｍが好ましく、０．４～０．６μｍがより好ましい。

【００１４】

複合粒子は、本発明の課題を解決できる範囲内で公知の化粧料成分と使用される粉末を含有することができる。

公知の化粧料成分と使用される粉末としては、各種無機顔料および有機顔料などを挙げることができる。

前記粉末を含有するときの含有割合は、複合粒子中に５質量％以下が好ましく、３質量％以下がより好ましく、１質量％以下がさらに好ましい。

【００１５】

複合粒子は、球状でもよいし、球状でなくてもよいが、球状であるものが好ましい。「球状」は、長径と短径の比（短径／長径または長径／短径）が０．８～１．２程度のものを意味する。

【００１６】

複合粒子は、青い波長の光（450nm）と赤い波長の光（700nm）を同一強度で照射したとき、青い光の方をより強く吸収し、赤い光の方をより強く反射できるものであることが好ましい。

【００１７】

複合粒子は、ポリウレタンの重合反応時にシリコーン樹脂粉末を添加して重合反応させることで製造することができる。

【００１８】

＜化粧料＞

本発明の化粧料は、上記した複合粒子を含むものである。

本発明の化粧料は、剤型に応じて、以下に列挙した一般に化粧料に配合される各種成分を含有することができる。

炭化水素、スクワラン、流動パラフィン、ワセリン、固形パラフィン、マイクロクリスタリンワックス、セレシン、アルキッド、アクリル、スルホンアミド樹脂、ニトロセルロース；

ミネラルオイル、オリーブ油、アーモンド油、カカオ脂、マカデミアナッツ油、アボカド油、硬化パーム油、ヒマシ油、ヒマワリ油、月見草油、合成トリグリセライド、ロウ、ヒマワリ種子ロウ、ミツロウ、カルナバロウ、キャンデリラロウ、ラノリン、酢酸ラノリン、高級脂肪酸、高級アルコール、合成エステル、直鎖・環状シリコーンオイル、ジメチルポリシロキサン、モノステアリン酸グリセリン、デカメチルシクロペンタンシロキサン、ポリオキシエチレン変性ジメチルポリシロキサン、オクタメチルシクロテトラシロキサン、ポリフェニルメチルシロキサン、ロジンペンタエリスリトットエステル、ジイソオクタン酸ネオペンチルグリコール、トリイソオクタン酸グリセリン、ミリスチン酸イソプロピル、モノラウリン酸プロピレングリコール、トリ(カプリル酸/カプリン酸)グリセリルなどの油剤；

【００１９】

精製水、エタノール、イソプロパノール、多価アルコール、水溶性高分子、ベントナイト、モノステアリン酸ポリオキシエチレンソルビタン、セスキイソステアリン酸ソルビタン、酢酸エチル、酢酸ブチル、ブタノール；

グリセリン、プロピレングリコール、ソルビット、ポリエチレングリコール、ジプロピレングリコール、１，３-ブチレングリコール、ジグリセリン、マンニトール、ＰＯＥメチルグリコシド、生体高分子、蔗糖などの保湿剤；

エチルヘキサン酸セチル、リンゴ酸ジイソステアリル、トリポリヒドロキシステアリン酸ジペンタエリスリチルなどのエモリエント成分；

クインスシード、ペクチン、セルロース誘導体、キサンタンガム、アルギン酸ナトリウム、ソアギーナ、カルボキシビニルポリマー；

ミリスチン酸オクチルドデシル、ジイソオクタン酸ネオペンチルグリコール、モノオレイン酸ソルビタン、トリイソオクタン酸グリセリン、オクチルメトキシシンナメート、モノオレイン酸ＰＯＥソルビタン、イソセチル、イソステアリン酸、ステアリン酸、パルミチン酸イソプロピル、クエン酸アセチルトリブチル、ジ安息香酸トリメチルペンタンジイル、ステアリルコニウムベントナイト；、

増粘剤、防腐剤、乳化剤、安定化剤、可塑剤；

陰イオン界面活性剤、陽イオン界面活性剤、非イオン界面活性剤、両性イオン界面活性剤、蛋白質系界面活性剤；

【００２０】

薬効成分、ビタミンＣジパルミテート、ビタミン類、アミノ酸、美白剤、殺菌剤；

タルク、カオリン、マイカ、セリサイト、アルミナ、シリカ、ガラスフレーク、炭酸カ

ルシウム、炭酸マグネシウム、無水ケイ酸、硫酸バリウム、化粧品用タール色素、有機色素、βカロチン、カルサミン、カルミン、クロロフィル、ベンガラ、黄酸化鉄、黒酸化鉄、群青、紺青、酸化クロム、カーボンブラック、白色顔料、パール顔料などの顔料、

ナイロンパウダー、ポリエチレン粉末、ポリメタクリル酸メチル、ウールパウダー、セルロースパウダー、シルクパウダー、シリコーンパウダー、でんぷん粉、アルミニウム粉末、球状ナイロン、球状ポリスチレン、雲母チタン、二酸化チタン、酸化チタン、酸化鉄、その他の粉体；

ｐＨ調整剤、水酸化カリウム、水酸化ナトリウム、トリエタノールアミン、ステアリン酸マグネシウム、ステアリン酸亜鉛、金属イオン封止剤、クエン酸、クエン酸ナトリウム、乳酸、乳酸ナトリウム、

紫外線吸収剤、抗酸化剤、香料、防腐剤、キレート剤、酸化防止剤、分散剤、褐色防止剤、緩衝剤、沈殿防止成分、ゲル化剤、有機変性粘土鉱物、使用性改質剤。

【００２１】

本発明の化粧料は、パウダー状、エアゾール、液状、ジェル状、クリーム状、泡状、ムース状、ペースト状などの各種形態のものに使用することができるが、これらの中でもパウダー状の化粧料（粉体化粧料）であることが好ましい。

粉体粧料は、プレストパウダー（固形状のもの）、ルースパウダー（粉体状のもの）の両方を含む。

具体的には、ボディパウダー、フェイスパウダー、ファンデーション、チーク、アイシャドウ、アイブロウ、粉白粉、ベビーパウダーなどを挙げることができる。

【００２２】

また、本発明の化粧料は、前記粉体化粧料以外の化粧料、例えば、ローション、クリーム、ジェル、オイルなどのベースコントロール化粧品、制汗剤などのエアゾール製剤、リップクリーム、口紅、アイライナーやマスカラなどのメイクアップ化粧料、ネイルエナメル、ネイルトリートメントなどの美爪料、日焼け止め化粧料、パックなどにすることができるが、メイクアップ化粧料が好ましい。

【実施例】

【００２３】

製造例１（ポリウレタン成分の製造）

窒素ガスで十分に置換し、乾燥させた2Lオートクレーブに、プラクセル308(ポリエステルポリオール、数平均分子量800、官能基数3、ダイセル化学工業株式会社製)854g とヘキサメチレンジイソシアネート1008gとを仕込み、さらに窒素ガスにて充分に上部を置換した後に密閉し、１２０℃で20時間撹拌・混合して反応させた。

その後、減圧下で未反応のヘキサメチレンジイソシアネートを除去した後、トルエンを加えて不揮発分90質量%とした。これにより、イソシアネート基含有8.1質量%の合成物・Ｉ・を得た。

【００２４】

製造例２（複合粒子の製造）

製造例１で得た合成物（Ｉ）３１０ｇ、トルエン　85g、ＭＳＰ－Ｎ０５０（ポリメチルシルセスオキサン、日興リカ株式会社，粒子径０．４～０．６μm) 22.5gを用意した。これらを反応器に入れ、混合して原材料を調製した。

別に2L攪拌機付セパラブルフラスコに水600gを仕込み、この中にメトローズ90SH-100(ヒドロキシプロピルメチルセルロース、信越化学工業株式会社製)18.0gを溶解して分散媒を調製した。

前記分散媒を400r/mで攪拌しながら、原材料を添加して、懸濁液を調製した。

次に、攪拌継続下、懸濁液を５０℃に昇温して、同温度で3時間反応させた。

その後、６０℃に昇温し、同温度で2時間反応させ、更に９５℃に昇温し、同温度で1時間保持して熟成させた。その後、室温まで冷却して固液分離し、水で充分洗浄し、７０℃で20時間乾燥して球状の複合粒子を得た。

複合粒子は、ポリウレタン成分９２．５質量%、シリコーン樹脂成分（ポリメチルシル

セスオキサン）７．５質量％（原料基準）である。

【００２５】

得られた複合粒子のＳＥＭ写真（３０００倍）を図１に示す。

複合粒子の表面側の層中にシリコーン樹脂（ポリメチルシルセスオキサン）の小さな粒が分散して存在していることが確認できた。

【００２６】

試験例１

複合粒子の粒度分布（d50）は１８．１μ¥ochm 真比重は１．１６、屈折率は１．５、吸油量（特開2017-48323号公報の段落番号0039に記載の方法）は６３．２ml/100g、嵩比重は０．３９g/mlであった。

【００２７】

試験例２（微小圧縮試験）

微小圧縮試験機(MCT-W500(株)島津製作所製)を使用して、複合粒子1個に対し直径が１０％及び３０％変形するまでの圧力を測定した。数値が小さい程、粒子が柔らかいことを示す。

試料の粒子1個に試験力9.8mNをかけた時の圧縮率と復元率を測定し、反発弾性を評価した。粒子の直径を100%とし、圧縮率は粒子の変形した割合、復元率は粒子径の復元された割合を測定した。圧縮率と復元率の割合が等しいほど粉体に反発弾性があることを示している。

比較として、シリコーン樹脂（ポリメチルシルセスオキサン）を使用しないほかは同様にして製造したポリウレタン粉末を使用した。結果を表１に示す。

【００２８】

【表１】

	10%強度 (MPa)	30%強度 (MPa)	圧縮率 (%)	復元率 (%)
複合粒子	2.0	5.0	48.7	12.3
ポリウレタン粉末	2.0	5.3	46.6	11.0

【００２９】

試験例３

変角分光光度計（株式会社カラーテクノシステム社製）にて複合粒子を測定し、青色（450nm）、黄色(580nm)、赤色（700nm）に対する反射の程度を図２のグラフに示した。

図２から明らかなとおり、赤色の波長の光と黄色の波長の光の反射は大きく、青色の波長の光の反射は小さかった（即ち、青色の波長の光の吸収が最も大きかった）。

【００３０】

以下においてパウダー状化粧料を調製し、下記の各項目を試験評価した。

（１）自然な仕上がり評価

実施例および比較例の各パウダー状化粧料を化粧品評価のパネラーの顔表面に塗布し、6時間後に前記塗布面を目視観察した。

評価は、自然な仕上がりと自然な感じ（透明感）を下記基準により評価した。

【００３１】

◎：非常に良好

○：良好

△：普通

×：不良

【００３２】

（２）シミ・毛穴の隠し効果の評価

実施例および比較例の各パウダー状化粧料を化粧品評価のパネラーの顔表面に塗布し、6時間後に前記塗布面を目視観察した。

評価は、シミや毛穴が目立たないかどうかを下記基準により評価した。

【００３３】

◎：非常に良好

○：良好

△：普通

×：不良

【００３４】

（３）伸びの良さの評価

実施例および比較例の各パウダー状化粧料を化粧品評価のパネラーの顔表面に塗布するときの塗布のし易さを下記基準により評価した。

【００３５】

◎：非常に良好

○：良好

△：普通

×：不良

【００３６】

（４）使用感（柔らかさ）の評価

実施例および比較例の各パウダー状化粧料を化粧品評価のパネラーの顔表面に塗布するときの使用感（柔らかさ）を下記基準により評価した。

【００３７】

◎：非常に良好

○：良好

△：普通

×：不良

【００３８】

実施例１、比較例１（Ａ，Ｂ）（リキッドファンデーション）

表２に示す１～１１までの成分を秤量して容器に入れた後、混合して溶解させた。

次に、前記１～１１の混合物が入った容器内に予め混合分散させた１２～２０を加えて混合分散した。

次に、予め混合溶解させた２１～２４をゆっくりと加えながら乳化機により乳化させた。その後、冷却してリキッドファンデーションとなる乳化物を得た。

表２に示す数値の単位は重量％である。

【００３９】

【 表２ 】

	成分	実施例1	比較例1	
			A	B
1	ポリエーテル変性シリコーンゲル	0.15	0.15	0.15
2	ポリエーテル変性シリコーン	3.00	3.00	3.00
3	トリメチルシロキシケイ酸	3.00	3.00	3.00
4	シリコーン油	11.00	11.00	11.00
5	デカメチルシクロペンタシロキサン	16.85	16.85	16.85
6	有機変性ベントナイト	0.40	0.40	0.40
7	トリエチルヘキサノイン	6.80	6.80	6.80
8	メトキシケイヒ酸エチルヘキシル	8.00	8.00	8.00
9	トリイソステアリン酸ジグリセリル	0.50	0.50	0.50
10	マカデミア種子油	1.00	1.00	1.00
11	オクチルドデカノール	1.00	1.00	1.00
12	タルク	0.45	0.45	0.45
13	セリサイト	2.90	2.90	2.90
14	ステアリン酸亜鉛	1.75	1.75	1.75
15	ベンガラ	0.30	0.30	0.30
16	黄酸化鉄	1.45	1.45	1.45
17	黒酸化鉄	0.15	0.15	0.15
18	酸化チタン	8.00	8.00	8.00
19	複合粒子	10.00	−	−
20	ウレタンパウダー	−	−	10.00
21	ポリオール	5.30	5.30	5.30
22	フェノキシエタノール	0.20	0.20	0.20
23	クエン酸ナトリウム	0.50	0.50	0.50
24	精製水	17.30	27.30	17.30
評価	自然な仕上がり	◎	△	○
	シミ･毛穴隠し効果	◎	△	○
	伸びの良さ	◎	×	◎
	柔らかい使用感	◎	×	◎

【００４０】

実施例２、比較例２（Ａ，Ｂ）（パウダーファンデーション）

表３に示す１～９までの成分を秤量し、高速混合機に入れて混合分散させた。

次に表３に示す１０を加えて混合分散させた後、皿に移して圧縮成形して、パウダーファンデーションを得た。

表３に示す数値の単位は重量％である。

【００４１】

【表３】

	成分	実施例2	比較例2	
			A	B
1	タルク(シリコーン処理)	0.15	0.15	0.15
2	セリサイト(シリコーン処理)	3.00	3.00	3.00
3	雲母チタン(シリコーン処理)	3.00	3.00	3.00
4	酸化チタン(シリコーン処理)	11.00	11.00	11.00
5	ベンガラ(シリコーン処理)	16.85	16.85	16.85
6	黄酸化鉄(シリコーン処理)	0.40	0.40	0.40
7	黒酸化鉄(シリコーン処理)	6.80	6.80	6.80
8	複合粒子	10.00	-	-
9	ウレタンパウダー	-	-	10.00
10	シリコーン油	5.30	5.30	5.30
評価	自然な仕上がり	◎	△	○
	シミ・毛穴隠し効果	◎	△	○
	伸びの良さ	◎	×	○
	柔らかい使用感	◎	×	○

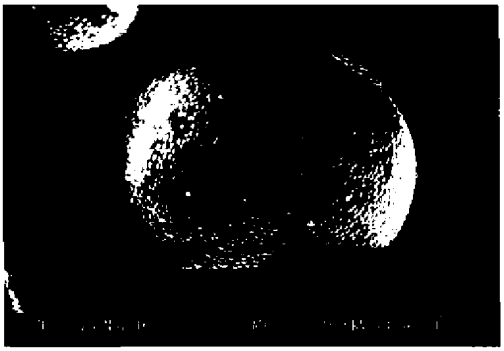
【００４２】
実施例３、比較例３（Ａ，Ｂ）（粉白粉）
表４に示す１～９までの成分を秤量し、高速混合機に入れて混合分散させた。
次に表４に示す１０を加えて混合分散させた粉白粉を得た。
表４に示す数値の単位は重量％である。
【００４３】
【表４】

	成分	実施例3	比較例3	
			A	B
1	タルク	42.85	52.85	42.85
2	セリサイト	30.00	30.00	30.00
3	合成金雲母	10.00	10.00	10.00
4	窒化ホウ素	3.00	3.00	3.00
5	ベンガラ	0.03	0.03	0.03
6	黄酸化鉄	0.12	0.12	0.12
7	酸化チタン	1.00	1.00	1.00
8	複合粒子	10.00	-	-
9	ウレタンパウダー	-	-	10.00
10	シリコーン油	3.00	3.00	3.00
評価	自然な仕上がり	◎	△	○
	シミ・毛穴隠し効果	○	△	○
	伸びの良さ	○	×	○
	柔らかい使用感	○	×	○

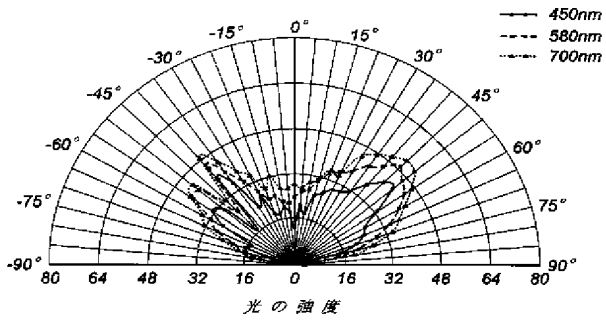
【産業上の利用可能性】
【００４４】
本発明の化粧料は、粉体化粧料、メイクアップ化粧料として好適に利用することができ

る。

【 図１ 】



【 図２ 】


450nm
580nm
700nm
-15°
0°
15°
-30°
30°
-45°
45°
-60°
60°
-75°
75°
-90°
90°
80 64 48 32 16 0 16 32 48 64 80
光の強度

フロントページの続き

(72) 発明者　伊藤　恵司
東京都葛飾区立石６－３７－１４　東色ピグメント株式会社内
(72) 発明者　鈴木　利宏
東京都葛飾区立石６－３７－１４　東色ピグメント株式会社内
(72) 発明者　西田　恵子
石川県能美市道林町ロ２２番地　根上工業株式会社内
(72) 発明者　田村　要
石川県能美市道林町ロ２２番地　根上工業株式会社内

Ｆターム(参考)　4C083 AA122 AB132 AB232 AB242 AB432 AB442 AC092 AC112 AC172 AC242
AC302 AC342 AC392 AC422 AC912 AD071 AD072 AD151 AD152 AD162
AD172 CC12　DD17　DD23　DD81　EE06　EE07

Europäisches Patentamt
European Patent Office
Office européen des brevets

Espacenet

JP2008239542A COSMETIC

Applicants: DAINICHISEIKA COLOR CHEM,UKIMA CHEM & COLOUR MFG

Inventors: SATO HIROMASA,TAKAHASHI KENICHI,WATANABE AKIHIRO,HANADA KAZUYUKI

Classifications:
IPC ***A61K8/87; A61Q1/02; A61Q19/00;***

Priorities: JP2007081711A 2007-03-27

Application: JP2007081711A·2007-03-27

Publication: JP2008239542A·2008-10-09

Published as: JP2008239542A;**JP4782719B2**

COSMETIC

Abstract

PROBLEM TO BE SOLVED: To provide a cosmetic containing organic fine particles which has solved the current shortcomings. SOLUTION: In a cosmetic which includes a functional component and/or a designing component, and contains polyurethane gelled particles, this cosmetic contains polyurethane gelled particles which are prepared by copolymerization of a polyisocyanate of which at least either one of its component is not less than trifunctional and a compound having an active hydrogen group in its molecule, and the surface of the three-dimensionally crosslinked polyurethane gelled particle is coated with polyurea colloid particles precipitated from a polyurea colloid nonaqueous solvent solution. COPYRIGHT: (C)2009,JPO&INPIT

(19)日本国特許庁(JP)　(12)公開特許公報(A)　(11)特許出願公開番号
特開2008-239542
(P2008-239542A)
(43)公開日　平成20年10月9日(2008.10.9)

(51)Int.Cl.		F I		テーマコード（参考）
A61K 8/87	(2006.01)	A61K	8/87	4C083
A61Q 1/02	(2006.01)	A61Q	1/02	
A61Q 19/00	(2006.01)	A61Q	19/00	

審査請求 未請求　請求項の数 9　ＯＬ　（全 22 頁）

(21)出願番号　特願2007-81711 (P2007-81711)
(22)出願日　平成19年3月27日 (2007.3.27)

(71)出願人　000002820
大日精化工業株式会社
東京都中央区日本橋馬喰町１丁目７番６号
(71)出願人　000238256
浮間合成株式会社
東京都中央区日本橋馬喰町１丁目７番６号
(74)代理人　100098707
弁理士　近藤　利英子
(74)代理人　100077698
弁理士　吉田　勝広
(74)代理人　100146042
弁理士　梶原　克哲
(72)発明者　佐藤　浩正
東京都中央区日本橋馬喰町１丁目７番６号
大日精化工業株式会社内
最終頁に続く

(54)【発明の名称】化粧料

(57)【要約】
【課題】従来の欠点を解決した有機微粒子を含む化粧料を提供すること。
【解決手段】機能性成分および／または意匠性成分を内包しているポリウレタンゲル粒子を含有する化粧料において、該ゲル粒子が、少なくともいずれか一方が３官能以上である、ポリイソシアネートと、分子内に活性水素基を有する化合物とを共重合してなる三次元架橋したポリウレタンゲル粒子の表面が、ポリウレアコロイド非水溶媒溶液から析出したポリウレアコロイド粒子により被覆されているポリウレタンゲル粒子であることを特徴とする化粧料。
【選択図】なし

【特許請求の範囲】
【請求項1】
機能性成分および／または意匠性成分を内包しているポリウレタンゲル粒子を含有する化粧料において、該ゲル粒子が、少なくともいずれか一方が３官能以上である、ポリイソシアネートと、分子内に活性水素基を有する化合物とを共重合してなる三次元架橋したポリウレタンゲル粒子（粒子Ａ）の表面が、ポリウレアコロイド非水溶媒溶液から析出したポリウレアコロイド粒子（粒子Ｂ）により被覆されているポリウレタンゲル粒子（粒子Ｃ）であることを特徴とする化粧料。
【請求項2】
機能性成分および／または意匠性成分が、粒子Ａおよび／または粒子Ｂに含まれている請求項１に記載の化粧料。
【請求項3】
機能性成分が、保湿成分、ビタミン成分、抗酸化成分、血行促進成分、紫外線吸収成分、紫外線カット成分、抗菌、美白成分および老化防止から選ばれる少なくとも１種であり、意匠性成分が、顔料、染料、パール、マイカおよび金属ペーストから選ばれる少なくとも１種であり、上記成分割合が、粒子Ｃを構成している樹脂１００重量部あたり０．１～３００質量部である請求項１に記載の化粧料。
【請求項4】
粒子Ｂが、溶媒に対して溶媒和されている部分と非溶媒和部分とから構成されており、非溶媒和部分の粒子径が０．０１～１．０μｍである請求項１に記載の化粧料。
【請求項5】
粒子Ｂが、油脂変性ポリオールとポリイソシアネートとポリアミンとの反応で得られるポリウレアコロイド粒子であって、非溶媒和部分がウレア結合の水素結合からなっている請求項１に記載の化粧料。
【請求項6】
粒子Ｃの粒子径が、０．５～１００μｍの範囲である請求項１に記載の化粧料。
【請求項7】
下記式１で示される粒子Ｃの円形度が、０．９～１．０の範囲である請求項１に記載の化粧料。
［式１］　円形度＝円相当径から求めた円の周囲長／粒子投影の周囲長
【請求項8】
粒子Ｃの圧縮強度が、０．０１～１．０ＭＰａの範囲であり、回復率が６０～１００％の範囲である請求項１に記載の化粧料。
【請求項9】
粒子Ｃの熱軟化点温度が、２５０℃以上である請求項１に記載の化粧料。

【発明の詳細な説明】
【技術分野】
【0001】
本発明は、機能性成分および／または意匠性成分を内包しているポリウレタンゲル粒子を含む化粧料に関し、さらに詳しくは均一な粒子径であり、かつ機械強度、耐屈曲性、耐熱性、低温特性、耐摩耗性、耐薬品性に優れており、特に化粧料成分として必要とされる柔軟性（ソフトタッチ感）、滑り性、しっとり感、弾性、変形回復性、透過性、光拡散性、適度な光沢性、肌への伸展性、耐媒体性（膨潤しない）、耐油性（膨潤しない）、皮脂吸収性、皮膚への安全性などに優れ、さらには機能性成分などを内包してなるポリウレタンゲル粒子を含有するメイクアップ化粧料やスキンケアー化粧料などの化粧料に関する。
【背景技術】
【0002】
従来、化粧料に使用される微粒子としては、タルク、カオリン、マイカ、顔料などの微粒子が多く使用されている。さらに有機微粒子としては、ナイロン、結晶セルロース、ウレタン、アクリル、シリコーン、ポリスチレン、ポリエチレン、エチレン・メチルメタク

リラート共重合体などの有機微粒子が挙げられる。
【0003】
上記種々の有機微粒子に関しては、粒形においては真球状や非真球状なもの、多孔質球状微粒子、種々の粒子径、粒度分布、比重、硬度、表面処理（表面性質）など、様々な材料が検討されている。化粧料に使用される代表的な微粒子について述べる。
【0004】
ナイロン１２微粒子は伸展性に優れ、高硬度のためサラサラ感があり、好評であるとともに、真球状で単一な粒度分布であり、耐溶剤性、耐薬品性、耐圧縮性、非熱流動性などの特性がある。しかしながら、ナイロン１２微粒子は、高コストであり、防腐剤であるパラヒドロキシ安息香酸エステルやパラヒドロキシ安息香酸エチルなどを吸収しやすく、防腐効果をなくすことや、口紅など、高温加工する際に融点の問題から、化粧料成分と融着すると云った問題を引き起こす。
【0005】
アクリル微粒子は、低コストで伸展性がよくスライド感も良好で、メイクアップ化粧料、制汗剤やローションなどに使用されているが、上記アクリル微粒子は、柔軟性、フィット感、肌への密着性（化粧持ち）に乏しいといった課題もある。
【0006】
シリコーン微粒子は、高硬度のため伸展性がよく（動摩擦係数が低い）、撥水性、光拡散性や隠蔽性があるのでメイクアップ化粧料に使用される。しかしながら、上記シリコーン微粒子は柔軟性に乏しいことや皮脂の吸収性が悪いことなどが課題としてある。
【0007】
真球状有機微粒子を含有している化粧料は、皮膚に対する刺激性がなく、人体の安全性に問題がない素材であるとともに、滑らかで柔軟な感触性、皮膚への伸展性（ローリング性）、汗や皮脂の吸収性、通気性を付与させたり、透過性、光拡散性、隠蔽効果、光沢性などの光学特性を活かして、皺やしみを隠した自然な肌を演出したナチュラルカバー効果を発揮させたり、テカリ防止、色むら隠し、化粧持ち、小皺や毛穴を隠す機能などを目的に利用される。
【0008】
さらに上記微粒子は、化粧料としての機能の他に化粧料配合において、例えば、化粧料に使用される揮発性シリコンオイル、精製水、油剤、防腐剤などとの相溶性が良好で、かつ揮発性シリコンオイル、油剤、防腐剤の吸収性が少なく長期安定性が求められる。
【0009】
また、パウダーファンデーションなどは各製造方式（乾式法、湿式法）での成型性が重要であり、口紅では高温で加工するため、上記微粒子は耐熱性（加工温度で軟化しないこと）や極性が少なく粘着しないことなどの化粧料の加工適性が求められる。
【0010】
かかる問題を解決する方法として、化粧料に球状ポリウレタン粒子を配合する手法が提案されている（特許文献１）。この化粧料は、伸展性、感触性などには問題ないが、化粧料の特性である光拡散性や隠蔽性が乏しく、光学特性としては満足するものではない。
【0011】
また、化粧料にアクリル共重合体微粒子を配合する手法が提案されている（特許文献２）。該アクリル共重合体微粒子を含有させた化粧料は、伸展性などは良好であるものの、微粒子自体が高硬度（ガラス転移温度が高い）であり、人肌とは遠い感触となる。これらの従来の方法では、現在主流と言われる人肌に近い柔軟性が求められるとともに、自然に近いナチュラルカバー効果が得られないと云う問題が解決されない。
【特許文献1】特開平５－２６２６２２号公報
【特許文献2】特開２００１－１５１６２６公報
【発明の開示】
【発明が解決しようとする課題】
【0012】

上記有機微粒子は化粧料において各素材独自の優れた特徴があるものの、幾つかの問題があり、前記した全ての機能を満足するものでない。そのうえ、従来よりも高機能である有機微粒子素材および化粧料が要望されている。従って本発明の目的は、従来の上記の欠点を解決した有機微粒子を含む化粧料を提供することである。

【課題を解決するための手段】

【0013】

上記目的は以下の本発明によって達成される。すなわち、本発明は、機能性成分および／または意匠性成分（以下両者を「機能性成分など」と云う場合がある）を内包しているポリウレタンゲル粒子を含有する化粧料において、該ゲル粒子が、少なくともいずれか一方が３官能以上である、ポリイソシアネートと、分子内に活性水素基を有する化合物（以下単に「ポリオール」と云う場合がある）とを共重合してなる三次元架橋したポリウレタンゲル粒子（以下単に「粒子Ａ」と云う場合がある）の表面が、ポリウレアコロイド非水溶媒溶液から析出したポリウレアコロイド粒子（以下単に「粒子Ｂ」と云う場合がある）により被覆されているポリウレタンゲル粒子（以下単に「粒子Ｃ」と云う場合がある）であることを特徴とする化粧料を提供する。上記機能性成分などは、粒子Ａおよび／または粒子Ｂに含まれている。

【0014】

上記機能性成分などとしては、保湿成分、ビタミン成分、抗酸化成分、血行促進成分、紫外線吸収成分、紫外線カット成分、抗菌、美白成分、老化防止、顔料、染料、パール、マイカおよび金属ペーストから選ばれる少なくとも１種であることが好ましく、上記成分割合が、粒子Ｃを構成している樹脂１００重量部あたり０．１～３００質量部であることが好ましい。

【0015】

また、上記粒子Ｂが、溶媒に対して溶媒和されている部分と非溶媒和部分とから構成されており、非溶媒和部分の粒子径が０．０１～１．０μｍであること；粒子Ｂが、油脂変性ポリオールとポリイソシアネートとポリアミンとの反応で得られるポリウレアコロイド粒子であって、非溶媒和部分がウレア結合の水素結合からなっていること；粒子Ｃの粒子径が、０．５～１００μｍの範囲であることが好ましい。

【0016】

また、下記式１で示される粒子Ｃの円形度が、０．９～１．０の範囲であること；上記粒子Ｃの圧縮強度が、０．０１～１．０ＭＰａの範囲であり、回復率が６０～１００％の範囲であること；および粒子Ｃの熱軟化点温度が、２５０℃以上であることが好ましい。

［式１］　円形度＝円相当径から求めた円の周囲長／粒子投影の周囲長

【発明の効果】

【0017】

本発明者らは、前記課題を解決すべく鋭意検討を重ねた結果、上記粒子Ｃが、機械強度、耐屈曲性、耐熱性、低温特性、耐摩耗性、耐薬品性などに優れており、化粧料成分として必要とされるナチュラルカバー効果のある適度な透明性、適度な光拡散性、適度な隠蔽性、適度な光沢性であり、テカリ防止、色むら隠し、小皺、毛穴隠し効果および感触（柔軟性（ソフトタッチ感）、滑り性、しっとり感）に優れており、弾性、変形回復性、肌への伸展性、吸油性、皮脂吸収性、皮膚への安全性などに優れ、特に柔軟性（ソフト性）、変形回復力および皮脂（オレイン酸）の吸収性能が高く、かつ粒度分布が狭いことから、これらの粒子に機能性成分などを含有させることで、前記従来技術の課題が解決されることを見いだした。

【発明を実施するための最良の形態】

【0018】

次に発明を実施するための最良の形態を挙げて本発明をさらに詳しく説明する。本発明で用いる粒子Ｃは、ポリイソシアネートおよびポリオール（これらの少なくとも一方には、機能性成分などを内包させてある、以下同じ）を、ポリウレアコロイド溶液の存在下に不活性溶媒中で乳化分散後、重合させることによって得られる。このようにして得られる

粒子Ｃは、粒子Ａの表面が、ポリウレアコロイド溶液から析出した粒子Ｂによって被覆されている。機能性成分などは粒子Ａに代えて、または加えて粒子Ｂ中に包含させることもできる。

【0019】

本発明で用いる粒子Ｃは上記方法によって得られるが、好ましい方法は、不活性溶媒中で撹拌機や乳化機付きのジャケット式合成釜に、ポリイソシアネートとポリオールとを仕込み、ポリウレアコロイド溶液により乳化分散し、これらの合成原料を反応させて粒子Ａを合成した後、粒子Ａの表面をポリウレアコロイド溶液から析出した粒子Ｂで均一に被覆させる方法である。

【0020】

合成温度は特に限定されないが、好ましい温度は４０℃～１４０℃である。また、合成時に使用するポリウレアコロイド溶液は、その固形分としての使用量で、粒子Ａの原料換算で１００質量部あたり０．０１質量部以上を使用することができ、好ましくは０．１～２０質量部である。使用量が０．０１質量部未満では粒子の乳化が不十分で、合成過程で粒子の大きい凝集塊が発生し、目的とする微細な粒子Ｃの分散体が得難い。一方、使用量が２０質量部を越えると、粒子Ａの乳化性には問題はなく、粒子Ｃは製造することができるが、乳化剤としての作用として過剰な量であり、特に利点はない。

【0021】

ポリイソシアネートとポリオールとの不活性溶媒中における濃度は、低い程小さい粒径の粒子Ａまたは粒子Ｃが得られ易いが、生産性から好ましい濃度は２０～７０質量％である。

【0022】

粒子Ａについて以下に説明する。粒子Ａの原料であるポリイソシアネートとポリオールとの少なくとも一方には、機能性成分などが加えられている。ここで機能性成分は、少しずつ徐放されて、目的とする機能を発揮する成分であり、意匠性成分は、意匠性の高い色相や光拡散による特異的な反射光を利用して美しい化粧肌を作り上げる成分である。上記機能性成分などの含有量は、粒子Ｃを構成している樹脂１００重量部あたり０．１～３００質量部であることが好ましい。

【0023】

粒子Ａの合成に使用される活性水素基を有する化合物としてのポリオールとしては、好ましくはポリウレタンの製造に従来から使用されている短鎖ジオール、多価アルコールおよび高分子ポリオールなどの従来公知のものが、また、活性水素基を有する化合物としてのポリアミンとしてはポリウレタンの製造に従来から使用されている短鎖ジアミン、高分子ポリアミンなどが使用できるが、これらは特に限定されない。以下に使用するそれぞれの化合物について説明する。

【0024】

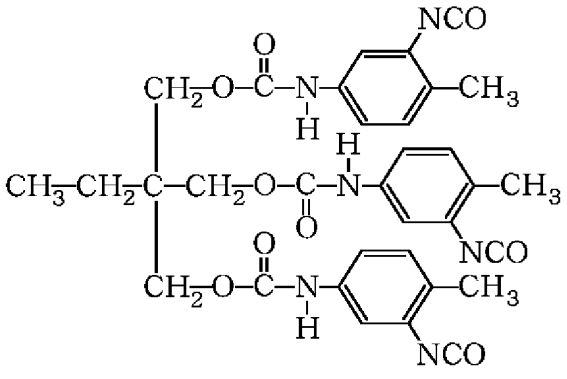
前記短鎖ジオールとしては、例えば、エチレングリコール、１，２－プロピレングリコール、１，３－プロピレングリコール、１，２－ブチレングリコール、１，３－ブチレングリコール、１，４－ブチレングリコール、１，６－ヘキサメチレングリコールおよびネオペンチルグリコールなどの脂肪族グリコールおよびそのアルキレンオキシド低モル付加物（数平均分子量５００未満）が挙げられる。

【0025】

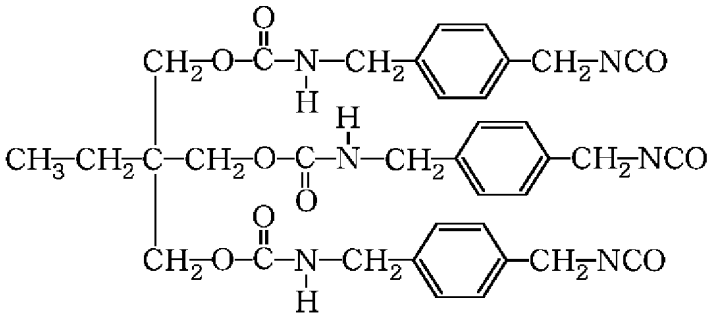
また、１，４－ビスヒドロキシメチルシクロヘキサンおよび２－メチル－１，１－シクロヘキサンジメタノールなどの脂環式系グリコールおよびそのアルキレンオキシド低モル付加物（数平均分子量５００未満）、キシリレングリコールなどの芳香族グリコールおよびそのアルキレンオキシド低モル付加物（数平均分子量５００未満）、ビスフェノールＡ、チオビスフェノールおよびスルホンビスフェノールなどのビスフェノールおよびそのアルキレンオキシド低モル付加物（数平均分子量５００未満）、およびＣ１～Ｃ１８のアルキルジエタノールアミンなどのアルキルジアルカノールアミンなどの化合物が挙げられる。

【0026】
　また、多価アルコールとしては、例えば、グリセリン、トリメチロールエタン、トリメチロールプロパン、ペンタエリトリトール、トリス－（２－ヒドロキシエチル）イソシアヌレート、１，１，１－トリメチロールエタンおよび１，１，１－トリメチロールプロパンなどが挙げられる。これらは単独或いは２種類以上を組み合わせて使用することができる。
【0027】
　前記高分子ポリオールとしては、例えば、以下のものが例示される。
（１）ポリエーテルポリオール、例えば、アルキレンオキシド（エチレンオキシド、プロピレンオキシド、ブチレンオキシドなど）および／または複素環式エーテル（テトラヒドロフランなど）を重合または共重合して得られるものが例示され、具体的にはポリエチレングリコール、ポリプロピレングリコール、ポリエチレングリコール－ポリテトラメチレングリコール（ブロックまたはランダム）、ポリテトラメチレンエーテルグリコールおよびポリヘキサメチレングリコールなどのジオールおよび／または３官能以上ポリエーテルポリオールなどが挙げられる。
【0028】
（２）ポリエステルポリオール、例えば、脂肪族系ジカルボン酸（例えば、コハク酸、アジピン酸、セバシン酸、グルタル酸およびアゼライン酸など）および／または芳香族系ジカルボン酸（例えば、イソフタル酸およびテレフタル酸など）と低分子量グリコール（例えば、エチレングリコール、１，２－プロピレングリコール、１，３－プロピレングリコール、１，４－ブチレングリコール、１，６－ヘキサメチレングリコール、ネオペンチルグリコールおよび１，４－ビスヒドロキシメチルシクロヘキサンなど）とを縮重合したものが例示され、具体的にはポリエチレンアジペートジオール、ポリブチレンアジペートジオール、ポリヘキサメチレンアジペートジオール、ポリネオペンチルアジペートジオール、ポリエチレン／ブチレンアジペートジオール、ポリネオペンチル／ヘキシルアジペートジオール、ポリ－３－メチルペンタンアジペートジオールおよびポリブチレンイソフタレートジオールなどのジオールおよび／または３官能以上のポリエステルポリオールなどが挙げられる。
【0029】
（３）ポリラクトンポリオール、例えば、ポリカプロラクトンジオールまたはポリカプロラクトントリオールおよびポリ－３－メチルバレロラクトンジオールなどのジオールおよび／または３官能以上のポリラクトンポリオールなどが挙げられる。
（４）ポリカーボネートジオール、例えば、ポリヘキサメチレンカーボネートジオールなどのジオールおよび／または３官能以上のポリカーボネートポリオールなどが挙げられる。
（５）ポリオレフィンポリオール、例えば、ポリブタジエングリコールおよびポリイソプレングリコール、または、その水素化物などのジオールおよび／または３官能以上のポリオレフィンポリオールなどが挙げられる。
【0030】
（６）水素添加ダイマーポリオール、ヒマシポリオールなどのジオールおよび／または３官能以上のダイマーポリオールなどが挙げられる。
（７）ポリメタクリレートジオール、例えば、α，ω－ポリメチルメタクリレートジオールおよびα，ω－ポリブチルメタクリレートジオールなどのジオールおよび３官能以上のポリメタクリレートポリオールなどが挙げられる。
【0031】
　これらのポリオールの分子量は特に限定されないが、ポリイソシアネートと反応するものは全て使用可能であり、通常、数平均分子量は５００～２，０００程度が好ましい。また、これらのポリオールは単独或いは２種類以上を組み合わせて使用することができる。ポリオールとしては、活性水素基が２個以上のポリオールが好ましく、特に好ましいのは３個以上の活性水素基を有するポリオールである。

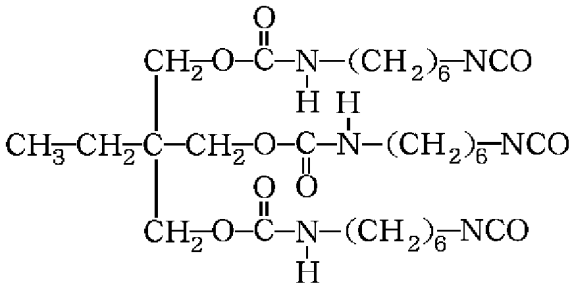
【0032】
前記粒子Ａまたは粒子Ｂの合成に使用するポリイソシアネートとしては、従来公知のポリウレタンの製造に使用されているものがいずれも使用でき特に限定されない。ポリイソシアネートとして好ましいものは、例えば、トルエン－２，４－ジイソシアネート、４－メトキシ－１，３－フェニレンジイソシアネート、４－イソプロピル－１，３－フェニレンジイソシアネート、４－クロル－１，３－フェニレンジイソシアネート、４－ブトキシ－１，３－フェニレンジイソシアネート、２，４－ジイソシアネートジフェニルエーテル、４，４’－メチレンビス（フェニレンイソシアネート）（ＭＤＩ）、ジュリレンジイソシアネート、トリレンジイソシアネート、キシリレンジイソシアネート（ＸＤＩ）、１，５－ナフタレンジイソシアネート、ベンジジンジイソシアネート、ｏ－ニトロベンジジンジイソシアネートおよび４，４’－ジイソシアネートジベンジルなどの芳香族ジイソシアネートが挙げられる。
【0033】
また、メチレンジイソシアネート、１，４－テトラメチレンジイソシアネート、１，６－ヘキサメチレンジイソシアネートおよび１，１０－デカメチレンジイソシアネートなどの脂肪族ジイソシアネート、１，４－シクロヘキシレンジイソシアネート、４，４’－メチレンビス（シクロヘキシルイソシアネート）、１，５－テトラヒドロナフタレンジイソシアネート、イソホロンジイソシアネート、水添ＭＤＩおよび水添ＸＤＩなどの脂環式ジイソシアネートなど、或いはこれらのジイソシアネートと低分子量のポリオールやポリアミンを末端がイソシアネートとなるように反応させて得られるポリウレタンプレポリマーなども当然使用することができる。
【0034】
また、これらの化合物をイソシアヌレート体、ビューレット体、アダクト体、ポリメリック体とした多官能のイソシアネート基を有するもので従来から使用されている公知のものが使用でき特に限定されない。例えば、２，４－トルイレンジイソシアネートの二量体、トリフェニルメタントリイソシアネート、トリス－（ｐ－イソシアネートフェニル）チオフォスファイト、多官能芳香族イソシアネート、多官能芳香族脂肪族イソシアネート、多官能脂肪族イソシアネート、脂肪酸変性多官能脂肪族イソシアネート、ブロック化多官能脂肪族イソシアネートなどのブロック型ポリイソシアネート、ポリイソシアネートプレポリマーなどが挙げられる。
【0035】
これらのうち、芳香族系或いは脂肪族系のどちらでも使用可能であり、好ましくは芳香族系ではジフェニルメタンジイソシアネートおよびトリレンジイソシアネート、脂肪族系ではヘキサメチレンジイソシアネートおよびイソホロンジイソシアネートなどの変性体であり、分子中にイソシアネート基を３個以上含むものが好ましく、前記ポリイソシアネートの多量体や他の化合物との付加体、さらには低分子量のポリオールやポリアミンとを末端イソシアネートになるように反応させたウレタンプレポリマーなども好ましく使用される。それらを下記に構造式を挙げて例示するが、これらに限定されるものではない。
【0036】



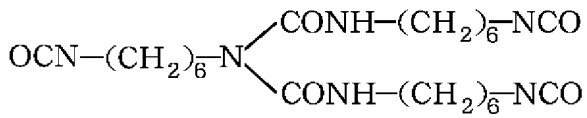
【0037】



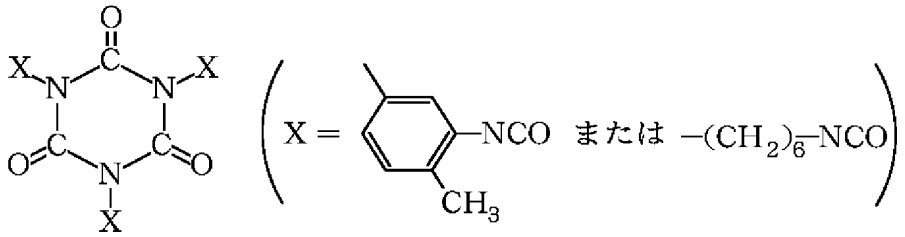
【0038】



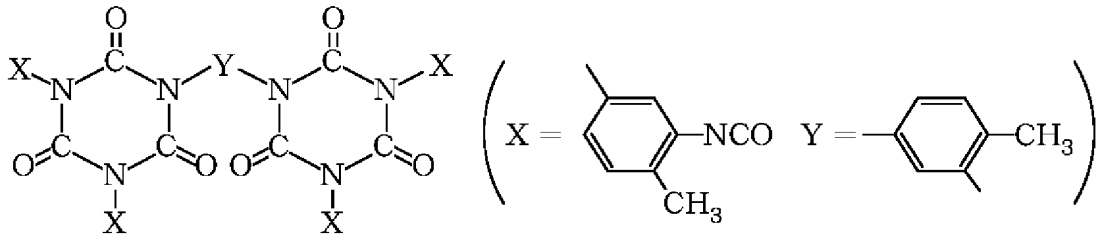
【0039】



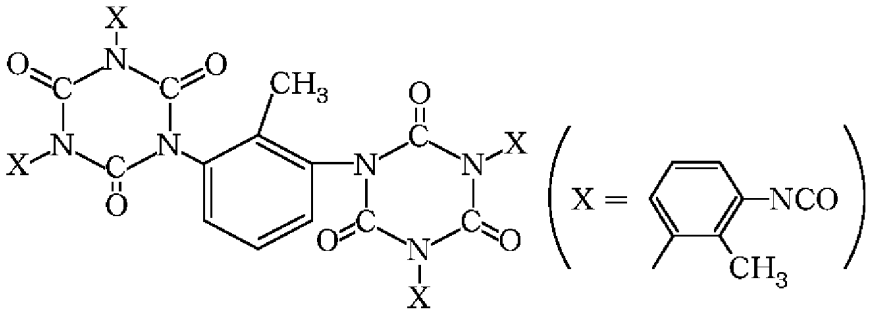
【0040】



【0041】



【0042】



【0043】
本発明で用いる機能性成分としては、保湿成分、ビタミン成分、抗酸化成分、血行促進成分、紫外線吸収成分、紫外線カット成分、抗菌、美白成分、老化防止などに効能がある薬剤が挙げられる。例えば、保湿成分としては、グリセリン、スクワラン、１，３－ブタンジオール（トウモロコシ由来も含む）、ソルビトール、コラーゲン、アミノ酸、尿素、セリン、ゼラチン、植物エキス、マリンミネラル、ヒアロン酸、ヒアルロン酸、キトサン、アルロン酸、単糖類、多糖類（トレハロース）、ロイヤルゼリー、天然セラミドなどが挙げられる。
【0044】
ビタミン成分としては、抗酸化作用、美白効果および老化防止を防ぐ機能がある、例えば、ビタミンＡ、Ｂ、Ｃ、Ｄ、Ｅ、Ｋおよびその誘導体、ポリフェノールなどが挙げられる。血行促進成分としては、ビタミンＥ、植物抽出エキス、酵母エキス、ロイヤルゼリーなどが挙げられる。抗酸化成分としては、ビタミンＣやビタミンＥおよびその誘導体、アルブチン、甘草エキス、植物抽出エキス、カロチン、白金ナノコロイドなどが挙げられる。
【0045】
美白成分としては、メラニン生成を抑える美白成分であり、ビタミンＣやその誘導体、アルブチン、エラグ酸、コウジ酸、甘草エキス、植物抽出エキスなどが挙げられる。紫外線吸収成分または紫外線カット成分としては、メトキシケイヒ酸オクチル、オキシベンゾン、サリチル酸オクチルおよびホモサレートなどの紫外線吸収剤や、酸化亜鉛、酸化チタン、アルミナ、酸化ジルコニウムなどの紫外線カット成分などが挙げられる。
【0046】
抗菌成分としては、パラベンなどを使用するが、肌の弱い人やアレルギー体質の人には向いていない。天然エキスやカテキンなどが良いとされる。老化防止成分としては、大豆由来のサポニンとイソフラボン、天然ビタミンＥ、コエンザイムＱ１０などが挙げられる。芳香成分や消臭成分は、肌のトラブルの原因となり得るので、無臭タイプを推奨するが、必要に応じて極微量の芳香成分や消臭成分も使用可能である。
【0047】
本発明に使用される意匠性成分としては、顔料、蛍光顔料、染料、パール、マイカ、金属素材など、体質顔料としては、マイカ、タルク、カオリン、セリライト、炭酸マグネシウム、炭酸カルシウム、無水珪酸、酸化アルミニウム、硫酸バリウムなど、天然色素としては、カロチノイド系、フラボノイド系、フラビン系など、有機合成色素としては、法定色素Ｉ、II、IIIグループおよびＦＤＡ承認色素など、無機顔料としては、酸化鉄、カーボンブラック、群青、紺青、酸化クロム、水酸化クロムなど、白色顔料としては、酸化チタン、酸化亜鉛などが挙げられる。
【0048】
また、アゾ系色素、ニトロ系色素、ニトロソ色素、キサンテン系色素、キノリン系色素、アントラキノン系色素、インジゴ系色素、トリフェニル系色素などのタール色素が挙げられる。
【0049】

パール顔料は、光を反射する微細な板状の物質からなり、化粧料の外観および塗布した際の皮膚表面にパールのような光沢感を出す顔料である。該パール顔料は、小さな板状の雲母を光反射する酸化チタン膜で覆った合成マイカと、ニシンや太刀魚の鱗から板状結晶を採取するものがある。特に、ホワイトパールを主剤とし、色材と混合して使用したり、シルバー調や様々な干渉色として使用している。金属素材としては、各種金属粉、金属のように光沢のある擬似加工品などが使用される。

【0050】

本発明に使用されるポリイソシアネートおよびポリオールなどの種類、使用量および使用比率は、得られる粒子Ｃの使用目的によって決定されるが、ポリイソシアネートおよびポリオールの少なくとも一方が３官能以上であることが必要である。例えば、ポリイソシアネートが２官能である場合には、ポリオールが３官能以上であり、また、ポリオールが２官能である場合には、３官能以上のポリイソシアネートが必要である。勿論、全ての成分が３官能以上であってもよい。また、ＮＣＯ／ＯＨ比は、使用する化合物と生成物に要求される性能によって決定されるが、好ましくは０．５～１．２の範囲である。

【0051】

上記全化合物の反応に使用し、生成する粒子の分散体の連続相を形成する不活性溶媒は、生成する粒子に対して実質的に非溶媒でありかつ、活性水素基を有さないものである。その例として、ペンタン、ヘキサン、ヘプタン、オクタン、デカン、石油エーテル、石油ベンジン、リグロイン、石油スピリット、シクロヘキサン、メチルシクロヘキサン、トルエン、キシレン、脂環族炭化水素の構造を有するエチルシクロヘキサン、ジメチルシクロヘキサンなどの炭化水素、ジメチルポリシロキサンなどの単独または混合物が挙げられ、これらの不活性溶媒は、該不活性溶媒と合成された粒子Ｃの分離工程や生産性の点からは１５０℃以下の沸点を有するものが好ましい。粒子Ｃの合成に際しては公知の触媒を使用すれば、反応温度は低温でもよいが、作業面から４０℃以上の反応温度が好ましい。

【0052】

上記粒子Ａの合成時に乳化剤として使用するポリウレアコロイド溶液中の粒子Ｂは、溶媒に対して溶媒和されている部分と非溶媒和部分とから構成されており、非溶媒和部分の粒子径が好ましくは０．０１～１．０μｍの粒子であり、かかるポリウレアコロイド溶液は、例えば、非水溶媒中で、油脂変性ポリオールとポリイソシアネート（またはこれらの化合物からなる末端ＮＣＯプレポリマー）とポリアミンとの反応で得られる。

【0053】

この反応では、反応が進むにつれて、ウレア結合同士の水素結合により、溶媒中に不溶解のウレアドメインが形成され、同時に油脂変性ポリオール鎖が溶媒中で溶媒和されることにより、非溶解性のウレアドメインの凝集などによる粒子Ｂの巨大化が防止され、安定なポリウレアコロイド溶液が容易に得られる。

【0054】

さらに、使用する油脂変性ポリオールが、非水溶媒中での結晶性が少なく、反応が進むにつれて生じる高分子化の過程でも、溶媒中で油脂変性ポリオールを主体とするポリマー鎖がある程度自由に動き得るために、非溶解性結晶部分と溶解性非結晶部分の分離が容易に行われ、ウレア結合同士の水素結合による非溶解性結晶部分を粒子の中心とするウレアドメインを形成し、その周囲に溶媒和されたポリマー鎖が規則正しく外向きに配向される。これは従来のミセル下に重合することにより得られる公知のコロイド溶液の製造方法における界面活性剤とは根本的に異なる作用である。

【0055】

上記ポリウレアコロイド溶液の製造方法をさらに具体的に説明する。先ず、最初に油脂変性ポリオールとポリイソシアネートとを非水溶媒中または無溶媒で反応させ、ＮＣＯ基を有するプレポリマーを合成する。次にこのプレポリマーを撹拌機付きのジャケット式合成釜に仕込み、濃度が５～７０質量％になるように非水系溶媒を添加して濃度を調整する。この溶液を撹拌しながら、予め１～２０質量％の濃度に調整したポリアミンの溶液を徐々に添加し反応を行い、ポリウレア化反応においてポリウレアコロイド溶液を製造する。

【0056】
ポリアミンの添加方法は、上記の方法の他にポリアミン溶液に前記プレポリマーまたはその溶液を添加する方法でもよい。ポリマー合成のための温度は特に限定されないが、好ましい温度は２０～１４０℃である。ポリマー合成のための反応濃度、温度、撹拌機の形態、撹拌力、ポリアミン溶液およびプレポリマーまたはその溶液の添加速度などは特に限定されないが、ポリアミンとプレポリマーのイソシアネート基との反応は速いので、急激な反応が行われないように、反応を制御することが好ましい。
【0057】
ポリウレアコロイド溶液の製造に使用する油脂変性ポリオールは、官能基が２個以下のポリオールであって、好ましい分子量は７００～３，０００であるが、これに限定されない。油脂変性ポリオールの具体例としては、例えば、各種の油脂を低級アルコールやグリコールを用いてアルコリシス化する方法、油脂を部分鹸化する方法、水酸基含有脂肪酸をグリコールによりエステル化する方法などによって、油脂に約２個以下の水酸基を含有させたものが好ましく、上記の水酸基含有脂肪酸としては、例えば、リシノレイン酸、１２－ヒドロキシステアリン酸、ヒマシ油脂肪酸、水添ヒマシ油脂肪酸などが挙げられる。
【0058】
油脂変性ポリオールとポリイソシアネートとの反応は、１＜ＮＣＯ／ＯＨ≦２の条件で行い、溶媒和されるプレポリマー鎖の分子量をコントロールする。このように合成されるプレポリマーの分子量は、特に限定されないが、好ましい範囲は約５００～１５，０００である。粒子Ｂの合成に使用されるポリイソシアネートとしては、公知のポリイソシアネートの全てが挙げられる。特に好ましいものはヘキサメチレンジイソシアネート、水添加ＴＤＩ、水添加ＭＤＩ、イソホロンジイソシアネート、水添ＸＤＩなどの脂肪族または脂環族系ジイソシアネートである。
【0059】
ポリウレアコロイド溶液の製造に使用する非水系溶媒としては、使用原料である油脂変性ポリオール、ポリイソシアネートおよびポリアミンを溶解するもので、活性水素基を有さない全ての非水系溶媒を使用することができる。特に好ましいものはペンタン、ヘキサン、ヘプタン、オクタン、デカン、石油エーテル、石油ベンジン、リグロイン、石油スピリット、シクロヘキサン、メチルシクロヘキサン、トルエン、キシレン、脂環族炭化水素の構造を有するエチルシクロヘキサン、ジメチルシクロヘキサンなどの炭化水素、ジメチルポリシロキサンなどの単独または混合物が挙げられる。なお、本発明において「溶解」とは常温および高温下での溶解の両方を包含する。
【0060】
ポリウレアコロイド溶液の製造に使用するポリアミンとして、例えば、短鎖ジアミン、脂肪族系ポリアミン、脂環式ポリアミン、芳香族系ポリアミンおよびヒドラジンなどが挙げられる。短鎖ジアミンおよび脂肪族系ポリアミンとしては、例えば、エチレンジアミン、ジアミノプロパン、ジアミノブタン、トリメチレンジアミン、トリメチルヘキサメチレンジアミン、ヘキサメチレンジアミン、オクタメチレンジアミン、ポリオキシプロピレンジアミンおよびポリオキシプロピレントリアミンなどの脂肪族ポリアミン、フェニレンジアミン、３，３’－ジクロロ－４，４’－ジアミノジフェニルメタン、４，４’－メチレンビス（フェニルアミン）、４，４’－ジアミノジフェニルエーテルおよび４，４’－ジアミノジフェニルスルホンなどの芳香族ポリアミンが挙げられる。
【0061】
また、シクロペンタンジアミン、シクロヘキシルジアミン、４，４－ジアミノジシクロヘキシルメタン、１，４－ジアミノシクロヘキサン、ビス－アミノプロピルピペラジン、チオ尿素、メチルイミノビスプロピルアミン、ノルボルナンジアミンおよびイソホロンジアミンなどの脂環式ジアミン化合物などが挙げられる。また、ヒドラジンとしては、ヒドラジン、カルボヒドラジド、アジピン酸ジヒドラジド、セバシン酸ジヒドラジドおよびフタル酸ジヒドラジドなどが挙げられる。これらは単独で或いは２種類以上を組み合わせて使用することができる。

【0062】
ポリウレアコロイド溶液の製造に使用する油脂変性ポリオール、ポリイソシアネート、ポリアミン、得られるプレポリマーの種類、使用量および使用比率は、使用する溶媒中での粒子Ｂの大きさおよび安定性などを制御する目的で決定される。すなわち、本発明で用いるポリウレアコロイド溶液中の粒子Ｂは、溶媒中で溶媒和されない結晶部分のウレアドメインと、そのウレアドメインから伸びて溶媒中で溶媒和されたポリマー鎖により形成されている。
【0063】
ポリウレアコロイド溶液中の粒子Ｂのウレアドメインの大きさおよび溶媒和されたポリマー鎖の大きさと形態がポリウレアコロイド溶液の性質を左右する。このように、ウレアドメインと溶媒和されたポリマー鎖とで形成された粒子Ｂは、溶媒中で安定なポリウレアコロイド溶液であり、その溶液中の粒子Ｂのウレアドメインの粒径は、通常０．０１～１．０μｍであり、溶媒和されているポリマー鎖の１個の分子量は約５００～１５，０００であり、両者の質量比はウレアドメイン（ウレア結合またはポリアミン）／ポリマー鎖が０．５～３０の範囲が好ましい。
【0064】
ウレア結合の割合が上記範囲未満であると、得られる粒子Ｂ中の非溶媒和性ウレアドメインが形成されにくく、粒子Ｂが非水溶媒に溶解し易くなり、良好なポリウレアコロイド溶液が生成されない。一方、ウレア結合の割合が上記範囲を越えると、非溶媒和性ウレアドメインが大きくなり、得られるポリウレアコロイド溶液の安定性が低下し、粒子Ｂの凝集が生じ易くなる。
【0065】
本発明で使用する粒子Ｂの溶媒中における形態は、図１に示すようなものと想像される。この粒子Ｂの粒径の制御については、溶媒和したポリマー部分とウレアドメインを含んだ粒子全体の大きさと、溶媒和したポリマー部分とウレアドメインのそれぞれの大きさについて、両者ともに制御が可能である。なお、先に記載の粒子Ｂの粒径は、ウレアドメイン部分を表現している。
【0066】
安定に制御されたポリウレアコロイド溶液を製造するためには、図１のように、溶媒和したポリマー部分とウレアドメイン部分が明瞭に相分離しているのが望ましく、そのためには溶媒和されるポリマー鎖と結晶部分のウレアドメインとが混在しないように製造することが必要である。このためには、合成過程で溶媒和したポリマー部分とウレアドメイン部分が分離しやすい合成条件が要求される。
【0067】
ポリウレアコロイド溶液の合成は、ＮＣＯ基を有するプレポリマーの溶液およびポリアミンの溶液の両方の濃度が低く、一方の溶液に他方の溶液を添加する添加速度が遅いほど良好な結果が得られ、撹拌はプロペラミキサー撹拌で充分である。また、原料溶液の濃度が高い場合や溶液の添加速度が速い場合には、ホモジナイザーなどの使用による高剪断力の混合を行いながら合成することが好ましい。反応温度は使用する溶媒の種類と、その溶媒に対するウレアドメインの溶解度により決まるが、好ましい温度は合成を制御し易い２０～１２０℃であるが、この温度範囲に特に限定されない。ウレアドメインの形成は合成過程で形成する方法、或いは高温で合成したものを冷却過程で形成する方法でもよい。
【0068】
ポリウレアコロイド溶液中の粒子Ｂの重要な因子は、その表面基の種類および濃度であり、さらには不活性溶媒中における分散性と分散粒径である。すなわち、ポリウレアコロイド溶液の乳化剤としての作用は、Ｗ／Ｏ、Ｏ／Ｏ型の乳化剤であり、ポリイソシアネートおよびポリオールの親水性、疎水性の強さと不活性溶媒との相関性で作用する。これらの条件を加味して検討を加えた結果として、ポリイソシアネートおよびポリオールに対するポリウレアコロイド溶液の添加量の調整で、粒子Ｃの粒径をコントロールすることが可能であり、前記の範囲で添加量が多い程粒径は小さくなり、少ない程粒径が大きくなる。

【0069】
以上の如き原材料から得られた粒子Ｃの分散溶液から、常圧または減圧下で不活性溶媒を分離することによって、本発明で使用する粒子Ｃが得られる。粒子化に用いる装置としてスプレイドライヤー、沪過装置付き真空乾燥機、撹拌装置付真空乾燥機、棚式乾燥機など公知のものがいずれも使用でき、好ましい乾燥温度は不活性溶媒の蒸気圧、ゲル粒子の軟化温度、粒径などに影響されるが、好ましくは減圧下４０～１３０℃である。
【0070】
このようにして製造された粒子Ｃの粒径は、０．５～１００μｍで真球状である。粒径のコントロールは、粒子Ｃの組成が同一の場合、合成釜の乳化型式（プロペラ式、錨型式、ホモジナイザー、螺旋帯式など）および撹拌力の大小に左右されるが、特に不活性溶媒中のポリイソシアネート、ポリオールの濃度および機能性成分などの濃度、ポリウレアコロイド溶液の種類および添加量に影響される。ポリイソシアネート、ポリオール、機能性成分などを乳化するための機械的撹拌や剪断力は乳化の初期段階で決定され、これが強力な程分散体の粒径が小さくなる。その後の撹拌および剪断力は大きくは影響しない。かえってその力が強すぎると分散体同士の凝集を促進することになり好ましくない。
【0071】
また、本発明では、上記の粒子Ｃの製造にあたり、原料の少なくとも一部または全部に機能性成分など以外の各種添加剤を混合して、粒子Ｃの合成を行い種々の用途に適した粒子Ｃを得ることも可能である。
【0072】
以上の如くして得られる粒子Ｃは、下記式１で示される粒子Ｃの円形度が、０．９～１．０の範囲であることが好ましい。
［式１］　円形度＝円相当径から求めた円の周囲長／粒子投影の周囲長
【0073】
ここで円形度は、株式会社セイシン企業の粒子形状画像解析装置ＰＩＴＡ－１により算出されるものであり、円形度を円相当径（実際に撮像された周囲長と同じ投影面積を持つ真円の直径）から算出された周囲長を実際に撮像された粒子の周囲長で割った値として定義し、真円で１になり、形状が複雑になるほど小さい値となる。このため、円形度は０．９以上の極めて球状性が高い粒子が好ましく、粒子を水などに分散した分散体は、電荷的反発により、極めて安定的に分散しており、製品に使用した際には分散安定性、増粘効果を有する。なお、円形度が０．９より小さい場合には球形でなくなり、安定的な分散性を喪失するとともに、化粧料成分として用いたときにざらつき感やきしみ感を生じる。
【0074】
さらに、前記粒子Ｃは、その圧縮強度は、０．０１から１．０ＭＰａであり、回復率は、８０％以上であることが好ましい。圧縮強度は、粒子Ｃが粒子Ｂによって被覆された粒子Ａであることから、化粧料成分として用いたときに０．０１ＭＰａ以上で十分なさらさら感を得ることができ、より肌に近い感触である柔軟性（ソフトタッチ感）、滑り性、しっとり感を得る観点から１ＭＰａ以下が好ましい。
【0075】
回復率は、圧力により変形した場合、力が解放されると同時に、元の形状に復元することが求められ、６０～１００％の範囲であることが好ましい。ここで圧縮強度、回復率とは、粒子Ｃを株式会社島津製作所の微小圧縮試験機ＭＣＴ－Ｗ５００にて圧縮試験を行った場合に、粒子径に対して１０％変形した時の荷重と粒子径から下記式２によって算出される値である。
［式２］　圧縮強度（ＭＰａ）＝２．８×荷重（Ｎ）／｛π×粒子径（ｍｍ）×粒子径（ｍｍ）｝
【0076】
回復率は、粒子に５０ｍＮの圧力をかけ、変位した距離（Ｌ１）と圧力を解放した時に変位した距離（Ｌ２）から下記式３によって計算される値である。なお、粒子Ｃの圧縮強度、回復率は、粒子Ａの構成成分であるポリイソシアネートおよびポリオールの種類と配

合量を制御することにより調節できる。
［式３］　回復率（％）＝Ｌ２／Ｌ１×１００
【0077】
粒子Ｃの熱軟化点は２５０℃以上であることが好ましい。熱軟化点が上記温度より低いと、化粧料成分として用いたときに口紅などのスティック剤に加工するときに高温で溶融などの不具合が起こることがある。熱軟化点は熱機械分析装置（ＴＭＡ、リガク（株））を用い、粒子と同じ樹脂組成のシートを作製し測定を行った。
【0078】
さらに、本発明においては、粒子Ｃを分散媒（重合媒体）から分離した状態において（乾燥粒子Ｃ）、通常の微粒子の場合、粘着性が強く二次凝集してしまうが、該粒子Ｃは、凝集物がなくサラサラした粒子の状態として取り出されるのが特徴である。この作用は従来公知の有機系乳化剤や分散安定剤とは根本的に異なる作用である。
【0079】
これらの粒子Ｃは、図２の電子顕微鏡写真（倍率５００倍）に示すように、ほぼ完全に真球状の粒子であり、図３の想像図に示す如く個々の粒子Ｃの表面にはポリウレアコロイド溶液から析出した粒子Ｂが付着或は被覆されておりかつ粒子Ｂが非粘着性と耐熱性に優れているため、該粒子Ｃを分散溶媒から単に除去するのみで極めて流動性に富んだ粒子となり、粒子化に当たっては従来技術における如き煩雑かつコスト高な粉砕工程や分級操作を何ら要しないなどの種々の利点を有している。
【実施例】
【0080】
以下に合成例、実施例および比較例を挙げて本発明をさらに具体的に説明するが、本発明はこれに限定されるものではない。また、以下の文中の「部」は質量部、「％」は質量％を示す。
【0081】
（ポリウレアコロイド溶液の作成）
［合成例１］
水酸基価１１９．５の２官能の油脂変性ポリオール（伊藤製油（株）製　ＵＲＩＣ　Ｙ－２０２）１００部中にグルコシルトレハロース２部（機能性成分）とホワイトパール（意匠性成分）０．２部および黄酸化鉄（意匠性成分）０．１部を均一に分散させたものと、ｎ－オクタン１００部とを撹拌機付き合成釜に仕込み上記ポリオールを溶解した。
【0082】
撹拌しながら温度を５０℃に制御し、ＮＣＯ／ＯＨ＝２になるように予め用意したイソホロンジイソシアネート４７．３部を１時間かけて徐々に添加し、この条件で３時間反応を続け、さらに８０℃、３時間の反応を行い合成した。次にｎ－オクタンで濃度５０％に調整し、ＮＣＯ基を３．０％含有するプレポリマー溶液（ＰＰ－１）を得た。この物の分子量は１，３８３である。
【0083】
上記のＰＰ－１の４０部と、ｎ－オクタン６０部を撹拌機付き合成釜に仕込み溶解した。撹拌しながら温度を７０℃に制御しながら、予め用意したイソホロンジアミンのｎ－オクタンの１０％溶液２４．３部を５時間掛けて徐々に添加し反応を完結して、（ポリアミン（ウレア結合部）／プレポリマー鎖）×１００＝１２．１５％のポリウレアコロイド溶液（固形分１８．０％）（Ｂ－１）を得た。この溶液は青い乳白色の安定な溶液であった。
【0084】
［合成例２］
水酸基価１１９．５の２官能の油脂変性ポリオール（伊藤製油（株）製　ＵＲＩＣ　Ｙ－２０２）１００部中にビタミンＥ（トコフェロール）（機能性成分）１部とホワイトパール（意匠性成分）０．５部を均一に分散させたものと、ｎ－オクタン１００部とを撹拌機付き合成釜に仕込み上記ポリオールを溶解した。撹拌しながら温度を５０℃に制御し、

ＮＣＯ／ＯＨ＝１．１になるように予め用意したイソホロンジイソシアネート２６．０部を１時間掛けて徐々に添加し、この条件で３時間反応を続け、さらに８０℃、４時間の反応を行い合成した。次にｎ－オクタンで濃度５０％に調整し、ＮＣＯ基を０．３６％含有するプレポリマー溶液（ＰＰ－２）を得た。この物の分子量は１１，８３４である。

【0085】

上記のＰＰ－２の２０部とｎ－オクタン８０部とを撹拌機付き合成釜に仕込み上記プレポリマー溶解した。撹拌しながら温度を７０℃に制御しながら、予め用意したイソホロンジアミンのｎ－オクタンの１％溶液１４．４部を８時間掛けて徐々に添加し反応を完結して、（ポリアミン／プレポリマー鎖）×１００＝１．４４％のポリウレアコロイド溶液（固形分８．９％）（Ｂ－２）を得た。この溶液は青い乳白色の安定な溶液であった。

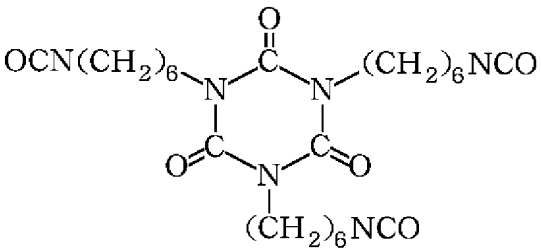
【0086】

（粒子Ｃの製造）

［合成例３］（実施例１）

平均分子量１，０００のポリブチレンアジペートジオール２０部中にヒアルロン酸（機能性成分）０．１部を均一に分散させたものを６０℃で溶解し、さらに下記の構造式（化１）で示されるヘキサメチレンジイソシアネートのイソシアヌレートポリイソシアネート（旭化成工業（株）製　デュラネートＴＰＡ－１００、ＮＣＯ％＝２３．１）７．３部を添加し均一に混合した。この物を予め１リットルのステンレス容器に準備した合成例１のポリウレアコロイド溶液（Ｂ－１）５．０部とｎ－オクタン２５部の混合液の中に徐々に加え、ホモジナイザーで１５分間乳化した。この乳化液は分散質の平均分散粒子径が５μｍで、分離もなく安定な乳化液であった。

【0087】



【0088】

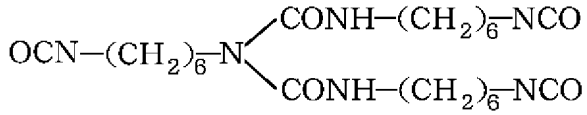
次にこれを錨型撹拌機付き反応釜に仕込み、４００ｒｐｍの回転をさせながら温度を８０℃まで上げ、６時間の反応を終了し、粒子Ｃの溶液を得た。この溶液を１００Ｔｏｒｒで真空乾燥を行ってｎ－オクタンを分離し、粒子Ｃ（１）を得た。このものは平均粒子径が５μｍで円形度が０．９２の真球状の白色粉末状であった。圧縮強度は、０．３５ＭＰａで回復率は８９％であった。

【0089】

［合成例４］（実施例２）

５００ミリリットルのセパラブルフラスコに、ポリウレアコロイド溶液（Ｂ－２）４部とイソオクタン１５０部とを仕込み混合した。次にこの液をホモミキサーで混合しながら予め５０℃に加温した平均分子量７８５の３官能のポリラクトンポリオール１００部中にビタミンＣ（機能性成分）１部と水酸化クロム（意匠性成分）０．２部を均一に分散した化合物を、徐々に添加して乳化させた。さらに下記の構造式で示されるヘキサメチレンジイソシアネートアダクトポリイソシアネート（旭化成工業（株）製　デュラネート２４Ａ－１００、ＮＣ０％＝２３．５）６８．３部を徐々に添加した。

【0090】



【0091】
次にホモミキサーを回転しながら、温度を８０℃に上げ、３時間の反応後に反応触媒としてジブチル錫ジラウレート０．００５部を加え、さらに４時間の反応を行ない、粒子Ｃの分散液を得た。この分散液から実施例１と同様にして粒子Ｃ（２）を得た。このものは平均粒子径が１５μｍで円形度が０．９４の真球状の白色粉末状であった。圧縮強度は、０．６０ＭＰａで回復率は９２％であった。
【0092】
［合成例５］（比較例１）
撹拌機および還流冷却器を具備した１，０００ミリリットルのセパラブルフラスコに、メチルメタクリレート５０部、エチルアクリレート３５部、プロピレングリコールジアクリレート５部、エチレングリコールジメタクリレート１０部およびベンゾイルパーオキサイド０．３部を仕込み、さらに、ポリビニルアルコール（ＧＨ－１７、日本合成化学工業社製）の５％水溶液３０部およびイオン交換水２５０部を添加し、ホモミキサーにて４，０００～６，０００ｒｐｍで１０分間分散処理し分散液（１）を調製した。さらに分散液（１）を、窒素雰囲気下で撹拌しながら８０℃、５時間ラジカル重合した。得られたアクリレート系粒子分散液を脱水、洗浄、乾燥後、解砕、篩いを掛けアクリル微粒子（３）を得た。このものは平均粒子径が１０μｍで円形度が０．９３の真球状の白色粉末状であった。圧縮強度は、７．１ＭＰａで回復率は４５％であった。
【0093】
（比較例２）
シリカ微粒子としてサイリシア３５０（富士シリシア化学社製、平均粒子径３．９μｍ、円形度０．７４）を用いた。圧縮強度は、１５．５ＭＰａで回復率は、破壊してしまったため０％とした。
【0094】
（実施例１、２および比較例１、２の各粒子の評価）
＜外観色調＞
乾燥粒子を外観で確認した際の意匠性
○：意匠性が高い。
×：意匠性が低い。
【0095】
＜分散性＞
ディゾルバー撹拌機（１，０００ｒｐｍ）中のＩＰＡ（イソプロピルアルコール）１００ｇに各粒子を５ｇ添加し、２０秒後の分散性を確認した。
評価基準；
○：均一に分散していた。
△：一部凝集物があった。
×：分散しない。
【0096】
＜吸油量＞
ＪＩＳ－Ｋ５１０１に準じて測定した。
各粒子が化粧料に使用する油剤や防腐剤などを吸収すると、それらの効果を発揮できなくなるので、油剤などの例として亜麻仁油を使用してその吸油量を測定した。亜麻仁油の吸収性が低い方がよいとされる。オレイン酸は、人の皮脂成分の代替材料として測定した。オレイン酸の吸収性が高いほど人の皮脂を吸収するので良好とされる。化粧料に使用する油剤、防腐剤の吸収性が少なく、かつ皮脂（オレイン酸）の吸収は必要とされる。

【0097】
＜分散安定性＞
１，３－ブタングリコール、揮発性シリコーン、ＩＰＡ１００ｇに対して、各粒子１０ｇを入れ、手撹拌で混合した際の分散安定性を確認した。
評価基準；
○：簡単に分散し３日間後、凝集・沈降もなく安定な溶液が保持できる。
△：簡単に分散するものの３日間後、一部に凝集・沈降が見られる。
×：分散しない。
【0098】
＜膨潤性＞
ＩＰＡ中に、各粒子を２４時間浸漬させた後、粒子径の増加率を比較した。
＜光学特性＞
試験片は、ニトロセルロースに各粒子を濃度１０ｐｈｒで調製した溶液を、塗布膜厚２０μｍでコーティングしたものの光学特性を測定した。全光線透過率は、数値が高いと透明感のある自然な肌を演出してよいとされる。また、拡散透過率は、適度な値（３０～５０）が求められ、光の拡散効果で小皺、しみなどを隠す作用がある。
【0099】
＜耐熱性＞
熱機械分析（ＴＭＡ、リガク（株））を用い、粒子と同じ樹脂組成のシートを作製して荷重１０ｇ、昇温速度１０℃／ｍｉｎ．の条件にて針進入法で測定を行った。
【0100】

表１：実施例１、２および比較例１、２の各粒子の評価

		実施例１	実施例２	比較例１	比較例２
外観色調		○	○	×	×
分散性		○	○	△	×
吸油量（ml/100g）	亜麻仁油	72	68	50	310
	オレイン酸	110	105	45	280
分散安定性	1,3－BG	○	○	△	△
	揮発性シリコーン	○	○	○	×
	IPA	○	○	○	△
膨潤性（IPA）		2％	1％	15％	0％
光学特性（％）	全光線透過率	90	88	90	87
	拡散透過率	33	30	40	65
耐熱性		250℃以上	250℃以上	220℃	250℃以上

1,3－BG；1,3－ブタングリコール
IPA；イソプロピルアルコール

【0101】
（実施例１、２および比較例１、２の各粒子の化粧料応用）
＜クリーム処方＞
・各粒子　　１２．０部
・シリコーン系界面活性剤　　１．０部

・スクワラン　　１２．０部
・揮発性シリコーン　　１２．０部
・１，３－ＢＧ　　５．０部
・精製水　　５８．０部
上記化粧処方にて以下の化粧料評価を行った。結果を表２に示す。

【0102】
＜柔軟性＞
適正量を手の甲に塗り、乾燥した状態で評価を行った。
○：ソフト性がある。
△：ソフト性が劣る。
×：ハード性が強い。
ソフト性が高いと人肌と近似した感覚であり評価される。

【0103】
＜伸展性（ローリング性）＞
適正量を手の甲に塗り、伸展性が良好であるか確認した。
○：伸展性がある。
△：伸展性が劣る。
×：伸展性が強い。

【0104】
＜毛穴隠し効果＞
適正量を手の甲に塗り、毛穴が隠れるか目視にて観察評価した。
○：毛穴隠し効果がある。
△：毛穴隠し効果が低い。
×：毛穴隠し効果がない。

【0105】
＜機能性＞
１０人の女性にクリーム処方、リキッドファンデーション処方にて調整したサンプルを腕に塗布してもらい、５名以上が効果を確認した場合を効果ありとした。

【0106】

表２

	実施例１	実施例２	比較例１	比較例２
柔軟性（ソフト性）	○	○	△	×
伸展性	○	○	△	×
毛穴隠し効果	○	○	△	×
機能性	保湿機能効果あり	抗酸化効果あり	なし	なし

【0107】
＜リキッドファンデーション処方＞
・各粒子　　１０．０部
・シリコーン系界面活性剤　　１．５部
・揮発性シリコーン　　２３．０部
・ジメチルシリコーン　　５．０部
・酸化チタン　　９．０部
・弁柄　　０．６部
・黄色酸化鉄　　０．２部
・タルク　　２．０部
・プロピルパラベン（防腐剤）　　０．５部

・１，３－ブタングリコール　　１０．０部
・ビタミンＥ　　０．２部
・精製水　　３８．０部
上記化粧処方にて前記と同様に化粧料評価を行った。結果を表３に示す。
【0108】

表３

	実施例１	実施例２	比較例１	比較例２
柔軟性（ソフト性）	○	○	△	×
伸展性	○	○	△	×
毛穴隠し効果	○	○	△	△
機能性	保湿機能効果あり	抗酸化効果あり	なし	なし

【0109】
＜パウダーファンデーション処方＞
・各粒子　　３．０部
・タルク　　３５．０部
・セリサイト　　２０．０部
・酸化チタン　　９．０部
・弁柄　　２．０部
・黄色酸化鉄　　３．５部
・黒色酸化鉄　　０．５部
・マイカ　　１５．０部
・スクワラン　　６．０部
・ステアリルアルコール　　３．０部
・ミツロウ　　３．０部
上記化粧処方にて前記と同様に化粧料評価を行った。結果を表４に示す。
【0110】

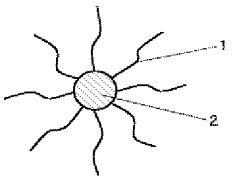
表４

	実施例１	実施例２	比較例１	比較例２
柔軟性（ソフト性）	○	○	△	×
伸展性	○	○	△	×
毛穴隠し効果	○	○	△	×
機能性	保湿機能効果あり	抗酸化効果あり	なし	なし

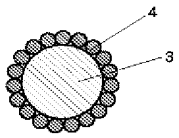
【産業上の利用可能性】
【0111】
本発明は下記の効果を奏する。
１．粒径がコントロールされ、機能性成分などを含む粒子Ｃを含む化粧料の提供が可能である。
２．得られた粒子Ｃは真球状であり、該粒子Ｃは、粒子Ａの表面にポリウレアコロイド溶液から析出した粒子Ｂが均一に付着または被覆されているものであるため、該粒子Ｃは極めて流動性に優れ、取り扱いが容易であり、化粧料として種々の応用が可能である。
３．以上の効果から、本発明の粒子Ｃは、化粧料成分として有益である。
【図面の簡単な説明】

【0112】
【図1】本発明で使用するポリウレアコロイド溶液中の粒子Ｂの断面の想像図。
【図2】本発明で使用する粒子Ｃの写真。
【図3】本発明で使用する粒子Ｃの断面の想像図。
【符号の説明】
【0113】
１：溶媒和されているポリマー鎖（油脂セグメント）
２：非溶媒和部分のウレアドメイン
３：粒子Ａ
４：粒子Ｂ

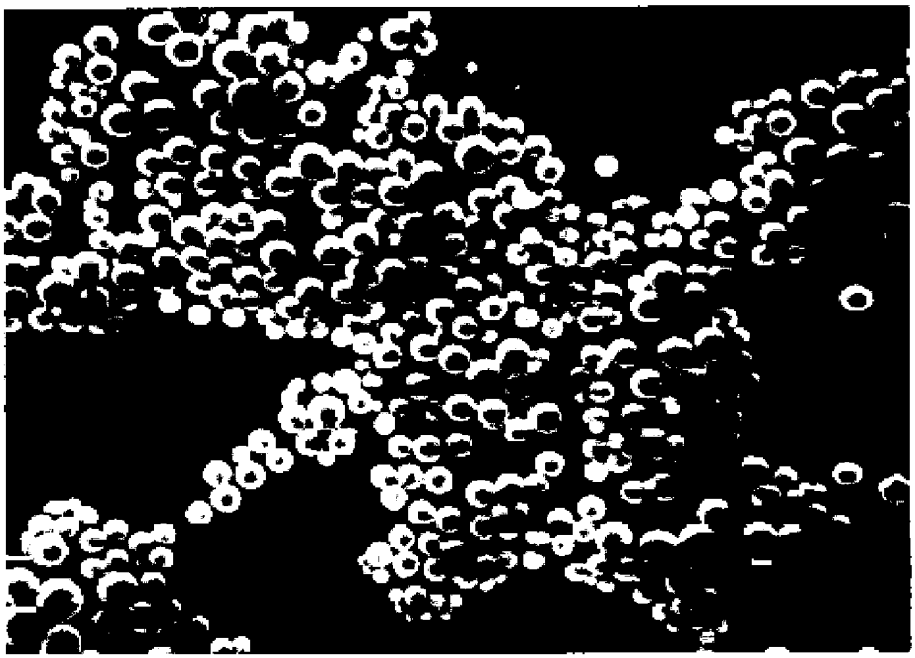
【図1】



【図3】



【図2】



(72)発明者　高橋　賢一
東京都中央区日本橋馬喰町１丁目７番６号　大日精化工業株式会社内
(72)発明者　渡辺　明弘
東京都中央区日本橋馬喰町１丁目７番６号　大日精化工業株式会社内
(72)発明者　花田　和行
東京都中央区日本橋馬喰町１丁目７番６号　大日精化工業株式会社内

Ｆターム(参考) 4C083 AA082 AB232 AB242 AB432 AC022 AC072 AC122 AC482 AD071 AD072
AD152 AD662 BB24 CC05 CC12

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 365 024 A1

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:
14.09.2011 Bulletin 2011/37

(21) Application number: **09830464.5**

(22) Date of filing: **04.12.2009**

(51) Int Cl.:
C08J 3/12 *(2006.01)* ***A61K 8/87*** *(2006.01)*
A61Q 13/00 *(2006.01)* ***B01J 2/00*** *(2006.01)*
B01J 2/04 *(2006.01)* ***B01J 20/26*** *(2006.01)*
C08G 18/10 *(2006.01)* ***C08G 18/48*** *(2006.01)*
C09K 3/00 *(2006.01)* ***A61L 9/01*** *(2006.01)*

(86) International application number:
PCT/JP2009/070378

(87) International publication number:
WO 2010/064698 (10.06.2010 Gazette 2010/23)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR

(30) Priority: **05.12.2008 JP 2008310341**

(71) Applicant: **Konishi Co., Ltd.**
Chuo-ku
Osaka-shi
Osaka 541-0045 (JP)

(72) Inventors:
- **ORIGUCHI Toshiki**
  Osaka-shi
  Osaka 538-0053 (JP)
- **NAKAYAMA Yoshitaka**
  Osaka-shi
  Osaka 538-0053 (JP)

(74) Representative: **HOFFMANN EITLE**
Patent- und Rechtsanwälte
Arabellastraße 4
81925 München (DE)

(54) POLYURETHANE PARTICLES AND METHOD FOR PRODUCING POLYURETHANE PARTICLE CLUSTER

(57) It is provided smooth polyurethane particles for oil absorption under producing, treating, keeping and transporting. A polyurethane particle consists of a body of the polyurethane particle and hydrophilic fine silica powders existing on the body. The body is obtained by three-dimensionally polymerizing an isocyanate-terminated urethane prepolymer with trifunctional or more functional amines. The isocyanate-terminated urethane prepolymer is obtained by reacting polyisocyanates and polyols including a poly(tetramethylene ether) glycol. The polyurethane particles are obtained by spray-drying a mixed aqueous dispersion in which the hydrophilic fine silica powders and the polyurethane spheres are dispersed in a water.

EP 2 365 024 A1

Description

Technical Field

[0001] The present invention relates to a polyurethane particle and a method for producing polyurethane particles. Especially, the invention relates to the polyurethane particle to superiorly absorb fats and oils such as sebums or oleic acids, and the method for producing them.

Background Art

[0002] In recent years, it is proposed an acrylic polymer particle easy to absorb fats and oils such as sebums or oleic acids. For example, the patent reference 1 discloses a swelling-type oil absorbent polymer particle consisting of a cross-linked acrylic polymer particle which is obtained by polymerizing an alkyl acrylate or alkyl methacrylate which has a liner or branched alkyl group having 18 to 24 carbon atoms, a vinyl monomer which is able to co-polymerize with the alkyl acrylate or alkyl methacrylate, and a cross-linkable monomer.

[0003] Patent reference 1: JP2006-8757 (the claims are referred.)

Summary of Invention

Technical Problem

[0004] The inventors have tried to obtain an oil absorbent particle with using a polyurethane but not acrylic polymer. The inventors have discovered that the polyurethane obtained by selecting a poly(tetramethylene ether)glycol as polyols superiorly absorbs fats and oils such as sebum or oleic acid. Concretely, the inventors have discovered the oil absorbent particle consisting of the polyurethane obtained with the following method. That is, it is obtained an isocyanate-terminated urethane prepolymer by reacting a poly(tetramethylene ether)glycol as polyols and polyisocyanates such as an isophorone diisocyanate. It is obtained an oil-in-water emulsion by dispersing the isocyanate-terminated urethane prepolymer in a water.
A trifunctional or more functional amines is added in the oil-in-water emulsion, and react with the isocyanate-terminated urethane prepolymer in droplets to three-dimensionally polymerize and convert droplets to polyurethane spheres. After that, removing the water of the emulsion with drying, polyurethane particles consisting of the polyurethane spheres are obtained.

[0005] However, removing the water of the emulsion with drying, the polyurethane spheres may be easy to cohere in the case the polyurethane sphere is soft or the surface of it is sticky. Furthermore, keeping the obtained polyurethane particles for a long time, the particles may be easy to cohere. The polyurethane particles for oil absorption are generally used as an aggregate of the polyurethane primary particles. Therefore, the polyurethane particles cohering, it is difficult to treat and an oil absorbability lowers because a total surface area of the polyurethane particles is small. Preventing to cohere, the polyurethane particles must be set in strict conditions under producing, treating, keeping and transporting them.

[0006] It is therefore the object of the invention to provide polyurethane particles which are difficult to cohere though they are not set in strict conditions under producing, treating, keeping and transporting them. Furthermore, it is the object of the invention to provide methods for producing such polyurethane particles,

Solution to Problem

[0007] The inventors have discovered to solve the problem by making an emulsion in which polyurethane spheres disperses, dispersing hydrophilic fine silica powders in the emulsion and spray-drying the emulsion to remove the water in it. The invention is based on the discovery. The invention is relates to the method for producing polyurethane particles comprising: preparing the hydrophilic fine silica powders, preparing an isocyanate-terminated urethane prepolymer obtained by reacting polyisocyanates and polyols including a poly(tetramethylene ether) glycol, preparing the polyurethane spheres obtained by three-dimensionally polymerizing the isocyanate-terminated urethane prepolymer with trifunctional or more functional amines, preparing a mixed aqueous dispersion by dispersing the hydrophilic fine silica powders and the polyurethane spheres in a water, and spraying the mixed aqueous dispersion in a high temperature atmosphere. Then, the polyurethane particles are obtained by vaporizing the water in the mixed aqueous dispersion, converting the polyurethane spheres to bodies of the polyurethane particles, and covering each surface of the bodies of the polyurethane particles with the hydrophilic fine silica powders. Furthermore, the invention relates to the polyurethane particle. Furthermore, the invention relates to an oil absorbent agent consisting of the polyurethane particles, a perfume comprising the polyurethane particles which hold a perfumed oil therein and chemicals comprising the polyurethane

particles which hold therein an oil-based chemical component selected from the group consisting of an oil-based agricultural chemical component, an oil-based attractant component and an oil-based repellent component.

[0008] The hydrophilic fine silica powder consists of mainly SiO_2, and has not substantially hydrophobic groups on the surface of it. The hydrophilic fine silica powders are well known, and sold by Nippon Aerosil Co. as AEROSIL® 200, 200V, 200CF, 200FAD, 300, 300CF, 380, 50, 90G, 130, 0X50, MOX80, MOX170, COK84 and etc.. Such hydrophilic fine silica powders are used in the invention. A particle size of the hydrophilic fine silica powder is finer than the particle size of the obtained polyurethane particle to cover the body of the polyurethane particle with the hydrophilic fine silica powders. Concretely, an average particle size of the obtained polyurethane particles is 1-500μ m, and an average particle size of the hydrophilic fine silica powders is 5-40 nm. Therefore, it is preferable that the particle size of the polyurethane particle is 30 or more times larger than the particle size of the hydrophilic fine silica powder. The average particle size of the hydrophilic fine silica powders is decided in nominal value.

[0009] It is used as the polyisocyanates for producing a polyurethane to be well known compounds which have two or more isocyanate groups in a molecule. It is preferably used alicyclic polyisocyanates or aliphatic polyisocyanates. Concretly, it is used an isophorone diisocyanate, a 1,6-hexamethylene diisocyanate and a hydrated MDI.

[0010] It is used as the polyols for producing a polyurethane to be a poly(tetramethylene ether)glycol. The other polyols may be mixed with the poly(tetramethylene ether)glycol. It may be used as the other polyols to be well known polyols for producing a polyurethane. A number average molecular weight of poly(tetramethylene ether)glycol is not limited, but preferably 650-3000.

[0011] Trifunctional or more functional amines for producing a polyurethane are used to three-dimensionally polymerize a urethane prepolymer obtained by reacting the polyols and the polyisocyanates.
It is used a diethylenetriamine, triethylenetetramine, tetraethylenepent amine and 3,3'-diaminodipropylamine as the trifunctional or more functional amines.

[0012] The polyurethane particle of the invention is obtained by the method described in the above paragraph 0007. The method is the following, describing concretely in the order of processes.

[0013] The processes comprise: a process to obtain an isocyanate-terminated urethane prepolymer by reacting polyisocyanates and polyols including a poly(tetramethylene ether)glycol, a process to obtain an oil-in-water emulsion by adding and mixing the isocyanate-terminated urethane prepolymer to an aqueous solution in which a dispersant dissolves, a process to obtain polyurethane spheres in the oil-in-water emulsion by that the isocyanate-terminated urethane prepolymer in oil droplets is three-dimensionally polymerized by adding the trifunctional or more functional amines in the oil-in-water emulsion, a process to obtain an aqueous polyurethane dispersion in which the polyurethane spheres disperse by removing the dispersant from the oil-in-water emulsion, a process to obtain a mixed aqueous dispersion by mixing the aqueous polyurethane dispersion with an aqueous silica dispersion in which hydrophilic fine silica powders disperse in a water, and a process to spray-dry the mixed aqueous dispersion in a high temperature atmosphere with a spray-dryer. Thereby, the water is vaporized in the mixed aqueous dispersion, the polyurethane spheres are converted to bodies of the polyurethane particles, and each surface of the bodies of the polyurethane particles is covered with the hydrophilic fine silica powders.

[0014] The processes are more described as the followings. The isocyanate-terminated urethane prepolymer is obtained by reacting conventionally the polyisocyanates and the polyols including a poly(tetramethylene ether)glycol. Then, an amount by mole of NCO group of the polyisocyanates exceeds an amount by mole of OH group of the polyols to terminate at the NCO group in the urethane prepolymer. The amount by mole of NCO group is conventionally 1.5-3.0 times to the amount by mole of OH group. Generally, the polyisocyanates and polyols are dissolved in an organic solvent such as ethyl acetate or methyl ethyl ketone, and react with a tin catalyst such as dibutyl tin dilaurate or an amine catalyst such as 1,8-diazabicyclo[5.4.0]undec-7-ene.

[0015] Conventionally, it is used only the poly(tetramethylene ether) glycol as the polyols, but may be mixed with the other polyols. It may be used a polyalcohol, polyetherpolyol, polyesterpolyol, polycarbonatepolyol, polyolefinpolyol, polyacrylicpolyol or castor oil as the other polyols. Mixing with the other polyols, it is preferable that the poly(tetramethylene ether)glycol occupies 50 or more mass% in the polyols. Less than 50 mass%, the polyurethane particle is insufficient to absorb oils because the poly(tetramethylene ether)glycol is a component to absorb oils. Using only the poly(tetramethylene ether)glycol, the body of the polyurethane particle tends to be soft. Mixing with the polycarbonatepolyol as the other polyols, the body of the polyurethane particle tends to be gradually hard with increase of the content.

[0016] The content of the isocyanate group (NCO group) of the isocyanate-terminated urethane prepolymer is 2.0-10 mass%, and preferably 2.5-3.5 mass%. More than 10 mass% in the content, the polyurethane particle is insufficient to absorb oils because a content of urethane linkage is much. Less than 2.0 mass% in the content, it may be difficult to treat the isocyanate-terminated urethane prepolymer because it becomes high molecular weight and high viscosity.

[0017] The obtained isocyanate-terminated urethane prepolymer is added and mixed to an aqueous solution in which a dispersant is dissolved to obtain an oil-in-water emulsion. Concretely, the oil-in-water emulsion is obtained by the following method.

[0018] It is prepared the aqueous solution in which the dispersant is dissolved. The dispersant is to emulsify the

isocyanate-terminated urethane prepolymer in a water. For example, as the dispersant, it is used general surfactants such as nonionic surfactant or usaul polymeric dispersants such as polyvinyl alcohol. The dispersant is dissolved in the water to obtain the aqueous solution. Dissolving the dispersant, it is preferable to heat the water so as to dissolve easily. After the dispersant is entirely dissolved in the water, it is preferable to cool the aqueous solution at room temperature. A temperature of the heated water is decided at a solubility of the dispersant. For example, using the polyvinyl alcohol having a saponification degree of about 86.5-89.0 mol%, the temperature of the heated water is about 90°C . A concentration of the dispersant is decided so as to emulsify the isocyanate-terminated urethane prepolymer in the water. It is conventionally about 3-20 mass%.

[0019] The isocyanate-terminated urethane prepolymer is added and mixed in the aqueous solution cooled at room temperature. An addition mass of the isocyanate-terminated urethane prepolymer is conventionally about 3-20 parts by mass to 100 parts by mass of the aqueous solution. The machine and degree for mixing are decided so as to emulsify the isocyanate-terminated urethane prepolymer in the water. It is used a homomixer, a homogenizer, a high-pressure homogenizer or an ultrasonic homogenizer as the machine for mixing. Using the homomixer, the degree for mixing is about 5 minutes at about 8000 rpm. Adding and mixing are conventionally executed at room temperature, but may be executed at a little heating temperature so as to mix easily.

[0020] A trifunctional or more functional amine is added in the oil-in-water emulsion. The trifunctional or more functional amine is used to obtain polyurethane having network structure by three-dimensionally polymerizing the isocyanate-terminated urethane prepolymer as described in paragraph 0011. It is used various poly-functional amine as the trifunctional or more functional amine. The poly-functional amine is added as it is or as solution dissolving it in a solvent such as water.

An addition mass of the poly-functional amine is preferably chemical equivalent to the isocyanate group of the isocyanate-terminated urethane prepolymer in the oil-in-water emulsion. That is, the poly-functional amine is preferably added such as an amino group of the poly-functional amine is chemical equivalent to the isocyanate group of the isocyanate-terminated urethane prepolymer. Thereby, the isocyanate group reacts with the amino group to three-dimensionally polymerize.

The addition mass of the poly-functional amine may be from 0.8 to less than the chemical equivalent to restraint three-dimensional polymerization. Furthermore, the addition mass of the poly-functional amine may be to 1.2 from more than the chemical equivalent to be densely three-dimensional polymerization.

[0021] Not only the poly-functional amine such as the trifunctional or more functional amine but also a difunctional amine or polyalcohol may be added with the poly-functional amine to react with isocyanate group.

Using the difunctional amine or polyalcohol, it may be controlled to three-dimensionally polymerize the isocyanate-terminated urethane prepolymer.

[0022] Three-dimensionally polymerizing the isocyanate-terminated urethane prepolymer in oil droplets with the addition of the poly-functional amine, the oil-in-water emulsion is conventionally heated to quicken the reaction of the polymerization. The temperature of the oil-in-water emulsion is decided on the reactivity of the poly-functional amine. For example, using the 3,3'-diaminodipropylamine as the poly-functional amine, the oil-in-water emulsion is heated at about 80 °C, then the three-dimensional polymerization has finished for about 20 hours.

[0023] After the three-dimensional polymerization is finished, the oil droplets in the oil-in-water emulsion are converted to the polyurethane spheres. That is, the polyurethane spheres are dispersed to be in a dispersion. The dispersant in the dispersion is removed. The method of removing the dispersant is the following. The polyurethane spheres are collected with filtering or centrifugal separating the dispersion. The collected polyurethane spheres are dispersed in a water again. The polyurethane spheres are again collected with filtering or centrifugal separating the second dispersion. By repeating the above method, it is obtained an aqueous polyurethane dispersion in which the polyurethane spheres disperse as dispersion medium of water.

[0024] It is prepared the aqueous silica dispersion in which the hydrophilic fine silica powders disperse into a water. It is easily prepared to add and mix the hydrophilic fine silica powders in the water. It is decided the condition of adding and mixing or the content of the powders so as to disperse the powders informally in the water, not cohering. For example, using the trade mark ｢Aerosil ® 200｣ which are the hydrophilic fine silica powders and dispersing them in a content of 5 mass%, the aqueous silica dispersion is easily obtained by mixing with a water for 10 minutes at 10000 rpm by a homomixer.

[0025] Mixing the above aqueous silica dispersion with the above aqueous polyurethane dispersion, the mixed aqueous dispersion is obtained. The mixing ratio of the both is decided on the ratio of the solid content of the both. Mixing the both, it is preferable to add a water so as to prevent that the hydrophilic fine silica powders and polyurethane spheres cohere. The addition mass of the water is optionally decided, conventionally being about equal to the mass of the aqueous polyurethane dispersion. Adding the water, it is preferable to mix so as to prevent coherence.

[0026] The mixed aqueous dispersion is dried with the spray-dryer having nozzles or disks. Using the spray-dryer having nozzles, the mixed aqueous dispersion is spray-dried through each nozzle in the high temperature atmosphere to dry. Using the spray-dryer having disks, the mixed aqueous dispersion is dropped on each rotating disk and spray-

dried on the centrifugal force of each disk in the high temperature atmosphere to dry. The spray-drying in the invention is characterized by spraying in remaining the form of each polyurethane sphere in the mixed aqueous dispersion, that is, not atomizing the polyurethane sphere. Because the polyurethane sphere is three-dimensionally polymerized in the mixed aqueous dispersion. Spraying the mixed aqueous dispersion, it is sprayed the polyurethane spheres and the hydrophilic fine silica powders with the water. Drying the water, the hydrophilic fine silica powders adhere onto each surface of the polyurethane spheres. The polyurethane spheres being softer, the hydrophilic fine silica powders adhere on the surface in implanting.

[0027] The condition of spraying is not strict because the polyurethane spheres are not atomized at spraying. It is not strict the condition of the pressure, centrifugal force and aperture of the nozzle for atomization. Therefore, the spray-dryer having nozzles or disks may be used. The condition of the high temperature atmosphere to dry after spraying is decided so as to vapor the spraying water. The condition is conventional, for example, the inlet of a hot air may be the temperature of about 140°C and the temperature of about 70°C into the dryer. Spraying and drying the polyurethane spheres, each body of the polyurethane particles is formed with one of them or joining two or more. The polyurethane sphere being softer or more stick surface, the body of the polyurethane particles tends to be formed with two or more of the polyurethane spheres. The polyurethane spheres being harder, the body of the polyurethane particles tends to be formed with one of the polyurethane spheres.

[0028] Spray-drying the mixed aqueous dispersion, the polyurethane sphere is converted to the body of the polyurethane particle, covering the surface of the body with the hydrophilic fine silica powders. The hydrophilic fine silica powders adhere on the body. Being softer the polyurethane sphere or the body of the polyurethane particle, the hydrophilic fine silica powders adhere on the body in implanting. An average particle size of the polyurethane particles is decided on an average particle size of the polyurethane sphere in the mixed aqueous dispersion, a softness or stickiness of the body or the condition of spray-drying. The average particle size of the polyurethane particles is conventionally about 1-500μm. The average particle size of the polyurethane particles means to be median size on volume basis. The average particle size is measured with the laser scattering type particle size distribution analyzer which is sold as trade name 「LA-920」 from HORIBA, Ltd in Japan, after dispersing the polyurethane particles in a deionized water.

[0029] The polyurethane particle is used as an oil absorbent particle, and the polyurethane particles are as an oil absorbent agent. The oil absorbent agent is used as a component for cosmetics to make-up, care skin, skin care cosmetics, deodorize, protect ultraviolet and treat hair because the oil absorbent agent superiorly absorbs sebum. Furthermore, the oil absorbent agent is used as a component for waste oil disposal because the oil absorbent agent superiorly absorbs oils such as oleic acid. The polyurethane particles superiorly absorb a perfumed oil. Therefore, the polyurethane particles absorbed the perfumed oil may be used as a perfume which is able to use for a long time, gradually releasing the perfumed oil therein. Furthermore, absorbing an oil-based chemical component such as oil-based agricultural chemical component, oil-based attractant component or oil-based repellent component, and scattering in an environment, chemicals comprising the absorbed polyurethane particles may be used for a long time, gradually releasing the oil-based chemical component.

Advantageous Effects of invention

[0030] The polyurethane particles are smooth because of covering on the body of the polyurethane particle with the hydrophilic fine silica powders. Therefore, the polyurethane particles are easily flowed for a long time because they are not cohered at keeping or transporting. The body of the polyurethane particle is formed by three-dimensionally polymerizing the isocyanate-terminated urethane prepolymer with the trifunctional or more functional amines. Further, the isocyanate-terminated urethane prepolymer is obtained by reacting the polyisocyanates and the polyols including the poly(tetramethylene ether)glycol. Therefore, the polyurethane particle superiorly absorbs the sebums and oils such as oleic acid because the body of the polyurethane particle comprises the poly(tetramethylene ether)glycol as an element of polymerization. Furthermore, absorbing the oils, the polyurethane particle is not solved but only swelled because the isocyanate-terminated urethane prepolymer comprising the element of the poly(tetramethylene ether)glycol is three-dimensionally polymerized with the trifunctional or more functional amines. Therefore, the body of the polyurethane particle remains to be covered with the hydrophilic fine silica powders, and the polyurethane particles are smooth, not sticky or liquidizing.

[0031] The method of producing polyurethane particles comprises of spraying the mixed aqueous dispersion in the high temperature atmosphere. Further, the mixed aqueous dispersion is obtained by dispersing the hydrophilic fine silica powders and the three-dimensionally polymerized polyurethane spheres in the water. Therefore, spraying the mixed aqueous dispersion, the polyurethane spheres are not atomizes because of the three-dimensionally polymerization. Adjusting the size of the polyurethane sphere which is then formed, it is obtained the polyurethane particle having the desired size after spraying. Furthermore, spraying the mixed aqueous dispersion, the hydrophilic fine silica powders are sprayed with the polyurethane spheres. Then, the hydrophilic fine silica powders and the water exist around the polyurethane sphere. Vaporizing the water by drying, the hydrophilic fine silica powders collide on the surface of the poly-

urethane sphere. Therefore, the polyurethane sphere which is the body of the polyurethane particle is covered with the hydrophilic fine silica powders. By the method, it is obtained the smooth polyurethane particles which are difficult to cohere.

Examples

Example 1

[Preparing an isocyanate-terminated urethane prepolymer]

[0032] 20 parts by mass of ethyl acetate and 300 parts by mass of poly(tetramethylene ether)glycol having a number average molecular weight of 1000 were charged in a four-necked flask fitted with a stirrer, nitrogen inlet, thermometer and condenser. 104.6 parts by mass of isophorone diisocyanate and 0.04 parts by mass of dibutyl tin dilaurate were added and reacted under a nitrogen stream at 75-80 °C for 5 hours to obtain the isocyanate-terminated urethane prepolymer containig 3.6% of isocyanate group.

[Preparing an oil-in-water emulsion]

[0033] 900 parts by mass of deionized water and 100 parts by mass of polyvinyl alcohol having a saponification degree of 86.5-89.0 mol% as a dispersant which was sold as a trade name of PVA-205 by Kuraray Co., Ltd. were charged and heated at 90 °C to obtain an aqueous solution of polyvinyl alcohol. 100 parts by mass of the above prepared isocyanate-terminated urethane prepolymer were added in the aqueous solution of polyvinyl alcohol, and they were mixed at 8000 rpm for 5 minutes with a homomixer to obtain the oil-in-water emulsion in which oils are consisted of the isocyanate-terminated urethane prepolymer.

[Preparing an aqueous polyurethane dispersion]

[0034] 35.7 parts by mass of 10% aqueous solution of 3, 3' - diaminodipropylamine were added in the above oil-in-water emulsion. They were heated at 80 °C with stirring, remained at the temperature and reacted for 20 hours. The isocyanate-terminated urethane prepolymer reacted with the 3,3'-diaminodipropylamine to be three-dimensionally polymerized, and polyurethane spheres were formed. The polyurethane spheres were sunk and collected with a centrifugation. The polyurethane spheres were again dispersed in a water and were sunk and collected with a centrifugation. Sixth dispersing and collecting were carried out to remove the polyvinyl alcohol as the dispersant from the water. It is obtained the aqueous polyurethane dispersion comprising the polyurethane spheres of 40% by mass.

[Preparing an aqueous silica dispersion]

[0035] 95 parts by mass of deionized water were charged and stirred at 10000 rpm in a homomixer. 5 parts by mass of hydrophilic fine silica powders having an average particle size of 20 nm which were sold as a trade name of AEROSIL 200 by Nippon Aerosil Co., Ltd. were added in the deionized water and mixed for 10 minutes to obtain the aqueous silica dispersion.

[Preparing a mixed aqueous dispersion]

[0036] 100 parts by mass of the above aqueous polyurethane dispersion, 80 parts by mass of the above aqueous silica dispersion and 110 parts by mass of deionized water were mixed to obtain the mixed aqueous dispersion.

[Producing polyurethane particles]

[0037] Spray-drying the above mixed aqueous dispersion with a spray-dryer which was sold as a trade name of L-8i by Ohkawara Kakohki Co., Ltd., the polyurethane particles were obtained. Each condition of the spray-drying was as the following. A pressure of spraying was 0.3MPa, a temperature of an inlet of a hot air was 140 °C and a temperature into a dryer was 70°C. Vaporizing the water in the mixed aqueous dispersion by the spray-drying, the polyurethane spheres were converted to bodies of the polyurethane particles and the hydrophilic fine silica powders were adhered to each surface of the bodies of the polyurethane particles in implanted. Therefore, each body of the polyurethane particles was covered with the hydrophilic fine silica powders to be the polyurethane particle. The polyurethane particles were not cohered and smooth because of separating from each one. An average particle size of the polyurethane particles is about 12 μm.

Example 2

[Preparing an isocyanate-terminated urethane prepolymer]

[0038] The isocyanate-terminated urethane prepolymer containing 2.5% of isocyanate group was obtained with the same method of the Example 1 except that a poly(tetramethylene ether)glycol having a number average molecular weight of 3000 was used in place of the number average molecular weight of 1000 and 45.0 parts by mass of isophorone diisocyanate were used in place of the 104.6 parts by mass.

[Preparing an oil-in-water emulsion]

[0039] The oil-in-water emulsion was obtained with the same method of the Example 1 except that the above isocyanate-terminated urethane prepolymer was used.

[Preparing an aqueous polyurethane dispersion]

[0040] The aqueous polyurethane dispersion was obtained with the same method of the Example 1 except that the above oil-in-water emulsion was used and 24.5 parts by mass of 10% aqueous solution of 3,3'-diaminodipropylamine were used in place of the 35.7 parts by mass.

[Preparing an aqueous silica dispersion]

[0041] The aqueous silica dispersion was obtained with the same method of the Example 1.

[Preparing a mixed aqueous dispersion]

[0042] The mixed aqueous dispersion was obtained with the same method of the Example 1 except that the above aqueous polyurethane dispersion was used.

[Producing polyurethane particles]

[0043] The polyurethane particles were obtained with the same method of the Example 1 except that the above mixed aqueous dispersion was used.
The properties of the polyurethane particles were the same as them of the Example 1. An average particle size of the polyurethane particles is about 15 μm.

Example 3

[Preparing an isocyanate-terminated urethane prepolymer]

[0044] The isocyanate-terminated urethane prepolymer was obtained with the same method of the Example 1.

[Preparing another isocyanate-terminated urethane prepolymer]

[0045] 20 parts by mass of ethyl acetate and 300 parts by mass of polycarbonatediol having a number average molecular weight of 2000 which was sold as a trade name PCDL T-6002 by Asahi Kasei Chemicals Co. were charged in a four-necked flask fitted with a stirrer, nitrogen inlet, thermometer and condenser. 67.4 parts by mass of isophorone diisocyanate and 0.04 parts by mass of dibutyl tin dilaurate were added and reacted under a nitrogen stream at 75-80 °C for 5 hours to obtain the another isocyanate-terminated urethane prepolymer containing 3.5% of isocyanate group.

[Preparing an oil-in-water emulsion]

[0046] The oil-in-water emulsion was obtained with the same method of the Example 1 except that 100 parts by mass of a mixture which consisted of 52 parts by mass of the isocyanate-terminated urethane prepolymer obtained in the Example 1 and 48 parts by mass of the above another isocyanate-terminated urethane prepolymer were used.

[Preparing an aqueous polyurethane dispersion]

[0047] The aqueous polyurethane dispersion was obtained with the same method of the Example 1 except that the above oil-in-water emulsion was used and 34.6 parts by mass of 10% aqueous solution of 3,3'-diaminodipropylamine were used in place of the 35.7 parts by mass.

[Preparing an aqueous silica dispersion]

[0048] The aqueous silica dispersion was obtained with the same method of the Example 1.

[Preparing a mixed aqueous dispersion]

[0049] The mixed aqueous dispersion was obtained with the same method of the Example 1 except that the above aqueous polyurethane dispersion was used.

[Producing polyurethane particles]

[0050] The polyurethane particles were obtained with the same method of the Example 1 except that the above mixed aqueous dispersion was used.
The properties of the polyurethane particles were the same as them of the Example 1. An average particle size of the polyurethane particles is about 14 μm.

Example 4

[Preparing an isocyanate-terminated urethane prepolymer]

[0051] 20 parts by mass of ethyl acetate, 150 parts by mass of poly(tetramethylene ether)glycol having a number average molecular weight of 1000 and 150 parts by mass of polycarbonatediol having a number average molecular weight of 2000 which was sold as a trade name PCDL T-6002 by Asahi Kasei Chemicals Co. were charged in a four-necked flask fitted with a stirrer, nitrogen inlet, thermometer and condenser. 85.4 parts by mass of isophorone diisocyanate and 0.1 parts by mass of 1,8-diazabicyclo[5.4.0]undec-7-ene were added and reacted under a nitrogen stream at 75-80 °C for 5 hours to obtain the isocyanate-terminated urethane prepolymer containing 3.5% of isocyanate group.

[Preparing an oil-in-water emulsion]

[0052] The oil-in-water emulsion was obtained with the same method of the Example 1 except that the above isocyanate-terminated urethane prepolymer was used.

[Preparing an aqueous polyurethane dispersion]

[0053] The aqueous polyurethane dispersion was obtained with the same method of the Example 1 except that the above oil-in-water emulsion was used and 34.7 parts by mass of 10% aqueous solution of 3,3'-diaminodipropylamine were used in place of the 35.7 parts by mass.

[Preparing an aqueous silica dispersion]

[0054] The aqueous silica dispersion was obtained with the same method of the Example 1.

[Preparing a mixed aqueous dispersion]

[0055] The mixed aqueous dispersion was obtained with the same method of the Example 1 except that the above aqueous polyurethane dispersion was used.

[Producing polyurethane particles]

[0056] The polyurethane particles were obtained with the same method of the Example 1 except that the above mixed aqueous dispersion was used.
The properties of the polyurethane particles were the same as them of the Example 1. An average particle size of the

polyurethane particles is about 13 μm.

Comparative Example 1

[Preparing another isocyanate-terminated urethane prepolymer]

[0057] Another isocyanate-terminated urethane prepolymer was obtained with the same method of the Example 3.

[Preparing an oil-in-water emulsion]

[0058] The oil-in-water emulsion was obtained with the same method of the Example 1 except that the above another isocyanate-terminated urethane prepolymer was used.

[Preparing an aqueous polyurethane dispersion]

[0059] The aqueous polyurethane dispersion was obtained with the same method of the Example 1 except that the above oil-in-water emulsion was used and 34.6 parts by mass of 10% aqueous solution of 3,3'-diaminodipropylamine were used in place of the 35.7 parts by mass.

[Preparing an aqueous silica dispersion]

[0060] The aqueous silica dispersion was obtained with the same method of the Example 1.

[Preparing a mixed aqueous dispersion]

[0061] The mixed aqueous dispersion was obtained with the same method of the Example 1 except that the above aqueous polyurethane dispersion was used.

[Producing polyurethane particles]

[0062] The polyurethane particles were obtained with the same method of the Example 1 except that the above mixed aqueous dispersion was used.
The properties of the polyurethane particles were the same as them of the Example 1. An average particle size of the polyurethane particles is about 16 μm.

[0063] Oil adsorption capacity was measured with an artificial sebum, oleic acid and squalane concerning the polyurethane particles obtained by the methods of Example 1-4 and Comparative Example 1. The oil adsorption capacity was measured by the following method. 0.2 grams of the polyurethane particles were dipped in 10 ml of the artificial sebum and left for 3 days under a room temperature. After the polyurethane particles sufficiently absorbed the artificial sebum, an excess quantity of the artificial sebum was removed with a vacuum filtration method for 10 minutes by using a membrane filter. After removing, the weight of the polyurethane particles absorbing the artificial sebum was measured. The increase of the polyurethane particles was the oil absorption capacity. The oil adsorption capacity was calculated with a unit of g/100g. Furthermore, the artificial sebum consisted of 29 parts by mass of trioleic acid, 28.5 parts by mass of oleic acid, 18.5 parts by mass of oleyl oleate, 14 parts by mass of squalane, 7 parts by mass of cholesterol and 3 parts by mass of myristyl myristate. Each adsorption capacity of the oleic acid and squalane was measured with the above method. The results were showed in the table 1.

[0064]

[Table 1]

	Example				Compar. Example
	1	2	3	4	1
artificial sebum	218	293	119	129	25
oleic acid	342	439	202	224	54
squalane	20	11	22	21	24

[0065] The polyurethane particles obtained by the methods of Example 1-4 selectively absorbed the artificial sebum

and oleic acid more than the polyurethane particles obtained by the method of the Comparative Example 1 as shown in the table 1. This reason may be the followings.
The polyurethane particles were produced by using the isocyanate-terminated urethane prepolymers which were obtained by reacting the polyisocyanates and the polyols including the poly(tetramethylene ether)glycol in the Example 1-4. The polyurethane particles were produced by using the isocyanate-terminated urethane prepolymer which was obtained by reacting the polyisocyanate and the polyols except a poly(tetramethylene ether) glycol in the Comparative Example 1.

Claims

1. A polyurethane particle the surface of the body of which is covered with hydrophilic fine silica powders, wherein;
the body of the polyurethane particle is obtained by three-dimensionally polymerizing an isocyanate-terminated urethane prepolymer with trifunctional or more functional amines, and the isocyanate-terminated urethane prepolymer is obtained by reacting polyisocyanates and polyols including a poly(tetramethylene ether)glycol.

2. The polyurethane particle according to the claim 1, wherein;
the surface of the body of the polyurethane particle is covered with hydrophilic fine silica powders which are implanted on the surface of the body.

3. The polyurethane particle according to the claim 1, wherein;
a number average molecular weight of poly(tetramethylene ether) glycol is 650-3000.

4. The polyurethane particle according to the claim 1, wherein;
an isophorone diisocyanate is used as the polyisocyanates and the poly(tetramethylene ether)glycol is used as the polyols.

5. The polyurethane particle according to the claim 1, wherein;
a 3,3'-diaminodipropylamine is used as trifunctional amines.

6. The polyurethane particle according to the claim 1, wherein;
a particle size of the polyurethane particle is 30 or more times larger than a particle size of the hydrophilic fine silica powder.

7. An oil absorbent agent comprising a large number of the polyurethane particles defined in the claim 1.

8. A perfume comprising a large number of the polyurethane particles defined in the claim 1 which hold a perfumed oil therein.

9. Chemicals comprising a large number of the polyurethane particles defined in the claim 1 which hold therein an oil-based chemical component selected from the group consisting of an oil-based agricultural chemical component, an oil-based attractant component and an oil-based repellent component.

10. A method for producing polyurethane particles comprising; preparing hydrophilic fine silica powders,
preparing an isocyanate-terminated urethane prepolymer obtained by reacting polyisocyanates and polyols including a poly(tetramethylene ether)glycol,
preparing polyurethane spheres obtained by three-dimensionally polymerizing the isocyanate-terminated urethane prepolymer with trifunctional or more functional amines,
preparing a mixed aqueous dispersion by dispersing the hydrophilic fine silica powders and the polyurethane spheres in a water, and
spraying the mixed aqueous dispersion in a high temperature atmosphere, thereby
vaporizing the water in the mixed aqueous dispersion, converting the polyurethane spheres to bodies of the polyurethane particles, and covering each surface of the bodies of the polyurethane particles with the hydrophilic fine silica powders.

11. A method for producing polyurethane particles comprising the following processes;
a process to obtain an isocyanate-terminated urethane prepolymer by reacting polyisocyanates and polyols including a poly(tetramethylene ether)glycol,

a process to obtain an oil-in-water emulsion by adding and mixing the isocyanate-terminated urethane prepolymer to an aqueous solution in which a dispersant dissolves,
a process to obtain polyurethane spheres in the oil-in-water emulsion by that the isocyanate-terminated urethane prepolymer in oil droplets is three-dimensionally polymerized by adding the trifunctional or more functional amines in the oil-in-water emulsion,
a process to obtain an aqueous polyurethane dispersion in which the polyurethane spheres disperse by removing the dispersant from the oil-in-water emulsion.
a process to obtain a mixed aqueous dispersion by mixing the aqueous polyurethane dispersion with an aqueous silica dispersion in which hydrophilic fine silica powders disperse into a water, and
a process to spray-dry the mixed aqueous dispersion in a high temperature atmosphere with a spray-dryer, thereby vaporizing the water in the mixed aqueous dispersion, converting the polyurethane spheres to bodies of the polyurethane particles, and covering each surface of the bodies of the polyurethane particles with the hydrophilic fine silica powders.

12. The method for producing polyurethane particles according to the claim 10 or 11, wherein;
each surface of the bodies of the polyurethane particles is covered with the hydrophilic fine silica powders which are implanted on each surface of the bodies.

13. The method for producing polyurethane particles according to the claim 11, wherein;
a polyvinyl alcohol is used as the dispersant.

14. The method for producing polyurethane particles according to the claim 11, wherein;
an average particle size of the hydrophilic fine silica powders is 5-40 nm, and an average particle size of the polyurethane particles is 1-500 μm.

15. An oil absorbent agent comprising the polyurethane particles obtained by the method defined in the claim 10 or 11.

16. Chemicals comprising the polyurethane particles obtained by the method defined in the claim 10 or 11, which hold therein an oil-based chemical component selected from the group consisting of an oil-based agricultural chemical component, an oil-based attractant component and an oil-based repellent component.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/070378

A. CLASSIFICATION OF SUBJECT MATTER
C08J3/12(2006.01)i, *A61K8/87*(2006.01)i, *A61Q13/00*(2006.01)i, *B01J2/00*(2006.01)i, *B01J2/04*(2006.01)i, *B01J20/26*(2006.01)i, *C08G18/10*(2006.01)i, *C08G18/48*(2006.01)i, *C09K3/00*(2006.01)i, *A61L9/01*(2006.01)n
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08J3/00-28, C08G18/00-87

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2010
Kokai Jitsuyo Shinan Koho	1971-2010	Toroku Jitsuyo Shinan Koho	1994-2010

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2006-321830 A (Sanyo Chemical Industries, Ltd.), 30 November 2006 (30.11.2006), entire text (Family: none)	1-16
A	JP 10-67958 A (Dainippon Ink And Chemicals, Inc.), 10 March 1998 (10.03.1998), entire text (Family: none)	1-16

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 26 February, 2010 (26.02.10)	Date of mailing of the international search report 09 March, 2010 (09.03.10)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/070378

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2004-176066 A (Bayer AG.), 24 June 2004 (24.06.2004), entire text & US 2004/0102599 A1 & EP 1422259 A1 & DE 10254600 A & KR 10-2004-0045318 A & CN 1502643 A & HK 1065054 A	1-16
A	JP 6-41419 A (Dainippon Ink And Chemicals, Inc.), 15 February 1994 (15.02.1994), entire text (Family: none)	1-16
P,A	JP 2009-29867 A (Konishi Co., Ltd.), 12 February 2009 (12.02.2009), entire text (Family: none)	1-16

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2006008757 A **[0003]**

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 778 689 A1

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:
17.02.2021 Bulletin 2021/07

(21) Application number: **19781145.8**

(22) Date of filing: **02.04.2019**

(51) Int Cl.:
C08G 18/73 *(2006.01)* ***C08G 18/08*** *(2006.01)*
C08G 18/48 *(2006.01)* ***C08G 18/79*** *(2006.01)*

(86) International application number:
PCT/JP2019/014588

(87) International publication number:
WO 2019/194161 (10.10.2019 Gazette 2019/41)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **05.04.2018 JP 2018073416**

(71) Applicant: **Mitsui Chemicals, Inc.**
Minato-ku
Tokyo 105-7122 (JP)

(72) Inventors:
- **TAGO, Hiroaki**
  Sodegaura-shi, Chiba 299-0265 (JP)
- **KANAYAMA, Hiroshi**
  Sodegaura-shi, Chiba 299-0265 (JP)
- **KAJIURA, Makoto**
  Sodegaura-shi, Chiba 299-0265 (JP)

(74) Representative: **Hoffmann Eitle**
Patent- und Rechtsanwälte PartmbB
Arabellastraße 30
81925 München (DE)

(54) POLYURETHANE GEL MATERIAL, POLYURETHANE GEL, PSEUDO-BIOLOGICAL MATERIAL, AND PRODUCTION METHOD FOR POLYURETHANE GEL

(57) A polyurethane gel material includes an aliphatic polyisocyanate (A) having an average functionality of 2.3 or more and 3.2 or less, a polyol (B) having an average functionality of 2.0 or more and 2.3 or less, and a plasticizer (C) having an ester group. The aliphatic polyisocyanate (A) contains an isocyanurate derivative of an aliphatic diisocyanate and/or an alcoholic modified isocyanurate derivative of an aliphatic diisocyanate. The polyol (B) contains a polyoxypropylene polyol and/or a polytetramethylene ether glycol. The polyol (B) has an average hydroxyl value of 73 mgKOH/g or more and 200 mgKOH/g or less. A ratio of the plasticizer (C) per 100 parts by mass of the polyol component (B) is 100 parts by mass or more and 500 parts by mass or less.

EP 3 778 689 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to a polyurethane gel material, a polyurethane gel, a pseudo-biomaterial, and a method for producing a polyurethane gel.

BACKGROUND ART

[0002] Conventionally, polyurethane gels of low hardness have been used in the fields of vibration-proof and quake-isolation members, shock absorbing members, cushioning members, surface protection members, and the like.

[0003] Specifically, a polyurethane gel has been proposed which includes a gel layer and a coating layer for covering the gel layer, wherein the gel layer is obtained by at least reacting an aliphatic polyisocyanate having an average functionality of above 2.0 with a polyol having an average functionality of 3.0 or less, and the coating layer is obtained by at least reacting an aliphatic diisocyanate and/or an alicyclic diisocyanate with a bifunctional active hydrogen compound (ref: for example, Patent Document 1 below).

Citation List

Patent Document

[0004] Patent Document 1: International Publication WO2017/010422

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0005] On the other hand, bleeding properties may be required in accordance with the application of the polyurethane gel because it imparts a moist feeling to the surface. However, when a plasticizer is simply added and bleeding is generated, there is a problem such as a large change in the dimension of the polyurethane gel.

[0006] In other words, the polyurethane gel is required to have both a moist feeling and excellent dimensional stability in accordance with its application.

[0007] Further, curability, mechanical properties (elongation etc.), appropriate hardness, and the like are required for the polyurethane gel in accordance with the application.

[0008] The present invention provides a polyurethane gel material capable of obtaining a polyurethane gel having both a moist feeling and dimensional stability and excellent in curability, mechanical properties, and hardness; a polyurethane gel obtained from the polyurethane gel material; a pseudo-biomaterial; and a method for producing a polyurethane gel.

MEANS FOR SOLVING THE PROBLEM

[0009] The present invention [1] includes a polyurethane gel material including an aliphatic polyisocyanate (A) having an average functionality of 2.3 or more and 3.2 or less, a polyol (B) having an average functionality of 2.0 or more and 2.3 or less, and a plasticizer (C) having an ester group, wherein the aliphatic polyisocyanate (A) contains an isocyanurate derivative of an aliphatic diisocyanate and/or an alcoholic modified isocyanurate derivative of an aliphatic diisocyanate, the polyol (B) contains a polyoxypropylene polyol and/or a polytetramethylene ether glycol, the polyol (B) has an average hydroxyl value of 73 mgKOH/g or more and 200 mgKOH/g or less, and a ratio of the plasticizer (C) per 100 parts by mass of the polyol component (B) is 100 parts by mass or more and 500 parts by mass or less.

[0010] The present invention [2] includes the polyurethane gel material described in the above-described [1], wherein the polyol (B) has an average functionality of 2.0.

[0011] The present invention [3] includes the polyurethane gel material described in the above-described [1] or [2], wherein the aliphatic polyisocyanate (A) has an average functionality of 2.3 or more and 3.0 or less.

[0012] The present invention [4] includes the polyurethane gel material described in any one of the above-described [1] to [3], wherein the aliphatic diisocyanate includes a pentamethylene diisocyanate and/or a hexamethylene diisocyanate.

[0013] The present invention [5] includes the polyurethane gel material described in any one of the above-described [1] to [4], wherein the plasticizer (C) is cyclohexanedicarboxylic acid esters and/or adipic acid esters.

[0014] The present invention [6] includes a polyurethane gel being a reaction product of the polyurethane gel material

described in any one of the above-described [1] to [5].

[0015] The present invention [7] includes the polyurethane gel described in the above-described [6], wherein in the polyurethane gel material, an equivalent ratio (NCO/ hydroxyl group) of an isocyanate group in an aliphatic polyisocyanate (A) to a hydroxyl group in a polyol (B) is 0.8 or more and 1.2 or less.

[0016] The present invention [8] includes the polyurethane gel described in the above-described [6] or [7], wherein a rate of weight change obtained by the following formula is 0.1% or more and 7% or less before and after a durability test under the following conditions.

- Durability test: left to stand at 80°C for five days, and then, further left to stand at 23°C with relative humidity of 55% for one day
- Rate of weight change [(weight W1 before durability test - weight W2 after durability test)/ (weight W1 before durability test)] × 100

[0017] The present invention [9] includes a pseudo-biomaterial including the polyurethane gel described in any one of the above-described [6] to [8].

[0018] The present invention [10] includes a method for producing a polyurethane gel including a preparation step of preparing the polyurethane gel material described in any one of above-described [1] to [5] and a reaction step of reacting and curing the polyurethane gel material to obtain a polyurethane gel, wherein in the reaction step, an equivalent ratio (NCO/ hydroxyl group) of an isocyanate group in an aliphatic polyisocyanate (A) to a hydroxyl group in a polyol (B) is 0.8 or more and 1.2 or less.

EFFECT OF THE INVENTION

[0019] According to the polyurethane gel material of the present invention, it is possible to obtain a polyurethane gel which has both a moist feeling and dimensional stability and is excellent in curability, mechanical properties, and hardness.

[0020] Further, the polyurethane gel of the present invention has both a moist feeling and dimensional stability, and is excellent in curability, mechanical properties, and hardness.

[0021] Further, according to the method for producing a polyurethane gel of the present invention, it is possible to obtain a polyurethane gel which has both a moist feeling and dimensional stability and is excellent in curability, mechanical properties, and hardness.

DESCRIPTION OF EMBODIMENTS

[0022] A polyurethane gel material of the present invention is a material which gels by a urethanization reaction to be described later and forms a polyurethane gel (described later). In other words, the polyurethane gel material is a raw material composition of a polyurethane gel (described later).

[0023] The polyurethane gel material contains an aliphatic polyisocyanate (A) having an average functionality of 2.3 or more and 3.2 or less, a polyol (B) having an average functionality of 2.0 or more and 2.3 or less, and a plasticizer (C) having an ester group. Preferably, the polyurethane gel material contains only an aliphatic polyisocyanate (A) having an average functionality of 2.3 or more and 3.2 or less, a polyol (B) having an average functionality of 2.0 or more and 2.3 or less, and a plasticizer (C) having an ester group.

[0024] A functional group of the aliphatic polyisocyanate (A) indicates an isocyanate group. The functional group of the polyol (B) indicates a hydroxyl group.

[0025] The aliphatic polyisocyanate (A) contains an isocyanurate derivative and/or an alcoholic modified isocyanurate derivative of an aliphatic diisocyanate, preferably, contains an alcoholic modified isocyanurate derivative.

[0026] Since the aliphatic polyisocyanate (A) has both an aliphatic hydrocarbon group and an isocyanurate group, it imparts appropriate flexibility to the polyurethane gel by the aliphatic hydrocarbon group, also imparts appropriate rigidity and polarity by the isocyanurate group, and can impart affinity to the plasticizer (C), and further, the average functionality can be adjusted within a range to be described later.

[0027] Examples of the aliphatic diisocyanate include trimethylene diisocyanate, 1,2-propylene diisocyanate, butylene diisocyanate (tetramethylene diisocyanate, 1,2-butylene diisocyanate, 2,3-butylene diisocyanate, 1,3-butylene diisocyanate), pentamethylene diisocyanate (PDI), hexamethylene diisocyanate (HDI), 2,4,4- or 2,2,4-trimethylhexamethylene diisocyanate, and 2,6-diisocyanatemethylcaproate.

[0028] These aliphatic diisocyanates may be used alone or in combination of two or more.

[0029] As the aliphatic diisocyanate, from the viewpoint of improvement of mechanical properties, preferably, a pentamethylene diisocyanate (PDI) and a hexamethylene diisocyanate (HDI) are used, and further, from the viewpoint of improvement of mechanical properties and hardness, more preferably, a pentamethylene diisocyanate (PDI) is used.

[0030] In other words, when the pentamethylene diisocyanate (PDI) is used as the aliphatic diisocyanate, the poly-

urethane gel excellent in mechanical properties and hardness can be obtained.

[0031] Then, the isocyanurate derivative of the aliphatic diisocyanate can be obtained by isocyanurating the above-described aliphatic diisocyanate by a known method.

[0032] More specifically, the isocyanurate derivative of the aliphatic diisocyanate can be obtained, for example, by reacting the aliphatic diisocyanate in the presence of a known isocyanuration catalyst (e.g., N-(2-hydroxypropyl)-N,N,N-trimethylammonium-2-ethylhexanoate etc.) and subjecting it to an isocyanuration reaction.

[0033] The reaction conditions in the isocyanuration reaction are not particularly limited and are appropriately set.

[0034] The alcoholic modified isocyanurate derivative of the aliphatic diisocyanate can be obtained by modifying the isocyanurate derivative of the aliphatic diisocyanate with alcohols.

[0035] The alcohols are not particularly limited, and examples thereof include aliphatic alcohols and aromatic alcohols. Preferably, aliphatic alcohols are used. Specific examples thereof include monohydric aliphatic alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol (isobutyl alcohol), sec-butanol, tert-butanol, pentanol, hexanol, 2-ethylhexanol, octanol, and decanol; dihydric aliphatic alcohols such as ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butylene glycol 1,4-butylene glycol, 1,5-pentanediol, and 1,6-hexanediol; trihydric aliphatic alcohols such as glycerine and trimethylolpropane; and tetrahydric or more aliphatic alcohols such as tetramethylolmethane.

[0036] These alcohols may be used alone or in combination of two or more. As the alcohols, preferably, a monohydric aliphatic alcohol is used, more preferably, a monohydric aliphatic alcohol having carbon number of 1 to 4 is used, further more preferably, isobutanol (another name: isobutyl alcohol) is used.

[0037] As a method for modifying the isocyanurate derivative of the aliphatic diisocyanate with the alcohols, for example, a method for first reacting the aliphatic diisocyanate with the alcohols and then, subjecting the obtained reaction product to an isocyanuration reaction in the presence of an isocyanuration catalyst, and a method for first isocyanurating only the aliphatic diisocyanate and then, reacting the obtained polyisocyanurate with the alcohols are used.

[0038] Preferably, first, an aliphatic diisocyanate and alcohols are reacted, and then, an isocyanuration reaction is carried out in the presence of an isocyanuration catalyst.

[0039] In such a reaction, a mixing ratio of the aliphatic diisocyanate to the alcohols is appropriately set in accordance with the purpose and the application, and the mixing ratio of the alcohols per 100 parts by mass of the aliphatic diisocyanate is, for example, 0.1 parts by mass or more, preferably 0.5 parts by mass or more, more preferably 1.0 part by mass or more, and for example, 10 parts by mass or less, preferably 5 parts by mass or less, more preferably 2 parts by mass or less, further more preferably 1.5 parts by mass or less.

[0040] Further, the reaction conditions of the aliphatic diisocyanate and the alcohols are appropriately set in accordance with the purpose and the application.

[0041] The reaction of the aliphatic diisocyanate with the alcohols is a urethanization reaction and an allophanatization reaction, and an allophanate derivative of the aliphatic diisocyanate may be generated as a by-product. In other words, the isocyanurate derivative of the aliphatic diisocyanate modified by the alcohols may have both an isocyanurate group and an allophanate group.

[0042] In such a case, a mole ratio of the allophanate group in the alcoholic modified isocyanurate derivative of the aliphatic diisocyanate is less than that of the isocyanurate group, and specifically, the mole ratio of the allophanate group per 1 mol of the isocyanurate group is, for example, 0.05 mol or more, preferably 0.1 mol or more, more preferably 0.2 mol or more, and for example, below 1.0 mol, preferably 0.5 mol or less.

[0043] When the mole ratio of the allophanate group is within the above-described range, improvement in mechanical properties and heat resistance can be achieved.

[0044] The mole ratio of the allophanate group to the isocyanurate group can be determined in conformity with Examples to be described later.

[0045] In addition, in the above-described reaction, if necessary, for example, a known additive such as a storage stabilizer (o-toluenesulfonamide, p-toluenesulfonamide, etc.), a reaction terminator (benzoyl chloride etc.), an anti-blocking agent, a heat-resistant stabilizer, a light-resistant stabilizer, an ultraviolet absorber, an antioxidant, a defoaming agent, a mold release agent, a pigment, a dye, a lubricant, a filler, and a hydrolysis inhibitor can be further blended at an appropriate ratio.

[0046] Further, after completion of the above-described reaction, if necessary, the unreacted aliphatic diisocyanate can be also, for example, removed by a known method such as distillation including thin film distillation (Smith distillation) or extraction.

[0047] A content ratio of the unreacted aliphatic diisocyanate (isocyanate monomer concentration) with respect to the total amount of the reaction liquid obtained in the above-described reaction is, for example, 1% by mass or less, preferably 0.5% by mass or less.

[0048] Further, the aliphatic polyisocyanate (A) may further contain another derivative as long as it contains the isocyanurate derivative and/or the alcoholic modified isocyanurate derivative of the aliphatic diisocyanate.

[0049] The other derivative is s derivative of the aliphatic diisocyanate excluding the isocyanurate derivative and the alcoholic modified isocyanurate derivative of the aliphatic diisocyanate. Examples thereof include an allophanate deriv-

ative of an aliphatic diisocyanate, a uretdione derivative of an aliphatic diisocyanate, a urea derivative of an aliphatic diisocyanate, a carbodiimide derivative of an aliphatic diisocyanate, a biuret derivative of an aliphatic diisocyanate, an oxadiazine trione derivative of an aliphatic diisocyanate, a uretonimine derivative of an aliphatic diisocyanate, and a polyol modified product of an aliphatic diisocyanate.

[0050] These other derivatives may be used alone or in combination of two or more.

[0051] As the other derivative, preferably, an allophanate derivative of an aliphatic diisocyanate is used.

[0052] The allophanate derivative of the aliphatic diisocyanate can be obtained by subjecting the above-described aliphatic diisocyanate and the above-described alcohols (preferably, the monohydric aliphatic alcohol) to a urethanization reaction, and then, subj ecting the reacted product to an allophanatization reaction in the presence of a known allophanatization catalyst (e.g., bismuth octylate, tris(2-ethylhexanoic acid) bismuth, etc.). The reaction conditions in the urethanization reaction and the allophanatization reaction are not particularly limited and are appropriately set.

[0053] A content ratio of the other derivative (preferably, an allophanate derivative) is appropriately set in accordance with the purpose and the application as long as it does not damage the excellent effect of the present invention. The content ratio of the other derivative per 100 parts by mass of the total amount of the aliphatic polyisocyanate (A) is, for example, 0 part by mass or more, and for example, 50 parts by mass or less, preferably 40 parts by mass or less, more preferably 20 parts by mass or less.

[0054] Further, the aliphatic polyisocyanate (A) may contain an aliphatic polyisocyanate monomer, if necessary.

[0055] An example of the aliphatic polyisocyanate monomer includes the above-described aliphatic diisocyanate (bifunctional aliphatic polyisocyanate monomer).

[0056] These aliphatic polyisocyanate monomers may be used alone or in combination of two or more.

[0057] A content ratio of the aliphatic polyisocyanate monomer is appropriately set in accordance with the purpose and the application as long as it does not damage the excellent effect of the present invention. The content ratio of the aliphatic polyisocyanate monomer per 100 parts by mass of the total amount of the aliphatic polyisocyanate (A) is, for example, 0 part by mass or more, and for example, 50 parts by mass or less, preferably 40 parts by mass or less, more preferably 20 parts by mass or less.

[0058] Then, in the aliphatic polyisocyanate (A), a ratio of the isocyanurate derivative and/or the alcoholic modified isocyanurate derivative of the aliphatic diisocyanate, the other derivative, and the aliphatic polyisocyanate monomer is appropriately adjusted so that the average functionality of the aliphatic polyisocyanate (A) is within a range of 2.3 to 3.2 as long as it does not damage the excellent effect of the present invention.

[0059] More specifically, the ratio of the isocyanurate derivative and/or the alcoholic modified isocyanurate derivative of the aliphatic diisocyanate per 100 parts by mass of the total amount of the aliphatic polyisocyanate (A) is, for example, 50 parts by mass or more, preferably 60 parts by mass or more, more preferably 80 parts by mass or more, and for example, 100 parts by mass or less. The ratio of the other derivative and/or the aliphatic polyisocyanate monomer per 100 parts by mass of the total amount of the aliphatic polyisocyanate (A) is, for example, 0 part by mass or more, and for example, 50 parts by mass or less, preferably 40 parts by mass or less, more preferably 20 parts by mass or less.

[0060] In addition, from the viewpoint of mechanical properties, preferably, the aliphatic polyisocyanate (A) consists of an isocyanurate derivative and/or an alcoholic modified isocyanurate derivative of an aliphatic diisocyanate, more preferably, an alcoholic modified isocyanurate derivative of an aliphatic diisocyanate, further more preferably, an alcoholic modified isocyanurate derivative of a pentamethylene diisocyanate (the inclusion of an allophanate derivative (allophanate derivative without containing an isocyanurate group) and a uretdione derivative by-produced at the time of producing an isocyanurate derivative is allowed).

[0061] From the viewpoint of curability and mechanical properties, an average functionality of the aliphatic polyisocyanate (A) is 2.3 or more, preferably 2.5 or more, more preferably 2.6 or more, further more preferably 2.7 or more, and 3.2 or less, preferably 3.1 or less, more preferably 3.0 or less, further more preferably 2.9 or less.

[0062] That average functionality of the aliphatic polyisocyanate (A) is calculated in conformity with Examples to be described later.

[0063] Further, the isocyanate group concentration of the aliphatic polyisocyanate (A) is, for example, 20.0% by mass or more, preferably 22.0% by mass or more, and for example, 30.0% by mass or less, preferably 25.0% by mass or less, more preferably 24.6% by mass or less.

[0064] The polyol (B) contains a polyoxypropylene polyol and/or a polytetramethylene ether glycol. When the polyol (B) contains these, a flexible polyurethane gel can be obtained.

[0065] The polyoxypropylene polyol is, for example, an addition polymer of a propylene oxide using a low molecular weight polyol, a known low molecular weight polyamine, or the like as an initiator.

[0066] A low molecular weight polyol is, for example, a compound having 2 or more hydroxyl groups in a molecule and having a molecular weight of 50 or more and 400 or less. Examples thereof include dihydric alcohols such as ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butylene glycol, 1,3-butylene glycol, 1,2-butylene glycol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 3-methyl-1,5-pentanediol, 2,2,2-trimethylpentanediol, 3,3-dimethylolheptane, alkane (C7-20) diol, 1,3- or 1,4-cyclohexanedimethanol and mixtures thereof, 1,3- or 1,4-cyclohexanediol and

mixtures thereof, hydrogenated bisphenol A, 1,4-dihydroxy-2-butene, 2,6-dimethyl-1-octen-3,8-diol, bisphenol A, diethylene glycol, triethylene glycol, and dipropylene glycol; trihydric alcohols such as glycerine, trimethylolpropane, and triisopropanolamine; and tetrahydric alcohols such as tetramethylolmethane (pentaerythritol) and diglycerine. These low molecular weight polyols may be used alone or in combination of two or more. As the low molecular weight polyol, preferably, a dihydric alcohol and a trihydric alcohol are used, more preferably, a dihydric alcohol is used.

[0067] The polyoxypropylene polyol is obtained as a polyoxypropylene polyol having an average functionality in accordance with a functionality of the initiator. For example, when an initiator having a functionality of 2 is used, a polyoxypropylene glycol having an average functionality of 2 is obtained, and when an initiator having a functionality of 3 is used, a polyoxypropylene triol having an average functionality of 3 is obtained.

[0068] These polyoxypropylene polyols may be used alone or in combination of two or more.

[0069] The polyoxypropylene polyol substantially does not contain a polyoxyethylene unit. "Substantially" means that it does not contain a polyoxyethylene unit, except for a polyoxyethylene unit which is unavoidably incorporated. More specifically, the content of the polyoxyethylene unit is below 1% by mass with respect to the total amount of the polyoxypropylene polyol.

[0070] Examples of the polytetramethylene ether glycol include a ring opening polymer (crystalline polytetramethylene ether glycol) obtained by cationic polymerization of a tetrahydrofuran, and an amorphous polytetramethylene ether glycol obtained by copolymerizing the above-described dihydric alcohol with a polymerization unit such as tetrahydrofuran. The crystallinity indicates solid at normal temperature (25°C), and the amorphousness indicates liquid at normal temperature (25°C).

[0071] The amorphous polytetramethylene ether glycol can be obtained, for example, as a copolymer (tetrahydrofuran/ alkyl substituted tetrahydrofuran (mole ratio) = 15/85 to 85/ 15) of a tetrahydrofuran and an alkyl substituted tetrahydrofuran (e.g., 3-methyltetrahydrofuran etc.) and a copolymer (tetrahydrofuran/ branched glycol (mole ratio) = 15/ 85 to 85/ 15) of a tetrahydrofuran and a branched glycol (e.g., neopentyl glycol etc.).

[0072] Further, as the amorphous polytetramethylene ether glycol, a commercially available product can be used, and examples of such a commercially available product include the "PTXG" series manufactured by ASAHI KASEI FIBERS CORPORATION and the "PTG-L" series manufactured by Hodogaya Chemical Co., Ltd.

[0073] Also, a plant-derived polytetramethylene ether glycol using a tetrahydrofuran produced based on a plant-derived raw material such as furfural as a starting material can be used.

[0074] As the polyol (B), from the viewpoint of a moist feeling, dimensional stability, mechanical properties, and hardness, preferably, a polyoxypropylene glycol is used.

[0075] The polyol (B) may contain another polyol as long as it contains the above-described polyoxypropylene glycol and/or the above-described polytetramethylene ether glycol.

[0076] Examples of the other polyol include the above-described low molecular weight polyol and a known high molecular weight polyol (excluding a polyoxypropylene glycol, and a polytetramethylene ether glycol). The high molecular weight polyol is a compound having a molecular weight (number average molecular weight in terms of polystyrene with GPC measurement) of above 400 and having two or more hydroxyl groups. Examples thereof include polyester polyol, polycarbonate polyol, polyurethane polyol, epoxy polyol, vegetable oil polyol, polyolefin polyol, acrylic polyol, and vinyl monomer-modified polyol.

[0077] These other polyols may be used alone or in combination of two or more.

[0078] In the polyol (B), a content ratio of the other polyol is appropriately adjusted as long as it does not damage the excellent effect of the present invention.

[0079] From the viewpoint of a moist feeling, dimensional stability, mechanical properties, and hardness, the polyol (B) preferably does not contain the other polyol and consists of a polyoxypropylene glycol and/or a polytetramethylene ether glycol, more preferably, consists of a polyoxypropylene glycol.

[0080] In addition, these polyols (B) are used alone or in combination of two or more so that its average functionality and an average hydroxyl value (OH value) are within a range to be described later.

[0081] Specifically, from the viewpoint of curability, the average functionality of the polyol (B) is 2.0 or more, and from the viewpoint of mechanical properties, the average functionality of the polyol (B) is 2.3 or less, preferably 2.2 or less, more preferably 2.1 or less. From the viewpoint of a moist feeling and dimensional stability, particularly preferably, the average functionality of the polyol (B) is 2.0.

[0082] In addition, from the viewpoint of a moist feeling and dimensional stability, the average hydroxyl value (OH value) of the polyol (B) is 73 mgKOH/g or more, preferably 84 mgKOH/g or more, more preferably 90 mgKOH/g or more, further more preferably 100 mgKOH/g or more, and 200 mgKOH/g or less, preferably 160 mgKOH/g or less, more preferably 150 mgKOH/g or less, further more preferably 130 mgKOH/g or less.

[0083] The average functionality of the polyol (B) is calculated from the mixing formulation of the charging, and the hydroxyl value of the polyol is measured in conformity with the description of JIS K 1557-1 (2007).

[0084] In addition, from the viewpoint of curability, mechanical properties, a moist feeling, and dimensional stability, the number average molecular weight (the number average molecular weight calculated from the average functionality

and the hydroxyl value) of the polyol (B) is, for example, 560 or more, preferably 600 or more, more preferably 800 or more, and for example, 1770 or less, preferably 1500 or less, more preferably 1300 or less, further more preferably 1200 or less.

[0085] When the hydroxyl value and the number average molecular weight are within the above-described range, appropriate hydrophobicity can be imparted to the obtained polyurethane gel, and appropriate affinity with the plasticizer (C) can be obtained.

[0086] In the polyurethane gel material, a content ratio of the aliphatic polyisocyanate (A) and the polyol (B) is adjusted so that an equivalent ratio (NCO/ hydroxyl group) of the isocyanate group in the aliphatic polyisocyanate (A) to the hydroxyl group in the polyol (B) is 0.8 to 1.2.

[0087] The plasticizer (C) has an ester group. By using the plasticizer (C) having an ester group, it is possible to improve the curability as compared with a case where a plasticizer without having an ester group (e.g., chloroparaffin etc.) is used.

[0088] Further, when the plasticizer (C) has an ester group, the affinity for a urethane group obtained by a reaction of the aliphatic polyisocyanate (A) with the polyol (B) can be obtained.

[0089] More specifically, examples of the plasticizer (C) having an ester group include cyclohexanedicarboxylic acid esters, phthalic acid esters, isophthalic acid esters, tetrahydrophthalic acid esters, adipic acid esters, azelaic acid esters, sebacic acid esters, fumaric acid esters, maleic acid esters, trimellitic acid esters, pyromellitic acid esters, citric acid esters, itaconic acid esters, oleic acid esters, ricinoleic acid esters, stearic acid esters, other fatty acid esters, and phosphoric acid esters.

[0090] Examples of the cyclohexanedicarboxylic acid esters include dimethylcyclohexane-1,2-dicarboxylate, diethylcyclohexane-1,2-dicarboxylate, dibutylcyclohexane-1,2-dicarboxylate, di(2-ethylhexyl)cyclohexane-1,2-dicarboxylate, dioctylcyclohexane-1,2-dicarboxylate, diisodecylcyclohexane-1,2-dicarboxylate, diisononylcyclohexane-1,2-dicarboxylate, dimethylcyclohexane-1,3-dicarboxylate, diethylcyclohexane-1,3-dicarboxylate, dibutylcyclohexane-1,3 -dicarboxylate, di(3-ethylhexyl)cyclohexane-1,3-dicarboxylate, dioctylcyclohexane-1,3-dicarboxylate, diisodecylcyclohexane-1,3-dicarboxylate, diisononylcyclohexane-1,3-dicarboxylate, dimethylcyclohexane-1,4-dicarboxylate, diethylcyclohexane-1,4-dicarboxylate, dibutylcyclohexane-1,4-dicarboxylate, di(4-ethylhexyl)cyclohexane-1,4-dicarboxylate, dioctylcyclohexane-1,4-dicarboxylate, diisodecylcyclohexane-1,4-dicarboxylate, diisononylcyclohexane-1,4-dicarboxylate, 3,4-epoxy-dimethylcyclohexane-1,2-dicarboxylate, 3,4-epoxy-diethylcyclohexane-1,2-dicarboxylate, 3,4-epoxy-dibutylcyclohexane-1,2-dicarboxylate, 3,4-epoxy-di(2-ethylhexyl)cyclohexane-1,2-dicarboxylate, 4,5-epoxy-dimethylcyclohexane-1,2-dicarboxylate, 4,5-epoxy-diethylcyclohexane-1,2-dicarboxylate, 4,5-epoxy-dibutylcyclohexane-1,2-dicarboxylate, and 4,5-epoxy-di(2-ethylhexyl)cyclohexane-1,2-dicarboxylate.

[0091] Examples of the phthalic acid esters include dibutyl phthalate, isobutyl phthalate, diheptyl phthalate, di-(2-ethylhexyl) phthalate, di-n-octyl phthalate, dinonyl phthalate, diisononyl phthalate, diisodecyl phthalate, diundecyl phthalate, ditridecyl phthalate, dicyclohexyl phthalate, and diphenyl phthalate.

[0092] Examples of the isophthalic acid esters include di-(2-ethylhexyl) isophthalate and diisooctyl isophthalate.

[0093] Examples of the tetrahydrophthalic acid esters include di-(2-ethylhexyl) tetrahydrophthalate.

[0094] Examples of the adipic acid esters include di-(2-ethylhexyl) adipate, dibutoxyethyl adipate, and diisononyl adipate.

[0095] Examples of the azelaic acid esters include di-n-hexylazelate and di-(2-ethylhexyl) azelate.

[0096] Examples of the sebacic acid esters include di-n-butylsebacate.

[0097] Examples of the fumaric acid esters include di-n-butylfumarate and di-(2-ethylhexyl) fumarate.

[0098] Examples of the maleic acid esters include di-n-butylmaleate and di-(2-ethylhexyl) maleate.

[0099] Examples of the trimellitic acid esters include tri-(2-ethylhexyl) trimellitate, tri-n-octyltrimellitate, and triisooctyltrimellitate.

[0100] Examples of the pyromellitic acid esters include tetra-(2-ethylhexyl) pyromellitate and tetra-n-octylpyromellitate.

[0101] Examples of the citric acid esters include tri-n-butylcitrate and acetyltributylcitrate.

[0102] Examples of the itaconic acid esters include dimethyl itaconate, diethyl itaconate, dibutyl itaconate, and di-(2-ethylhexyl) itaconate.

[0103] Examples of the oleic acid esters include glyceryl monoolate and diethylene glycol monooleate.

[0104] Examples of the ricinoleic acid esters include glyceryl monoricinoleate and diethylene glycol monoricinoleate.

[0105] Examples of the stearic acid esters include glycerine monostearate and diethylene glycol distearate.

[0106] Examples of the other fatty acid esters include diethylene glycol dipelargonate and pentaerythritol fatty acid ester.

[0107] Examples of the phosphoric acid esters include tributoxyethyl phosphate, triphenyl phosphate, tricresyl phosphate, diphenyl decyl phosphate, and diphenyl octyl phosphate.

[0108] These plasticizers (C) having an ester group may be used alone or in combination of two or more.

[0109] As the plasticizer (C) having an ester group, from the viewpoint of curability, preferably, cyclohexanedicarboxylic acid esters, phthalic acid esters, and adipic acid esters are used, more preferably, cyclohexanedicarboxylic acid esters, adipic acid esters, and combinations of these are used, further more preferably, cyclohexanedicarboxylic acid esters

are used.

[0110] A boiling point of the plasticizer (C) is, for example, 180°C or more, preferably 200°C or more, more preferably 220°C or more. The upper limit of the boiling point is about 400°C from the viewpoint of industrial availability.

[0111] In the polyurethane gel material, from the viewpoint of a moist feeling, dimensional stability, and hardness, a content ratio of the plasticizer (C) having an ester group per 100 parts by mass of the polyol component (B) is 100 parts by mass or more, preferably 150 parts by mass or more, more preferably 200 parts by mass or more, further more preferably 250 parts by mass or more, and 500 parts by mass or less, preferably 450 parts by mass or less, more preferably 400 parts by mass or less, further more preferably 350 parts by mass or less.

[0112] According to such a polyurethane gel material, it is possible to obtain the polyurethane gel which has both a moist feeling and dimensional stability and is excellent in curability, mechanical properties, and hardness.

[0113] Then, in order to obtain the polyurethane gel, first, the above-described polyurethane gel material is prepared (preparation step), then, the aliphatic polyisocyanate (A) and the polyol (B) are put into a predetermined metal mold together with the plasticizer (C) having an ester group, and preferably, the obtained mixture is subjected to a urethanization reaction (solvent-free reaction, bulk polymerization) in the absence of a solvent (reaction step).

[0114] In the urethanization reaction, for example, a known method such as a one-shot method and a prepolymer method is used, preferably, a one-shot method is used.

[0115] In the one-shot method, for example, the aliphatic polyisocyanate (A) and the polyol (B) are formulated (mixed) so that an equivalent ratio (NCO/ hydroxyl group) of the isocyanate group in the aliphatic polyisocyanate (A) to the hydroxyl group in the polyol (B) is 0.8 or more, preferably 0.9 or more, and 1.2 or less, preferably 1.1 or less, more preferably 1.05 or less, and then, the obtained mixture is subjected to a curing reaction at, for example, room temperature to 120°C, preferably at room temperature to 100°C, for, for example, from 5 minutes to 72 hours, preferably from 2 to 10 hours. The curing temperature may be a constant temperature, or may be raised or cooled in stages.

[0116] When the equivalent ratio (NCO/ hydroxyl group) of the isocyanate group in the aliphatic polyisocyanate (A) to the hydroxyl group in the polyol (B) is within the above-described range, both the flexibility and the shape-retaining properties (rigidity) of the polyurethane gel containing the plasticizer (C) can be achieved.

[0117] In addition, in the above-described reaction, if necessary, a known urethanization catalyst such as amines and an organic metal compound can be, for example, added.

[0118] Examples of the amines include tertiary amines such as triethylamine, triethylenediamine, bis-(2-dimethylaminoethyl) ether, and N-methylmorpholine; quaternary ammonium salts such as tetraethylhydroxylammonium; and imidazoles such as imidazole and 2-ethyl-4-methylimidazole.

[0119] Examples of the organic metal compound include organic tin compounds such as tin acetate, tin octylate, tin oleate, tin laurate, dibutyltin diacetate, dimethyltin dilaurate, dibutyltin dilaurate, dibutyltin dimercaptide, dibutyltin maleate, dibutyltin dilaurate (dibutyltin dilaurate (IV)), dibutyltin dineodecanoate, dioctyltin dimercaptide, dioctyltin dilaurate, and dibutyltin dichloride; organic lead compounds such as lead octanoate and lead naphthenate; organic nickel compounds such as nickel naphthenate; organic cobalt compounds such as cobalt naphthenate; organic copper compounds such as copper octenate; and organic bismuth compounds such as bismuth octylate and bismuth neodecanoate.

[0120] Further, examples of the urethanization catalyst include potassium salts such as potassium carbonate, potassium acetate, and potassium octylate.

[0121] These urethanization catalysts may be used alone or in combination of two or more.

[0122] As the urethanization catalyst, preferably, an organic metal compound is used, more preferably, an organic tin compound is used, further more preferably, dibutyltin dilaurate (dibutyltin dilaurate (IV)) is used.

[0123] The timing of addition of the urethanization catalyst is not particularly limited, and may be, for example, added in advance to both or either of the aliphatic polyisocyanate (A) and the polyol (B), may be added simultaneously with the formulation thereof, and further, may be added separately after blending them.

[0124] Further, an addition ratio of the urethanization catalyst is not particularly limited, and is appropriately set in accordance with the purpose and the application.

[0125] In addition, in the above-described reaction, if necessary, a known additive such as a storage stabilizer (o-toluenesulfonamide, p-toluenesulfonamide, etc.), an anti-blocking agent, a heat-resistant stabilizer, a light-resistant stabilizer, an ultraviolet absorber, an antioxidant, a defoaming agent, a mold release agent, a pigment, a dye, a lubricant, a filler, and a hydrolysis inhibitor can be, for example, further blended at an appropriate ratio.

[0126] The timing of addition of the additive is not particularly limited, and may be, for example, added in advance to both or either of the aliphatic polyisocyanate (A) and the polyol (B), may be added simultaneously with the formulation thereof, and further, may be added separately after blending them. Further, an addition ratio of the additive is not particularly limited, and is appropriately set in accordance with the purpose and the application.

[0127] Such a polyurethane gel contains a polyurethane which is a reaction product of the aliphatic polyisocyanate (A) and the polyol (B), and the plasticizer (C), has high viscosity due to the higher order structure (three dimensional network) of the polyurethane, loses fluidity due to the inclusion of the plasticizer (C) in the polyurethane, and becomes a solid state as a whole of the system.

[0128] A shear elastic modulus at 25°C of the polyurethane gel is 1×10^3 to 1×10^7 Pa. The shear elastic modulus is measured with a solid viscoelasticity measurement device.

[0129] Such a polyurethane gel includes the plasticizer (C) having an ester group at a specific ratio in a higher order structure (three dimensional network) of the polyurethane formed by a reaction of the aliphatic polyisocyanate (A) having a specific average functionality with the polyol (B) having a specific average functionality. As a result, the plasticizer (C) is not completely confined in the three dimensional network and appropriately bleeds without excessive bleeding. As a result, the polyurethane gel can achieve both a moist feeling and dimensional stability.

[0130] In other words, since the above-described polyurethane gel is obtained from the above-described polyurethane gel material, it has both a moist feeling and dimensional stability and is excellent in curability, mechanical properties, and hardness.

[0131] Further, according to the above-described method for producing a polyurethane gel, it is possible to obtain the polyurethane gel which has both a moist feeling and dimensional stability and is excellent in curability, mechanical properties, and hardness.

[0132] A size of the polyurethane gel is set in accordance with the type of the metal mold to be used, and the like, and the thickness thereof is, for example, 0.03 mm or more, preferably 0.05 mm or more, and for example, 500 mm or less, preferably 400 mm or less.

[0133] Further, the bleeding properties (degree of bleeding) of the polyurethane gel is evaluated, for example, by a rate of weight change (weight reduction rate) before and after a durability test. Specifically, the rate of weight change (weight reduction rate) is obtained by the following formulation before and after the durability test under the following conditions.

- Durability test: left to stand at 80°C for five days, and then, further left to stand at 23°C with relative humidity of 55% for one day
- Rate of weight change [(weight W1 before durability test - weight W2 after durability test)/ (weight W1 before durability test)] × 100

[0134] The rate of weight change (weight reduction rate) of the polyurethane gel is, for example, 0.1% or more, preferably 0.5% or more, more preferably 1% or more, further more preferably 1.5% or more, particularly preferably 2% or more, and for example, 7% or less, preferably 6% or less, more preferably 5% or less, further more preferably 4% or less.

[0135] Further, the dimensional stability of the polyurethane gel is evaluated, for example, by a rate of dimensional change (dimensional reduction rate) before and after the durability test. Specifically, the rate of dimensional change (dimensional reduction rate) is obtained by the following formula before and after the durability test under the following conditions.

- Durability test: left to stand at 80°C for five days, and then, further left to stand at 23°C with relative humidity of 55% for one day
- Rate of dimensional change [(dimension L1 before durability test - dimension L2 after durability test)/ (dimension L1 before durability test)] × 100

[0136] The dimensional stability of the polyurethane gel is, for example, 0% or more, preferably 0.1% or more, more preferably 0.2% or more, further more preferably 0.5% or more, and for example, 8% or less, preferably 6% or less, more preferably 4% or less, further more preferably 3% or less, still more preferably 2% or less, particularly more preferably 1% or less.

[0137] Also, the above-described polyurethane gel may be also, for example, coated on a substrate such as leather, artificial or synthetic leather, nonwoven fabric, felt, sheet, film, or the like.

[0138] Specifically, the polyurethane gel is an ultra-low hardness polyurethane elastomer, and the Asker C hardness (JIS K 7312 (1996)) thereof is, for example, 0 or more, and for example, 40 or less, preferably 30 or less, more preferably 20 or less, further more preferably 15 or less, still more preferably 12 or less, particularly preferably 10 or less.

[0139] When the Asker C hardness is within the above-described range, especially 40 or less, it can be particularly preferably used as a gel with a feel, elasticity and flexibility that is close to human skin.

[0140] Further, such a polyurethane gel can be also further used by being encapsulated in a fabric such as cotton, silk, and synthetic fibers, a natural leather, a synthetic leather, paper, a nonwoven fabric, a resin film, a flexible foam, or the like.

[0141] The polyurethane gel can be preferably used as vibration-proof and quake-isolation members, shock absorbing members, cushioning members, surface protection members, cushioning, elbow rests, arm rests, switches, robotic components, robotic skin, manikins, members of mobility, pads, clothing components, aircraft components, cosmetics, medical devices, care and clothing materials such as diapers and floor misalignment prevention materials, wearable materials, eyewears such as frames, ear and nose pads of eyewear, earphones, headphones, grips and other sporting

components, toys, playground equipment, protectors such as helmets, furniture, flexible sensors, sheets, flexible rods, non-woven fabrics, composite materials with felt, shoe soles, shoe friction prevention, actuators, pseudo-biomaterials, and the like. Among all, the polyurethane gel can be preferably used as pseudo-biomaterials.

[0142] Since the polyurethane gel of the present invention has a touch, elasticity, and flexibility close to various organs and various internal organs constituting a human body in particular, and tissues constituting them, it is preferably used as a pseudo-biomaterial or the like in a medical field, a healthcare field, or the like.

[0143] More specifically, the pseudo-biomaterial made from the above-described polyurethane gel is formed as pseudo-biological models of cartilage and joints constituting a skeletal system; muscle, skeletal muscle, smooth muscle, and cardiac muscle constituting a muscular system; heart and blood constituting a circulatory system; upper airway, lower airway, and lung constituting a respiratory system; skin, ear, and nose constituting a sensory system; oral cavity, pharynx, esophagus, stomach, small intestine, large intestine, anal canal, anal, digestive gland, liver, biliary gland, and pancreas constituting a digestive system; kidney, renal pelvis, urinary tract, urinary bladder, and urethra constituting a urinary system; testis, prostate, seminal vesicle, penis, ovary, oviduct, uterus, and vagina constituting a genital organ; hypothalamus, pituitary, thyroid, accessory thyroid, adrenal, pancreas, testis, and ovary constituting an endocrine system; and brain, spinal cord, cerebrospinal nerve, and autonomic nerve constituting a nervous system. For example, the pseudo-biomaterial is preferably used as pseudo-biological models for training in various types of medical surgeries and pseudo-biological models for training in various types of inspections (ultrasonography, CT scan, etc.), pseudo-biological models in telemedicine and medical treatment, wearable equipment and terminal equipment in the field of health care, and as exhibition samples, equipment for education, toys, and the like.

Examples

[0144] Next, the present invention is described based on Production Examples, Examples, and Comparative Examples. The present invention is however not limited by the following Examples. All designations of "part" or "parts" and "%" mean part or parts by mass and % by mass, respectively, unless otherwise particularly specified in the following description. The specific numerical values in mixing ratio (content ratio), property value, and parameter used in the following description can be replaced with upper limit values (numerical values defined as "or less" or "below") or lower limit values (numerical values defined as "or more" or "above") of corresponding numerical values in mixing ratio (content ratio), property value, and parameter described in the above-described "DESCRIPTION OF EMBODIMENTS".

[0145] The measurement methods used in the respective Production Examples, the respective Examples, and the respective Comparative Examples are described below.

1. Measurement method

<Isocyanate Group Concentration (Unit: % by mass), Conversion Rate of Isocyanate Group (Unit: % by mass)>

[0146] By using a potentiometric titrator (manufactured by KYOTO ELECTRONICS MANUFACTURING CO., LTD., model number: AT-510), the isocyanate group concentration (isocyanate group content ratio) was measured by a toluene/dibutylamine hydrochloric acid method in conformity with JIS K-1603-1 (2007), and a conversion rate of an isocyanate group of a measurement sample was calculated by the following formula.

$$\text{Conversion rate of isocyanate group} = 100 - (\text{isocyanate group concentration in reaction liquid mixture after completion of reaction} / \text{isocyanate group concentration in reaction liquid before reaction} \times 100)$$

<Isocyanate Monomer Concentration (Unit: % by mass)>

[0147] The concentration of an unreacted isocyanate monomer (pentamethylene diisocyanate monomer or hexamethylene diisocyanate monomer) was calculated by using a pentamethylene diisocyanate produced in the same manner as in Example 1 in International Publication WO2012/121291 or a commercially available hexamethylene diisocyanate as a standard substance, being labelled with a dibenzylamine, and using a calibration curve prepared from the area values of chromatogram obtained under the following HPLC measurement conditions.

Device: Prominence (manufactured by Shimadzu Corporation)
Pumping: LC-20AT

Degasser: DGU-20A3
Autosampler: SIL-20A
Column thermostat: COT-20 A
Detector: SPD-20A
Column: SHISEIDO SILICA SG-120
Column temperature: 40°C
Eluent: n-hexane/ methanol/ 1,2-dichloroethane = 90/ 5/ 5 (volume ratio)
Flow rate: 0.2 mL/ min
Detecting method: UV 225 nm

<Viscosity (unit: mPa·s)>

[0148] The viscosity of the measurement sample was measured at 25°C in conformity with a cone plate viscometer method of JIS K5600-2-3 (2014) by using an E-type viscometer TV-30 (rotor angle: 1°34', rotor radius: 24 cm) manufactured by TOKI SANGYO CO., LTD. The number of revolutions of the cone plate at the time of measurement was sequentially changed between 100 rpm and 2.5 rpm as the viscosity increased.

<Mole Ratio of Allophanate Group to Isocyanurate Group by ^{1}H-NMR>

[0149] The ^{1}H-NMR was measured with the following device and conditions, and a content ratio (mole ratio of allophanate group/ isocyanurate group) of the allophanate group to 1 mol of the isocyanurate group in the aliphatic polyisocyanate was calculated by the following formula. As a reference of chemical shift ppm, a tetramethylsilane (0 ppm) in D^6-DMSO solvent was used.

Device: JNM-AL400 (manufactured by JEOL Ltd.)
Conditions: measurement frequency: 400 MHz, solvent: D^6-DMSO, solute concentration: 5% by mass
Assigned peak (6H) of proton of isocyanurate group (methylene group (CH_2 group) directly bonded to isocyanurate group): 3.8 ppm
Assigned peak (1H) of proton of allophanate group (NH group in allophanate group): 8.3 to 8.7 ppm

$$\text{Allophanate group/ isocyanurate group (mole ratio)} = \text{integrated value of assigned peak of proton of allophanate group/ (integrated value of assigned peak of proton of isocyanurate group/ 6)}$$

<Average Number of Isocyanate Group (Average Functionality)>

[0150] An average number of the isocyanate group of the aliphatic polyisocyanate was calculated from the isocyanate group concentration, the solid content concentration (NV), and a number average molecular weight of gel permeation chromatography measured by the following device and conditions according to the following formula.

$$\text{Average number of isocyanate group} = A/B \times C/42.02$$

(wherein A represents the isocyanate group concentration, B represents the solid content concentration, and C represents a number average molecular weight.)

Device: HLC-8220GPC (manufactured by TOSOH CORPORATION)
Column: series connection of TSKgelG1000HXL, TSKgelG2000HXL, and TSKgelG3000HXL (manufactured by TOSOH CORPORATION)
Detector: differential refractometer
Measurement conditions
Injection volume: 100 μm
Eluent: tetrahydrofuran
Flow rate: 0.8 mL/ min

Temperature: 40°C
Calibration curve: standard polyethylene oxide in a rage of 106 to 22450 (manufactured by TOSOH CORPORATION, trade name: TSK standard polyethylene oxide)

<Average Number of Hydroxyl Group (Average Functionality)>

[0151] A hydroxyl value was defined as the number of mg of potassium hydroxide corresponding to a hydroxyl group in 1 g of a polyoxyalkylene polyol. The hydroxyl value of the polyol was measured in conformity with "hydroxyl value" of Section 6.4 of JIS K1557 (2007).

2. Materials

(1) Aliphatic Polyisocyanate (A)

Preparation Example 1 (Isocyanate (a-1) (Alcoholic Modified Isocyanurate Derivative of PDI))

[0152] A four-neck flask equipped with a thermometer, a stirring device, a reflux tube, and a nitrogen introducing tube was charged with 500 parts by mass of pentamethylene diisocyanate produced in the same manner as in Example 1 in the specification of International Publication WO2012/121291 (hereinafter, referred to as PDI), 6.9 parts by mass of isobutyl alcohol, 0.3 parts by mass of 2,6-di(tert-butyl)-4-methylphenol, and 0.3 parts by mass of tris(tridecyl) phosphite to be reacted at 80°C for 2 hours.
[0153] Then, 0.05 parts by mass of N-(2-hydroxypropyl)-N,N,N-trimethylammonium-2-ethylhexanoate was blended as an isocyanuration catalyst. The isocyanate group concentration was measured, and the reaction was continued until its concentration reached 48.3% by mass (that is, conversion rate of 10% by mass). When a predetermined conversion rate (conversion rate of 10% by mass) was reached after 20 minutes, 0.12 parts by mass of o-toluenesulfonamide was added thereto. The obtained reaction liquid mixture was passed through a thin film distillation device (temperature: 150°C, vacuum degree: 0.093 kPa) to remove unreacted pentamethylene diisocyanate monomer, and further, 0.02 parts by mass of o-toluenesulfonamide and 0.003 parts by mass of benzoyl chloride were added to 100 parts by mass of the obtained residue to obtain an alcoholic modified isocyanurate derivative of PDI. This was referred to as an isocyanate (a-1).
[0154] In the isocyanate (a-1), the average number of the isocyanate group was 2.8, the isocyanate monomer concentration was 0.4% by mass, the isocyanate group concentration was 23.4% by mass, and the viscosity at 25°C was 950 mPa·s.
[0155] Further, the mole ratio of the allophanate group to the isocyanurate group by ^{1}H-NMR measurement was an allophanate group/ isocyanurate group = 33.0/100.

Preparation Example 2 (Isocyanate (a-2) (Alcoholic Modified Isocyanurate Derivative of PDI))

[0156] A four-neck flask equipped with a thermometer, a stirring device, a reflux tube, and a nitrogen introducing tube was charged with 500 parts by mass of PDI, 0.5 parts by mass of isobutyl alcohol, 0.3 parts by mass of 2,6-di(tert-butyl)-4-methylphenol, and 0.3 parts by mass of tris(tridecyl) phosphite to be reacted at 80°C for 2 hours.
[0157] Then, 0.05 parts by mass of N-(2-hydroxypropyl)-N,N,N-trimethylammonium-2-ethylhexanoate was blended as an isocyanuration catalyst. The isocyanate group concentration was measured, and the reaction was continued until its concentration reached 48.9% by mass (that is, conversion rate of 10% by mass). When a predetermined conversion rate (conversion rate of 10% by mass) was reached after 50 minutes, 0.12 parts by mass of o-toluenesulfonamide was added thereto. The obtained reaction liquid mixture was passed through a thin film distillation device (temperature: 150°C, vacuum degree: 0.093 kPa) to remove unreacted pentamethylene diisocyanate monomer, and further, 0.02 parts by mass of o-toluenesulfonamide and 0.003 parts by mass of benzoyl chloride were added to 100 parts by mass of the obtained residue to obtain an alcoholic modified isocyanurate derivative of PDI. This was referred to as an isocyanate (a-2).
[0158] In the isocyanate (a-2), the average number of the isocyanate group was 3.1, the isocyanate monomer concentration was 0.5% by mass, the isocyanate group concentration was 24.7% by mass, and the viscosity at 25°C was 2000 mPa·s.
[0159] Further, the mole ratio of the allophanate group to the isocyanurate group by ^{1}H-NMR measurement was an allophanate group/ isocyanurate group = 7.4/ 100.

Preparation Example 3 (Isocyanate (a-3) (Isocyanurate Derivative of PDI))

[0160] A four-neck flask equipped with a thermometer, a stirring device, a reflux tube, and a nitrogen introducing tube was charged with 500 parts by mass of PDI, 0.3 parts by mass of 2,6-di(tert-butyl)-4-methylphenol, and 0.3 parts by

mass of tris(tridecyl) phosphite to be heated to 80°C. Then, 0.05 parts by mass of N-(2-hydroxypropyl)-N,N,N-trimethylammonium-2-ethylhexanoate was blended as an isocyanuration catalyst. The isocyanate group concentration was measured, and the reaction was continued until its concentration reached 49.0% by mass (that is, conversion rate of 10% by mass). When a predetermined conversion rate (conversion rate of 10% by mass) was reached after 50 minutes, 0.12 parts by mass of o-toluenesulfonamide was added thereto. The obtained reaction liquid mixture was passed through a thin film distillation device (temperature: 150°C, vacuum degree: 0.093 kPa) to remove unreacted pentamethylene diisocyanate monomer, and further, 0.02 parts by mass of o-toluenesulfonamide and 0.003 parts by mass of benzoyl chloride were added to 100 parts by mass of the obtained residue to obtain an isocyanurate derivative of PDI. This was referred to as an isocyanate (a-3).

[0161] In the isocyanate (a-3), the average number of the isocyanate group was 3.2, the isocyanate monomer concentration was 0.5% by mass, the isocyanate group concentration was 24.9% by mass, and the viscosity at 25°C was 2800 mPa·s.

[0162] Further, the mole ratio of the allophanate group to the isocyanurate group by ^{1}H-NMR measurement was an allophanate group/ isocyanurate group = 0/100.

Preparation Example 4 (Isocyanate (a-4) (Alcoholic Modified Isocyanurate Derivative of PDI))

[0163] A four-neck flask equipped with a thermometer, a stirring device, a reflux tube, and a nitrogen introducing tube was charged with 500 parts by mass of PDI, 0.5 parts by mass of isobutyl alcohol, 0.3 parts by mass of 2,6-di(tert-butyl)-4-methylphenol, and 0.3 parts by mass of tris(tridecyl) phosphite to be reacted at 80°C for 2 hours.

[0164] Then, 0.05 parts by mass of N-(2-hydroxypropyl)-N,N,N-trimethylammonium-2-ethylhexanoate was blended as an isocyanuration catalyst. The isocyanate group concentration was measured, and the reaction was continued until its concentration reached 40.3% by mass (that is, conversion rate of 26% by mass). When a predetermined conversion rate (conversion rate of 26% by mass) was reached after 130 minutes, 0.12 parts by mass of o-toluenesulfonamide was added thereto. The obtained reaction liquid mixture was passed through a thin film distillation device (temperature: 150°C, vacuum degree: 0.093 kPa) to remove unreacted pentamethylene diisocyanate monomer, and further, 0.02 parts by mass of o-toluenesulfonamide and 0.003 parts by mass of benzoyl chloride were added to 100 parts by mass of the obtained residue to obtain an alcoholic modified isocyanurate derivative of PDI. This was referred to as an isocyanate (a-4).

[0165] In the isocyanate (a-4), the average number of the isocyanate group was 3.8, the isocyanate monomer concentration was 0.5% by mass, the isocyanate group concentration was 23.1% by mass, and the viscosity at 25°C was 9000 mPa·s.

[0166] Further, the mole ratio of the allophanate group to the isocyanurate group by ^{1}H-NMR measurement was an allophanate group/ isocyanurate group = 5.0/100.

Preparation Example 5 (Isocyanate (a-5) (Allophanate Derivative of PDI))

[0167] In a reactor equipped with a thermometer, a stirring device, a nitrogen introducing tube, and a cooling tube, 1500 parts by mass of PDI, 24 parts by mass of isobutanol, 0.3 parts by mass of 2,6-di(t-butyl)-4-methylphenol, and 0.3 parts by mass of tris(tridecyl) phosphite were charged under a nitrogen atmosphere to be subjected to a urethanization reaction at 85°C for 3 hours.

[0168] Then, 0.02 parts by mass of tris(2-ethylhexanoic acid) bismuth was added as an allophanatization catalyst, and the obtained mixture was reacted until the isocyanate group concentration reached a calculated value (46.7% by mass, that is, a conversion rate of 10% by mass), and then, 0.02 parts by mass of o-toluenesulfonamide was added thereto.

[0169] Thereafter, the obtained reaction liquid was passed through a thin film distillation device (vacuum degree of 0.093 KPa, temperature of 150°C) to remove unreacted pentamethylene diisocyanate, and further, 0.02 parts by mass of o-toluenesulfonamide was added to 100 parts by mass of the obtained residue to obtain an allophanate derivative of PDI. This was referred to as an isocyanate (a-5).

[0170] In the isocyanate (a-5), the average number of the isocyanate group was 2.0, the isocyanate group concentration was 20.4% by mass, the viscosity at 25°C was 24 mPa·s, and the isocyanate monomer concentration was 0.2% by mass.

[0171] Further, the mole ratio of the allophanate group to the isocyanurate group by ^{1}H-NMR measurement was an allophanate group/ isocyanurate group = 100/ 0.

Preparation Example 6 (Isocyanate (a-6) (Alcoholic Modified Isocyanurate Derivative of HDI))

[0172] An alcoholic modified isocyanurate derivative of HDI was obtained in the same manner as in Preparation Example 1, except that PDI was changed to a hexamethylene diisocyanate (manufactured by Mitsui Chemicals, Inc., trade name: Takenate 700 (hereinafter, referred to as HDI)). This was referred to as an isocyanate (a-6).

[0173] In the isocyanate (a-6), the average number of the isocyanate group was 2.9, the isocyanate monomer con-

centration was 0.5% by mass, the isocyanate group concentration was 22.1% by mass, and the viscosity at 25°C was 840 mPa·s.

[0174] Further, the mole ratio of the allophanate group to the isocyanurate group by ^{1}H-NMR measurement was an allophanate group/ isocyanurate group = 34.3/ 100.

Preparation Example 7 (Isocyanate (a-7) (Polyol Derivative of PDI (TMP Modified Product))

[0175] A four-neck flask equipped with a stirring device, a thermometer, a reflux tube, and a nitrogen introducing tube was charged with 200 parts by mass of PDI to be heated to 95°C under a nitrogen atmosphere with stirring. Next, 21.1 parts by mass of trimethylolpropane (hereinafter, referred to as TMP) was charged into a dropping funnel to be heated with a ribbon heater.

[0176] The melted TMP was added dropwise over a period of about 60 minutes. Thereafter, the urethanization reaction was continued for about 3 hours until the isocyanate group concentration reached a calculated value. The obtained reaction liquid was passed through a thin film distillation device (vacuum degree of 50 Pa, temperature of 130°C) to remove unreacted PDI, thereby obtaining a polyol derivative of PDI (TMP modified product). This was referred to as an isocyanate (a-7).

[0177] In the isocyanate (a-7), the average number of the isocyanate group was 3.7, the isocyanate group concentration was 13.8% by mass, and the viscosity at 25°C was 450 mPa·s.

(2) Polyol (B)

Preparation Example 1 (Polyol (b-1))

[0178] A polyoxypropylene glycol (polyether polyol (PPG) obtained by subjecting propylene glycol to addition polymerization of propylene oxide, number average molecular weight (Mn) = 1000, average functionality of 2, hydroxyl value of 112 mgKOH/g) was referred to as a polyol (b-1).

Preparation Example 2 (Polyol (b-2))

[0179] A polyoxypropylene glycol (polyether polyol (PPG) obtained by subjecting propylene glycol to addition polymerization of propylene oxide, number average molecular weight (Mn) = 2000, average functionality of 2, hydroxyl value of 56 mgKOH/g) was referred to as a polyol (b-2).

Preparation Example 2-1 (Polyol (b-2-1))

[0180] The polyol (b-1) having a number average molecular weight of 1000 and the polyol (b-2) having a number average molecular weight of 2000 were mixed so as to have 1: 1 (b-1: b-2 (mass ratio)), and as a mixture, a polyol (b-2-1) was obtained. The polyol (b-2-1) had a number average molecular weight of about 1300 (1335), an average functionality of 2, and a hydroxyl value of 84 mgKOH/g.

Preparation Example 3 (Polyol (b-3))

[0181] A polyoxypropylene glycol (polyether polyol (PPG) obtained by subjecting propylene glycol to addition polymerization of propylene oxide, number average molecular weight (Mn) = 700, average functionality of 2, hydroxyl value of 160 mgKOH/g) was referred to as a polyol (b-3).

Preparation Example 4 (Polyol (b-4))

[0182] A polyoxypropylene glycol (polyether polyol (PPG) obtained by subjecting propylene glycol to addition polymerization of propylene oxide, number average molecular weight (Mn) = 400, average functionality of 2, hydroxyl value of 281 mgKOH/g) was referred to as a polyol (b-4).

Preparation Example 5 (Polyol (b-5))

[0183] A polyoxypropylene triol (polyether polyol (PPT) obtained by subjecting glycerine to addition polymerization of propylene oxide, number average molecular weight (Mn) = 1000, average functionality of 3, hydroxyl value of 168 mgKOH/g) was referred to as a polyol (b-5).

Preparation Example 6 (Polyol (b-6))

[0184] A polytetramethylene ether glycol having a number average molecular weight of 1000 (PTMEG, manufactured by Hodogaya Chemical Co., Ltd., trade name: PTG-1000, hydroxyl value of 112 mgKOH/g, average functionality of 2) was referred to as a polyol (b-6).

(3) Plasticizer (c)

Preparation Example 11 (Plasticizer (c-1))

[0185] A diisononylcyclohexane-1,2-dicarboxylate (manufactured by BASF SE, trade name: Hexamol DINCH, boiling point of 394°C) was referred to as a plasticizer (c-1).

Preparation Example 12 (Plasticizer (c-2))

[0186] A diisononyl adipate (manufactured by Mitsubishi Chemical Corporation, trade name: DINA, boiling point of 250°C) was referred to as a plasticizer (c-2).

Preparation Example 13 (Plasticizer (c-3))

[0187] A di-(2-ethylhexyl) phthalate (manufactured by Mitsubishi Chemical Corporation, trade name: DOP, boiling point of 386°C) was referred to as a plasticizer (c-3).

Preparation Example 14 (Plasticizer (c-4))

[0188] A chloroparaffin (manufactured by Sigma-Aldrich Co. LLC, trade name: Chloroparaffin) was referred to as a plasticizer (c-4).

(4) Catalyst (d)

[0189] Manufactured by TOKYO CHEMICAL INDUSTRY CO., LTD., reagent, dibutyltin dilaurate

(5) Antifoaming Agent (e)

[0190] Manufactured by BYK Japan KK, trade name: BYK-088

3. Production of Polyurethane Gel

Example 1

[0191] The isocyanate (a-1), the polyol (b-1), and the plasticizer (c-1) were prepared at the mass ratio shown in Table 1 to obtain a polyurethane gel material (preparation step).

[0192] Then, 100 parts by mass of the polyol (b-1) adjusted at 25°C, 35.85 parts by mass of the polyisocyanate (a-1) (equivalent ratio of isocyanate group to hydroxyl group (NCO/ hydroxyl group = 1.0)), 300 parts by weight of the plasticizer (c-1), 0.03 parts by weight of the dibutyltin dilaurate (d) of the catalyst, and 0.2 parts by weight of the defoaming agent (e) were put into a plastic container, and the mixture was stirred and mixed for one minute under stirring at 7000 rpm by using a three-one motor (manufactured by SHINTO Scientific Co., Ltd., trade name: HEIDOM FBL3000).

[0193] Thereafter, the liquid mixture was immediately defoamed under a reduced pressure, and after removing the foam of the liquid mixture, it was poured into the following metal mold which was previously coated with Teflon (registered trademark) and heated to 80°C without contamination of bubbles. Then, the liquid mixture was allowed to react at 80°C for 2 hours to obtain a urethane gel.

[0194]

- Sheet metal mold having a thickness of 2 mm
- Square block metal mold having a size of 5 cm × 5 cm × height of 15 mm
- Columnar metal mold having a diameter of 29 mm × height of 13 mm

[0195] This polyurethane gel was left to stand in a room at 23°C with relative humidity of 55% for seven days and

then, subjected to various property measurement.

Examples 2 to 14 and Comparative Examples 1 to 9

[0196] A polyurethane gel was obtained in the same manner as in Example 1, except that the formulation was changed to those shown in Tables 1 to 3.

4. Evaluation

<Curability of Polyurethane Gel>

[0197] A liquid mixture of a polyurethane gel material was poured into a block metal mold, and the mixture was reacted at 80°C for 2 hours. Then, the flowability of the polyurethane gel material was confirmed, and the curability of the polyurethane gel was evaluated. Criteria for evaluation are as follows.

[0198] Bad: the polyurethane gel material has flowability and cannot retain its shape after demolding.

[0199] Excellent: the polyurethane gel material has flowability and can retain its shape after demolding.

<Mechanical Properties of Polyurethane Gel (Elongation at Break (EL) (unit: %)>

[0200] A polyurethane gel prepared with a 2 mm-sheet metal mold was punched into a No. 3 test piece shape to prepare a measurement sample. The measurement sample was subjected to a tensile test by using a tensile compressive tester (manufactured by INTESCO co., ltd., Model 205N) in conformity with JIS K-6400 (2012) to calculate the elongation at break.

<Moist Feeling>

[0201] A moist feeling of the polyurethane gel obtained by the block metal mold was evaluated by visual and finger touch. Criteria for evaluation are as follows.

Bad: the surface of the polyurethane gel is dry and does not stick liquid to the fingers when touched.
Good: the surface of the polyurethane gel is dry and the liquid adheres to the fingers when touched.
Excellent: the surface of the polyurethane gel is moist and the liquid adheres to the fingers when touched.

<Bleeding Properties of Polyurethane Gel>

[0202] A polyurethane gel obtained with a columnar metal mold was punched into a columnar test piece to prepare a measurement sample, and the weight thereof was measured (W1).

[0203] After the upper and the lower surfaces of the sample were sandwiched between filter papers (manufactured by Advantec Tokyo Kaisha, Ltd., FILTER PAPER No. 5C) and treated in an oven at 80°C for five days, they were left to stand in a room at 23°C with relative humidity of 55% for one day, and then, the surface was further thoroughly wiped off with the filter paper to measure the weight thereof again (W2).

Bleeding properties were evaluated by a weight change before and after treatment (W: $W = (W1 - W2)/W1 \times 100$ (unit: %)).

<Dimensional Stability of Polyurethane Gel>

[0204] A length (dimension) of a width of the polyurethane gel obtained by the block metal mold was measured (LI).

[0205] After the upper and the lower surfaces of the sample were sandwiched between filter papers (manufactured by Advantec Tokyo Kaisha, Ltd., FILTER PAPER No. 5C) and treated in an oven at 80°C for five days, they were left to stand in a room at 23°C with relative humidity of 55% for one day, and then, the surface was further thoroughly wiped off with the filter paper to measure a length of a width (dimension) thereof again (L2).

[0206] A rate of dimensional change before and after the above-described durability test (left to stand at 80°C for five days, and then, further left to stand at 23°C with relative humidity of 55% for one day) was calculated by the following formula.

Rate of dimensional change (%) = [(dimension L1 before durability test – dimension L2 after durability test)/ (dimension L1 before durability test)] × 100

<Asker C Hardness of Polyurethane Gel>

[0207] The Asker C hardness of the polyurethane gel obtained with the block metal mold was measured by a type C hardness test of JIS K 7312 (1996).

[Table 1]

[0208]

Table 1

No.				Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comparative Ex. 1	Comparative Ex. 2	Comparative Ex. 3
Mixing Formulation (parts by mass)	Polyisocyanate (A)	Preparation Ex. 1 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-1	100	-	-	60	-	-	30	-
		Preparation Ex. 2 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-2	-	100	-	-	-	-	-	-
		Preparation Ex. 3 (Isocyanurate Derivative of PDI)	a-3	-	-	100	-	-	-	-	-
		Preparation Ex. 4 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-4	-	-	-	-	-	100	-	-
		Preparation Ex. 5 (Allophanate Derivative of PDI)	a-5	-	-	-	40	-	-	70	-
		Preparation Ex. 6 (Alcoholic Modified Isocyanurate Derivative of HDI)	a-6	-	-	-	-	100	-	-	-
		Preparation Ex. 7 (Polyol Derivative of PDI)	a-7	-	-	-	-	-	-	-	100
		Average Functionality		2.8	3.1	3.2	2.5	2.9	3.8	2.2	3.7
		Preparation Ex. 1 (PPG: Mn1000)	b-1	100	100	100	100	100	100	100	100

(continued)

No.				Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comparative Ex. 1	Comparative Ex. 2	Comparative Ex. 3
	Polyol (B)	Preparation Ex. 2-1 (PPG: Mn1300)	b-2-1	-	-	-	-	-	-	-	-
		Preparation Ex. 2 (PPG: Mn2000)	b-2	-	-	-	-	-	-	-	-
		Preparation Ex. 3 (PPG: Mn700)	b-3	-	-	-	-	-	-	-	-
		Preparation Ex. 4 (PPG: Mn400)	b-4	-	-	-	-	-	-	-	-
		Preparation Ex. 5 (PPT: Mn1000)	b-5	-	-	-	-	-	-	-	-
		Preparation Ex. 6 (PTMEG: Mn1000)	b-6	-	-	-	-	-	-	-	-
		Average Functionality		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
		Average Hydroxyl Value (mgKOH/g)		112	112	112	112	112	112	112	112
Plasticizer (c) (parts by mass per 100 parts by mass of polyol)		Diisononylcyclohexane-1,2-dicarboxylate (DINCH)	c-1	300	300	300	300	300	300	300	300
		Diisononyl Adipate (DINA)	c-2	-	-	-	-	-	-	-	-
		Di-(2-ethylhexyl) phthalate (DOP)	c-3	-	-	-	-	-	-	-	-
		Chloroparaffin	c-4	-	-	-	-	-	-	-	-
Bleeding Properties (weight reduction rate: %)				2.9	2.5	2.1	4.6	3.1	1.9	-	3.5

(continued)

No.		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comparative Ex. 1	Comparative Ex. 2	Comparative Ex. 3
Evaluation	Curability	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Bad	Excellent
	Elongation at Break (%)	110	89	73	138	104	55	-	46
	Moist Feeling	Excellent	Excellent	Good	Excellent	Excellent	Good	-	Excellent
	Dimensional Stability (Dimensinal Reduction Rate: %)	1	1	1	2	1	1	-	2
	Asker C Hardness	10	23	29	3	12	37	-	19

[Table 2]

[0209]

Table 2

No.				Ex. 6	Ex. 7	Ex. 8	Ex. 9	Comparative Ex. 4	Comparative Ex. 5	Comparative Ex. 6
Mixing Formulation (parts by mass)	Polyisocyanate (A)	Preparation Ex. 1 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-1	100	100	100	100	100	100	100
		Preparation Ex. 2 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-2	-	-	-	-	-	-	-
		Preparation Ex. 3 (Isocyanurate Derivative of PDI)	a-3	-	-	-	-	-	-	-
		Preparation Ex. 4 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-4	-	-	-	-	-	-	-
		Preparation Ex. 5 (Allophanate Derivative of PDI)	a-5	-	-	-	-	-	-	-
		Preparation Ex. 6 (Alcoholic Modified Isocyanurate Derivative of HDI)	a-6	-	-	-	-	-	-	-
		Preparation Ex. 7 (Polyol Derivative of PDI)	a-7	-	-	-	-	-	-	-
		Average Functionality		2.8	2.8	2.8	2.8	2.8	2.8	2.8

(continued)

No.				Ex. 6	Ex. 7	Ex. 8	Ex. 9	Comparative Ex. 4	Comparative Ex. 5	Comparative Ex. 6
	Polyol (B)	Preparation Ex. 1 (PPG: Mn1000)	b-1	-	-	-	90	-	-	50
		Preparation Ex. 2-1 (PPG: Mn1300)	b-2-1	100	-	-	-	-	-	-
		Preparation Ex. 2 (PPG: Mn2000)	b-2	-	-	-	-	100	-	-
		Preparation Ex. 3 (PPG: Mn700)	b-3	-	100	-	-	-	-	-
		Preparation Ex. 4 (PPG: Mn400)	b-4	-	-	-	-	-	100	-
		Preparation Ex. 5 (PPT: Mn1000)	b-5	-	-	-	10	-	-	50
		Preparation Ex. 6 (PTMEG: Mn1000)	b-6	-	-	100	-	-	-	-
		Average Functionality		2.0	2.0	2.0	2.1	2.0	2.0	2.5
		Average Hydroxyl Value (mgKOH/g)		84	160	112	106	56	281	84
Plasticizer (c) (parts by mass per 100 parts by mass of polyol)		Diisononylcyclohexane-1,2-dicarboxylate (DINCH)	c-1	300	300	300	300	300	300	300
		Diisononyl Adipate (DINA)	c-2	-	-	-	-	-	-	-
		Di-(2-ethylhexyl)phthalate (DOP)	c-3	-	-	-	-	-	-	-
		Chloroparaffin	c-4	-	-	-	-	-	-	-
Bleeding Properties (weight reduction rate: %)				2.0	7.1	3.5	2.5	1.0	-	3.4

(continued)

No.		Ex. 6	Ex. 7	Ex. 8	Ex. 9	Comparative Ex. 4	Comparative Ex. 5	Comparative Ex. 6
Evaluation	Curability	Excellent	Excellent	Excellent	Excellent	Excellent	Bad	Excellent
	Elongation at Break (%)	140	91	101	95	194	-	45
	Moist Feeling	Good	Excellent	Good	Excellent	Bad	-	Good
	Dimensional Stability (Dimensinal Reduction Rate: %)	1	4	1	1	0	-	1
	Asker C Hardness	7	19	13	16	<1	-	24

[Table 3]

[0210]

Table 3

No.				Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Comparative Ex. 7	Comparative Ex. 8	Comparative Ex. 9
Mixing Formulation (parts by mass)	Polyisocyanate (A)	Preparation Ex. 1 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-1	100	100	100	100	100	100	100	100
		Preparation Ex. 2 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-2	-	-	-	-	-	-	-	-
		Preparation Ex. 3 (Isocyanurate Derivative of PDI)	a-3	-	-	-	-	-	-	-	-
		Preparation Ex. 4 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-4	-	-	-	-	-	-	-	-
		Preparation Ex. 5 (Allophanate Derivative of PDI)	a-5	-	-	-	-	-	-	-	-
		Preparation Ex. 6 (Alcoholic Modified Isocyanurate Derivative of HDI)	a-6	-	-	-	-	-	-	-	-
		Preparation Ex. 7 (Polyol Derivative of PDI)	a-7	-	-	-	-	-	-	-	-
		Average Functionality		2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
		Preparation Ex. 1 (PPG: Mn1000)	b-1	100	100	100	100	100	100	100	100

(continued)

No.				Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Comparative Ex. 7	Comparative Ex. 8	Comparative Ex. 9
	Polyol (B)	Preparation Ex. 2-1 (PPG: Mn1300)	b-2-1	-	-	-	-	-	-	-	-
		Preparation Ex. 2 (PPG: Mn2000)	b-2	-	-	-	-	-	-	-	-
		Preparation Ex. 3 (PPG: Mn700)	b-3	-	-	-	-	-	-	-	-
		Preparation Ex. 4 (PPG: Mn400)	b-4	-	-	-	-	-	-	-	-
		Preparation Ex. 5 (PPT: Mn1000)	b-5	-	-	-	-	-	-	-	-
		Preparation Ex. 6 (PTMEG: Mn1000)	b-6	-	-	-	-	-	-	-	-
		Average Functionality		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
		Average Hydroxyl Value (mgKOH/g)		112	112	112	112	112	112	112	112
Plasticizer (c) (parts by mass per 100 parts by mass of polyol)		Diisononylcyclohexane-1,2-dicarboxylate (DINCH)	c-1	500	100	-	-	150	10	600	-
		Diisononyl Adipate (DINA)	c-2	-	-	300	-	150	-	-	-
		Di-(2-ethylhexyl) phthalate (DOP)	c-3	-	-	-	300	-	-	-	-
		Chloroparaffin	c-4	-	-	-	-	-	-	-	300
Bleeding Properties (weight reduction rate: %)				5.7	0.3	2.7	5.2	2.8	0.0	7.1	-

(continued)

No.		Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Comparative Ex. 7	Comparative Ex. 8	Comparative Ex. 9
Evaluation	Curability	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Bad
	Elongation at Break (%)	118	98	113	105	112	93	120	-
	Moist Feeling	Excellent	Good	Excellent	Excellent	Excellent	Bad	Excellent	-
	Dimensional Stability (Dimensinal Reduction Rate: %)	3	1	1	3	1	0	9	-
	Asker C Hardness	<1	48	13	15	11	79	<1	-

[0211] While the illustrative embodiments of the present invention are provided in the above description, such is for illustrative purpose only and it is not to be construed as limiting the scope of the present invention. Modification and variation of the present invention that will be obvious to those skilled in the art is to be covered by the following claims.

INDUSTRIAL APPLICATION

[0212] The polyurethane gel material, the polyurethane gel, the pseudo-biomaterial, and the method for producing a polyurethane gel of the present invention are, for example, preferably used in the field of pseudo-biomaterials such as a medical field and a healthcare field.

Claims

1. A polyurethane gel material comprising:

an aliphatic polyisocyanate (A) having an average functionality of 2.3 or more and 3.2 or less,
a polyol (B) having an average functionality of 2.0 or more and 2.3 or less, and
a plasticizer (C) having an ester group, wherein
the aliphatic polyisocyanate (A) contains an isocyanurate derivative of an aliphatic diisocyanate and/or an alcoholic modified isocyanurate derivative of an aliphatic diisocyanate,
the polyol (B) contains a polyoxypropylene polyol and/or a polytetramethylene ether glycol,
the polyol (B) has an average hydroxyl value of 73 mgKOH/g or more and 200 mgKOH/g or less, and
a ratio of the plasticizer (C) per 100 parts by mass of the polyol component (B) is 100 parts by mass or more and 500 parts by mass or less.

2. The polyurethane gel material according to claim 1, wherein
the polyol (B) has an average functionality of 2.0.

3. The polyurethane gel material according to claim 1, wherein
the aliphatic polyisocyanate (A) has an average functionality of 2.3 or more and 3.0 or less.

4. The polyurethane gel material according to claim 1, wherein
the aliphatic diisocyanate includes a pentamethylene diisocyanate and/or a hexamethylene diisocyanate.

5. The polyurethane gel material according to claim 1, wherein
the plasticizer (C) is cyclohexanedicarboxylic acid esters and/or adipic acid esters.

6. A polyurethane gel being a reaction product of the polyurethane gel material according to claim 1.

7. The polyurethane gel according to claim 6, wherein
in the polyurethane gel material, an equivalent ratio (NCO/ hydroxyl group) of an isocyanate group in an aliphatic polyisocyanate (A) to a hydroxyl group in a polyol (B) is 0.8 or more and 1.2 or less.

8. The polyurethane gel according to claim 6, wherein
a rate of weight change obtained by the following formula is 0.1% or more and 7% or less before and after a durability test under the following conditions.

- Durability test: left to stand at 80°C for five days, and then, further left to stand at 23°C with relative humidity of 55% for one day
- Rate of weight change [(weight W1 before durability test - weight W2 after durability test)/ (weight W1 before durability test)] × 100

9. A pseudo-biomaterial comprising the polyurethane gel according to claim 6.

10. A method for producing a polyurethane gel comprising:

a preparation step of preparing the polyurethane gel material according to claim 1 and
a reaction step of reacting and curing the polyurethane gel material to obtain a polyurethane gel, wherein

in the reaction step,
an equivalent ratio (NCO/ hydroxyl group) of an isocyanate group in an aliphatic polyisocyanate (A) to a hydroxyl group in a polyol (B) is 0.8 or more and 1.2 or less.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/014588

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C08G18/73(2006.01)i, C08G18/08(2006.01)i, C08G18/48(2006.01)i, C08G18/79(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. C08G18/73, C08G18/08, C08G18/48, C08G18/79

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAplus/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2017/010422 A1 (MITSUI CHEMICALS, INC.) 19 January 2017, entire text & US 2018/0208720 A1, entire text & EP 3321086 A1 & CN 107848285 A	1-10
A	JP 2013-067757 A (DIC CORPORATION) 18 April 2013, entire text (Family: none)	1-10
A	WO 2016/190131 A1 (BANDO CHEMICAL INDUSTRIES, LTD.) 01 December 2016, entire text & US 2018/0171139 A1, entire text & EP 3305823 A1 & CN 107614558 A & KR 10-2018-0011790 A	1-10
P, A	JP 2018-090662 A (MITSUI CHEMICALS, INC.) 14 June 2018, entire text (Family: none)	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 25 June 2019 (25.06.2019)	Date of mailing of the international search report 02 July 2019 (02.07.2019)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2017010422 A **[0004]**
- WO 2012121291 A **[0147] [0152]**

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference		FOR FURTHER ACTION
0113-0006WO1		see Form PCT/ISA/220 as well as, where applicable, item 5 below.
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US 20/41540	10 July 2020 (10.07.2020)	10 July 2019 (10.07.2019)
Applicant NANOMETICS LLC (D.B.A. PHD BIOSCIENCES)		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of:

☒ the international application in the language in which it was filed.

☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).

c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (see Box No. II).

3. ☐ **Unity of invention is lacking** (see Box No. III).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the **drawings**,

a. the figure of the **drawings** to be published with the abstract is Figure No. 1

☒ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

b. ☐ none of the figures is to be published with the abstract.

Form PCT/ISA/210 (first sheet) (July 2019)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 20/41540

A. CLASSIFICATION OF SUBJECT MATTER
IPC - A61K 8/87; A61Q 19/00; C08G 18/72 (2020.01)
CPC - A61K 8/87; A61Q 19/00; C08G 18/72; C08G 18/32; C08G 2220/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,661,099 A (von Bittera et al.) 28 April 1987 (28.04.1987); entire document, but especially: col 1 lines 7-16, col 6 lines 42-44, col 7 lines 39-41, col 7 lines 44-45, col 7 line 57, example 1, example 5	1, 5, 22, 27, 33/(1), 36/(1), 37/(1)
X	US 2018/0208720 A1 (Mitsui Chemicals, Inc.) 26 July 2018 (26.07.2018); para [0013], entire document, but especially: para [0013], para [0014], para [0084], para [0111], para [0112], para [0114], para [0129], para [0204], para [0255]- para [0259], para [0353], table 1, production example 3, example 6	1, 6, 10-11, 22, 26, 28, 35
X --- Y	EP 1 142 959 A1 (Dai-Ichi Kogyo Seiyaku Co., Ltd.) 10 October 2001 (10.10.2001); entire document, but especially: para [0002], para [0013], para [0017], para [0023], para [0024], para [0026], table 1	1, 5-6, 14-17, 22, 33/(6), 37/(6) --- 2-4, 7-9, 12-13, 18-21, 23-25, 29-32, 34
Y	JP 3631542 B2 (Dai-Ichi Kogyo Seiyaku Co., Ltd.) 24 December 2004 (24.12.2004); entire document, but especially: para [0001], para [0006], para [0014]	2-4, 7-9, 12-13, 23-25

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 September 2020	16 OCT 2020
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Lee Young Telephone No. PCT Helpdesk: 571-272-4300

Form PCT/ISA/210 (second sheet) (July 2019)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 20/41540

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2011/0014139 A1 (Viala et al.) 20 January 2011 (20.01.2011); entire document, but especially: para [0001], para [0031]- para [0035], para [0048], para [0113], para [0133], para [0140], para [0227]	18-21, 29-32, 34
Y	US 2012/0046358 A1 (Cheng et al.) 23 February 2012 (23.02.2012); para [0020], para [0021], para [0024], para [0034]	8, 24
A	Jones, Charla. "What Is Coco-Caprylate Doing In My Natural Skin Care Products?" Eu2Be (08 May 2015): pages 1-2 <https://eu2be.com/blogs/discover/19389252-what-is-coco-caprylate-doing-in-my-natural-skin-care-products>; page 2	8, 24
A	US 2009/0232752 A1 (Carson et al.) 17 September 2009 (17.09.2009); entire document	1-37
A	US 2019/0169390 A1 (Peterson Chemical Technology LLC) 06 June 2019 (06.07.2019); entire document	1-37
A	JP 2018-90662 A2 (Mitsui Chemicals, Inc.) 14 June 2018 (14.06.2018); entire document	1-37

Form PCT/ISA/210 (continuation of second sheet) (July 2019)

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
18/066,105	**01/09/2025 08:09:51 AM Z ET**	**GRAN-1012-U-D**

Title of Invention

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	1563	FILED BY	Yu Jin In
PATENT CENTER #	68648899	FILING DATE	12/14/2022
CUSTOMER #	20311	FIRST NAMED INVENTOR	Anna K. CROOM
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Michael Mercanti

Documents

TOTAL DOCUMENTS: 21

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
JPH05262622A.pdf	6	Foreign Reference	352 KB
JPH04320457A.pdf	6	Foreign Reference	814 KB
JP2008201698A.pdf	15	Foreign Reference	787 KB
JP2017114773A.pdf	33	Foreign Reference	1605 KB
JP2011178693A.pdf	28	Foreign Reference	1584 KB
EP2759572A1.pdf	38	Foreign Reference	2198 KB
JP2008260722A.pdf	28	Foreign Reference	1326 KB
JP2018199653A.pdf	12	Foreign Reference	543 KB
JP2008239542A.pdf	23	Foreign Reference	1176 KB
WO2018122532A1.pdf	31	Foreign Reference	2150 KB

EP_3778690_A1.pdf	35	Foreign Reference	2419 KB
EP_2365024_A1.pdf	14	Foreign Reference	1028 KB
EP_3778689_A1.pdf	32	Foreign Reference	2241 KB
EP_2380557_A1.pdf	20	Foreign Reference	1172 KB
WO_2016090081_A1.pdf	58	Foreign Reference	4340 KB
WO_2008039466_A1.pdf	48	Foreign Reference	3902 KB
Srivastava.pdf	12	Non Patent Literature	664 KB
ISR_PCTUS2020041540.pdf	3	Other reference-Patent/Application/Search Documents	129 KB
EPSearchReport.pdf	13	Other reference-Patent/Application/Search Documents	466 KB
MUTLU.pdf	21	Non Patent Literature	2672 KB
GRAN-1012-U-D_SUPPL-IDS.pdf	6	Information Disclosure Statement (IDS) Form (SB08)	1314 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
JPH05262622A.pdf	6B9BAF692B00FF84370DFA22A9A82F11071C096AC9F1349B442BA4701DBDBD6CAC59248786DD003CD46B5DF50DB9F3985646ED8EF225EB85BE518B0F86B60E80
JPH04320457A.pdf	94A2BF5AF0CEEFC91CDC2D80C6B5F6EDDB965CD99A8422BAC72465ACEE3560F3F884EAB220C9C1D225DD2D7C70E80D3E4555D978D0FD7D6D1B99D40FBB0A109A
JP2008201698A.pdf	07AAC500977FB01CEBEB37484241322E7AEF7D0E009FCFF04DE3E2CE4D1DA6F3564F36CB2BB0BE92A57B6DA5B9435BA0F1DAAED25D2D0279C174DF5DC99ED20D
JP2017114773A.pdf	92E3D81ED55D8DEF393D99C8D303DEFC726E5D71CBC861E6B7D6894E6357A789341A6E7414B377F5E1B654F79D73CDA495059694A244E8F19FC4B42836CEDF4B
JP2011178693A.pdf	292EF7BFCFB8702EF61155243A722823CDC678AABD048B5C57E0ECC75E4972096DF0B09065FCD20A68DCF557C1CB64B0E4CB80D2945A890126A85D87FA7871E3
EP2759572A1.pdf	C3AC93CEFC789AE612E74ED3D4CD1221BEC2BAA818638908FA9A15EDBD4A368E1B57A640619F1428634A6A0095002789D

	0BD09DD4D476AC101487E0960AA6B0A
JP2008260722A.pdf	63213132269769D678BB5848502F659C6AE8CC9896000AEF5C 8D0B3EAFB26FAD5CD187016330BFD8C1517BB4319779ED20 0F9CE35BCF8B2347E797B774A0677D
JP2018199653A.pdf	5061529EDB1B5F1EE5CA9E564542AC6DC5522EC99AC673C4 79083EEE50AE14749207AA8448ADF60BC17780DFBC00B2A36 A9E4D0D9B9019272D92AA2BFC704005
JP2008239542A.pdf	CBBBD287E99483B49AB489AB3DFABC9227C12F95AD7E52B7 8594B428E5D0A103FD874A1A9470FB287CC3605484D2A1896 1FDFC1BC6EB38EDA9605D0E2C65451F
WO2018122532A1.pdf	35D86B86E014C7EBF54A8C8C6523523B42A55D320DF939E5D 0A26710A860EEA1077487B3037FB4651EBC18F2D4472A462A1 739D9173782C2A22E4A5D66CC9AB2
EP_3778690_A1.pdf	63DF3A52BB6A45D7348B77297EC0EFC1FCD92BD1BD9C1FF8 8906354628E128FAD8AB77BC3BF2637665025BE67879C02B69 827C92DF005910A45465597CF102D8
EP_2365024_A1.pdf	75C45985EF7275EC52F08D28CE74755BE92A07CA433C56AF4 5DBD99117FD66645321DF064115D1BC8CF05FAD835BFDEB0 D4C5D9E68A26C364CFC5884A10BE692
EP_3778689_A1.pdf	7B5A5AD7938BA79331218B51A3D504C111DFDB2CE8AB2B3C C315EDB3723997F0D9DC8B0BAEFA472FF3295F134E53495A8 5572832E64F0FE0631FB6E6823D4D38
EP_2380557_A1.pdf	0EAD2FF5C10A49837438490532222E4D6A29036DC293DB47B CF276986E63C75E79C1F04E6E5154E9A61ED46086086860544 0584DE0961F7E1F840B959D799EC3
WO_2016090081_A1.pdf	7C4B5316618D71C1B92BC62083342A2770750049FA1E35B558 370E9FB4D571EE37F6F9DD0E4B417F4459A0544A26596F219 E964F8097A0A45220CFD0589A9443
WO_2008039466_A1.pdf	22022A4005A77F85F17A2918E0C58D80AA1D2F151DFFFDEF8 491329A983758CB8B16B81C978F8CBC6ECA0227210110B54A 91F0909BBE4FD7FAA577F09DA2A451
Srivastava.pdf	40C6F70B21A1BDA59ABCC8305A801F8029D8E35560C683C7F 2B99C1E04A4E7DE9D3EA2860A281E43B2D65F8F2FA3E03802 FD73F5D7D24B4C17244B864D2006AD
ISR_PCTUS2020041540.pdf	9A3DB255982E6661EA81C1147747386D5E602C1CE4E6CF72B D954CA62FA067B290129FD3B3A0366BF22751DB58F2FCAC02 E1E4ADEB63E98B982872AB4D00A548
EPSearchReport.pdf	B0566488E278E9ABC9855B0930909A41CDB34F0D2BAD6EB0 ABA6ACA7E424BAC7CDFC5F8379AFEA6B604AE27F858FC4E 7FD4F335B2D1D218931EB418B387C6C55

MUTLU.pdf	80E70074701E732CB39C3FEAA67343D5235233FE86DC1BB5A C695D91B727E73F706D356F41A4C3692EF042B761204168B57 952096E116534A2CAACA3152949C2
GRAN-1012-U-D_SUPPL-IDS.pdf	FCB2E49D9F1FB7A352D86E99CA7F816BE72A4EA9CCD89828 E1A779DF125F355091D1F2982343A51113A5B444158004BBDF 160B271CB4D0914BF3B28393CE8318

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 778 690 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
17.02.2021 Bulletin 2021/07

(21) Application number: **19781383.5**

(22) Date of filing: **02.04.2019**

(51) Int Cl.:
C08G 18/73 *(2006.01)* ***C08G 18/08*** *(2006.01)*
C08G 18/48 *(2006.01)* ***C08G 18/79*** *(2006.01)*

(86) International application number:
PCT/JP2019/014590

(87) International publication number:
WO 2019/194162 (10.10.2019 Gazette 2019/41)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **05.04.2018 JP 2018073421**

(71) Applicant: **Mitsui Chemicals, Inc.**
Minato-ku
Tokyo 105-7122 (JP)

(72) Inventors:
- **TAGO, Hiroaki**
  Sodegaura-shi, Chiba 299-0265 (JP)
- **KANAYAMA, Hiroshi**
  Sodegaura-shi, Chiba 299-0265 (JP)
- **KAJIURA, Makoto**
  Sodegaura-shi, Chiba 299-0265 (JP)

(74) Representative: **Hoffmann Eitle**
Patent- und Rechtsanwälte PartmbB
Arabellastraße 30
81925 München (DE)

(54) POLYURETHANE GEL MATERIAL, POLYURETHANE GEL, PSEUDO-BIOLOGICAL MATERIAL, AND PRODUCTION METHOD FOR POLYURETHANE GEL

(57) A polyurethane gel material includes an aliphatic polyisocyanate (A) having an average functionality of 2.3 or more and 3.2 or less, a polyol (B) having an average functionality of 2.0 or more and 2.3 or less, and a plasticizer (C) having an ester group. The aliphatic polyisocyanate (A) contains an isocyanurate derivative of an aliphatic diisocyanate and/or an alcoholic modified isocyanurate derivative of an aliphatic diisocyanate. The polyol (B) contains a polyoxyalkylene (carbon number of 2 to 3) polyol having an ethylene oxide content of 30% by mass or less, and/or a polytetramethylene ether glycol. The polyol (B) has an average hydroxyl value of 30 mgKOH/g or more and 70 mgKOH/g or less. A ratio of the plasticizer (C) per 100 parts by mass of the polyol component (B) is 50 parts by mass or more and 400 parts by mass or less.

EP 3 778 690 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to a polyurethane gel material, a polyurethane gel, a pseudo-biomaterial, and a method for producing a polyurethane gel.

BACKGROUND ART

[0002] Conventionally, polyurethane gels of low hardness have been used in the fields of vibration-proof and quake-isolation members, shock absorbing members, cushioning members, surface protection members, and the like.

[0003] Since flexibility is required for such a polyurethane gel, a plasticizer is usually added thereto. However, the plasticizer may bleed, resulting in a problem that the surface of the polyurethane gel is greasy.

[0004] Therefore, for example, as a polyurethane gel without containing a plasticizer, an ultra-low hardness thermosetting polyurethane elastomer forming composition obtained by reacting a nurate-type polyisocyanate (A) having an average functionality of 2.5 to 3.5 with a modified polytetramethylene glycol (B) having a number average molecular weight of 800 to 5000 at a NCO/ OH equivalent ratio of (A) to (B) of below 1.0 and having an Asker C hardness of 50 or less has been proposed (ref: for example, Patent Document 1 below).

[0005] However, in the ultra-low hardness thermosetting polyurethane elastomer forming composition of Patent Document 1 described below, there is no bleeding of the plasticizer, while the pressure-sensitive adhesive properties (tackiness) of the surface is high, resulting in inconvenience in handleability. Therefore, it is required to suppress the bleeding of the plasticizer and to reduce the surface tackiness.

[0006] Therefore, it has been proposed to cover a polyurethane gel by a surface layer, and specifically, a polyurethane gel including a gel layer and a coating layer for covering the gel layer has been proposed (ref: for example, Patent Document 2 below). The gel layer is obtained by at least reacting an aliphatic polyisocyanate having an average functionality of above 2.0 with a polyol having an average functionality of 3.0 or less, and the coating layer is obtained by at least reacting an aliphatic diisocyanate and/or an alicyclic diisocyanate with a bifunctional active hydrogen compound.

Citation List

Patent Document

[0007]

Patent Document 1: Japanese Unexamined Patent Publication No. 2011-79985
Patent Document 2: International Publication WO2017/010422

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0008] On the other hand, in order to improve productivity of the polyurethane gel, it has been considered to remove a skin layer in the polyurethane gel described in Patent Document 2 described above.

[0009] In other words, there is a demand for the polyurethane gel capable of suppressing bleeding of the plasticizer and reducing the surface tackiness even without the skin layer.

[0010] In addition, curability, mechanical properties (elongation etc.), appropriate hardness, and the like are required for the polyurethane gel in accordance with the application.

[0011] The present invention provides a polyurethane gel material capable of suppressing bleeding of a plasticizer, reducing surface tackiness, and obtaining a polyurethane gel excellent in curability, mechanical properties, and hardness; a polyurethane gel obtained from the polyurethane gel material; a pseudo-biomaterial; and a method for producing a polyurethane gel.

MEANS FOR SOLVING THE PROBLEM

[0012] The present invention [1] includes a polyurethane gel material including an aliphatic polyisocyanate (A) having an average functionality of 2.3 or more and 3.2 or less, a polyol (B) having an average functionality of 2.0 or more and 2.3 or less, and a plasticizer (C) having an ester group, wherein the aliphatic polyisocyanate (A) contains an isocyanurate derivative of an aliphatic diisocyanate and/or an alcoholic modified isocyanurate derivative of an aliphatic diisocyanate,

the polyol (B) contains a polyoxyalkylene (carbon number of 2 to 3) polyol having an ethylene oxide content of 30% by mass or less, and/or a polytetramethylene ether glycol, the polyol (B) has an average hydroxyl value of 30 mgKOH/g or more and 70 mgKOH/g or less, and a ratio of the plasticizer (C) per 100 parts by mass of the polyol component (B) is 50 parts by mass or more and 400 parts by mass or less.

[0013] The present invention [2] includes the polyurethane gel material described in the above-described [1], wherein the polyol (B) has an average functionality of 2.0.

[0014] The present invention [3] includes the polyurethane gel material described in the above-described [1] or [2], wherein the polyol (B) has an average hydroxyl value of 37 mgKOH/g or more and 56 mgKOH/g or less.

[0015] The present invention [4] includes the polyurethane gel material described in any one of the above-described [1] to [3], wherein the aliphatic polyisocyanate (A) has an average functionality of 2.3 or more and 3.0 or less.

[0016] The present invention [5] includes the polyurethane gel material described in any one of the above-described [1] to [4], wherein the aliphatic diisocyanate includes a pentamethylene diisocyanate and/or a hexamethylene diisocyanate.

[0017] The present invention [6] includes the polyurethane gel material described in any one of the above-described [1] to [5], wherein a ratio of the plasticizer (C) per 100 parts by mass of the polyol component (B) is 100 parts by mass or more and 200 parts by mass or less.

[0018] The present invention [7] includes the polyurethane gel material described in any one of the above-described [1] to [6], wherein the plasticizer (C) is cyclohexanedicarboxylic acid esters and/or adipic acid esters.

[0019] The present invention [8] includes a polyurethane gel being a reaction product of the polyurethane gel material described in any one of the above-described [1] to [7].

[0020] The present invention [9] includes the polyurethane gel described in the above-described [8], wherein in the polyurethane gel material, an equivalent ratio (NCO/ hydroxyl group) of an isocyanate group in an aliphatic polyisocyanate (A) to a hydroxyl group in a polyol (B) is 0.8 or more and 1.2 or less.

[0021] The present invention [10] includes a pseudo-biomaterial including the polyurethane gel described in the above-described [8] or [9].

[0022] The present invention [11] includes a method for producing a polyurethane gel including a preparation step of preparing the polyurethane gel material described in any one of above-described [1] to [7] and a reaction step of reacting and curing the polyurethane gel material to obtain a polyurethane gel, wherein in the reaction step, an equivalent ratio (NCO/ hydroxyl group) of an isocyanate group in an aliphatic polyisocyanate (A) to a hydroxyl group in a polyol (B) is 0.8 or more and 1.2 or less.

EFFECT OF THE INVENTION

[0023] According to the polyurethane gel material of the present invention, it is possible to obtain a polyurethane gel which suppresses bleeding of a plasticizer, can reduce surface tackiness, and is excellent in curability, mechanical properties, and hardness.

[0024] In addition, the polyurethane gel of the present invention suppresses bleeding of a plasticizer, can reduce surface tackiness, and is excellent in curability, mechanical properties, and hardness.

[0025] Further, according to the method for producing a polyurethane gel of the present invention, it is possible to obtain a polyurethane gel which suppresses bleeding of a plasticizer, can reduce surface tackiness, and is excellent in curability, mechanical properties, and hardness.

DESCRIPTION OF EMBODIMENTS

[0026] A polyurethane gel material of the present invention is a material which gels by a urethanization reaction to be described later and forms a polyurethane gel (described later). In other words, the polyurethane gel material is a raw material composition of a polyurethane gel (described later).

[0027] The polyurethane gel material contains an aliphatic polyisocyanate (A) having an average functionality of 2.3 or more and 3.2 or less, a polyol (B) having an average functionality of 2.0 or more and 2.3 or less, and a plasticizer (C) having an ester group. Preferably, the polyurethane gel material contains only an aliphatic polyisocyanate (A) having an average functionality of 2.3 or more and 3.2 or less, a polyol (B) having an average functionality of 2.0 or more and 2.3 or less, and a plasticizer (C) having an ester group.

[0028] A functional group of the aliphatic polyisocyanate (A) indicates an isocyanate group. The functional group of the polyol (B) indicates a hydroxyl group.

[0029] The aliphatic polyisocyanate (A) contains an isocyanurate derivative and/or an alcoholic modified isocyanurate derivative of an aliphatic diisocyanate, preferably, contains an alcoholic modified isocyanurate derivative.

[0030] Since the aliphatic polyisocyanate (A) has both an aliphatic hydrocarbon group and an isocyanurate group, it imparts appropriate flexibility to the polyurethane gel by the aliphatic hydrocarbon group, also imparts appropriate rigidity

and polarity by the isocyanurate group, and can impart affinity to the plasticizer (C), and further, the average functionality can be adjusted within a range to be described later.

[0031] Examples of the aliphatic diisocyanate include trimethylene diisocyanate, 1,2-propylene diisocyanate, butylene diisocyanate (tetramethylene diisocyanate, 1,2-butylene diisocyanate, 2,3-butylene diisocyanate, 1,3-butylene diisocyanate), pentamethylene diisocyanate (PDI), hexamethylene diisocyanate (HDI), 2,4,4- or 2,2,4-trimethylhexamethylene diisocyanate, and 2,6-diisocyanatemethylcaproate.

[0032] These aliphatic diisocyanates may be used alone or in combination of two or more.

[0033] As the aliphatic diisocyanate, from the viewpoint of improvement of mechanical properties, preferably, a pentamethylene diisocyanate (PDI) and a hexamethylene diisocyanate (HDI) are used, and further, from the viewpoint of improvement of bleeding resistance, low tackiness, mechanical properties, and hardness, more preferably, a pentamethylene diisocyanate (PDI) is used.

[0034] In other words, when the pentamethylene diisocyanate (PDI) is used as the aliphatic diisocyanate, the polyurethane gel excellent in bleeding resistance, low tackiness, mechanical properties, and hardness can be obtained.

[0035] Then, the isocyanurate derivative of the aliphatic diisocyanate can be obtained by isocyanurating the above-described aliphatic diisocyanate by a known method.

[0036] More specifically, the isocyanurate derivative of the aliphatic diisocyanate can be obtained, for example, by reacting the aliphatic diisocyanate in the presence of a known isocyanuration catalyst (e.g., N-(2-hydroxypropyl)-N,N,N-trimethylammonium-2-ethylhexanoate etc.) and subjecting it to an isocyanuration reaction.

[0037] The reaction conditions in the isocyanuration reaction are not particularly limited and are appropriately set.

[0038] The alcoholic modified isocyanurate derivative of the aliphatic diisocyanate can be obtained by modifying the isocyanurate derivative of the aliphatic diisocyanate with alcohols.

[0039] The alcohols are not particularly limited, and examples thereof include aliphatic alcohols and aromatic alcohols. Preferably, aliphatic alcohols are used. Specific examples thereof include monohydric aliphatic alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol (isobutyl alcohol), sec-butanol, tert-butanol, pentanol, hexanol, 2-ethylhexanol, octanol, and decanol; dihydric aliphatic alcohols such as ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butylene glycol 1,4-butylene glycol, 1,5-pentanediol, and 1,6-hexanediol; trihydric aliphatic alcohols such as glycerine and trimethylolpropane; and tetrahydric or more aliphatic alcohols such as tetramethylolmethane.

[0040] These alcohols may be used alone or in combination of two or more. As the alcohols, preferably, a monohydric aliphatic alcohol is used, more preferably, a monohydric aliphatic alcohol having carbon number of 1 to 4 is used, further more preferably, isobutanol (another name: isobutyl alcohol) is used.

[0041] As a method for modifying the isocyanurate derivative of the aliphatic diisocyanate with the alcohols, for example, a method for first reacting the aliphatic diisocyanate with the alcohols and then, subjecting the obtained reaction product to an isocyanuration reaction in the presence of an isocyanuration catalyst, and a method for first isocyanurating only the aliphatic diisocyanate and then, reacting the obtained polyisocyanurate with the alcohols are used.

[0042] Preferably, first, an aliphatic diisocyanate and alcohols are reacted, and then, an isocyanuration reaction is carried out in the presence of an isocyanuration catalyst.

[0043] In such a reaction, a mixing ratio of the aliphatic diisocyanate to the alcohols is appropriately set in accordance with the purpose and the application, and the mixing ratio of the alcohols per 100 parts by mass of the aliphatic diisocyanate is, for example, 0.1 parts by mass or more, preferably 0.5 parts by mass or more, more preferably 1.0 part by mass or more, and for example, 10 parts by mass or less, preferably 5 parts by mass or less, more preferably 2 parts by mass or less, further more preferably 1.5 parts by mass or less.

[0044] Further, the reaction conditions of the aliphatic diisocyanate and the alcohols are appropriately set in accordance with the purpose and the application.

[0045] The reaction of the aliphatic diisocyanate with the alcohols is a urethanization reaction and an allophanatization reaction, and an allophanate derivative of the aliphatic diisocyanate may be generated as a by-product. In other words, the isocyanurate derivative of the aliphatic diisocyanate modified by the alcohols may have both an isocyanurate group and an allophanate group.

[0046] In such a case, a mole ratio of the allophanate group in the alcoholic modified isocyanurate derivative of the aliphatic diisocyanate is less than that of the isocyanurate group, and specifically, the mole ratio of the allophanate group per 1 mol of the isocyanurate group is, for example, 0.05 mol or more, preferably 0.1 mol or more, more preferably 0.2 mol or more, and for example, below 1.0 mol, preferably 0.5 mol or less.

[0047] When the mole ratio of the allophanate group is within the above-described range, improvement in mechanical properties and heat resistance can be achieved.

[0048] The mole ratio of the allophanate group to the isocyanurate group can be determined in conformity with Examples to be described later.

[0049] In addition, in the above-described reaction, if necessary, for example, a known additive such as a storage stabilizer (o-toluenesulfonamide, p-toluenesulfonamide, etc.), a reaction terminator (benzoyl chloride etc.), an anti-blocking agent, a heat-resistant stabilizer, a light-resistant stabilizer, an ultraviolet absorber, an antioxidant, a defoaming

agent, a mold release agent, a pigment, a dye, a lubricant, a filler, and a hydrolysis inhibitor can be further blended at an appropriate ratio.

[0050] Further, after completion of the above-described reaction, if necessary, the unreacted aliphatic diisocyanate can be also, for example, removed by a known method such as distillation including thin film distillation (Smith distillation) or extraction.

[0051] A content ratio of the unreacted aliphatic diisocyanate (isocyanate monomer concentration) with respect to the total amount of the reaction liquid obtained in the above-described reaction is, for example, 1% by mass or less, preferably 0.5% by mass or less.

[0052] Further, the aliphatic polyisocyanate (A) may further contain another derivative as long as it contains the isocyanurate derivative and/or the alcoholic modified isocyanurate derivative of the aliphatic diisocyanate.

[0053] The other derivative is s derivative of the aliphatic diisocyanate excluding the isocyanurate derivative and the alcoholic modified isocyanurate derivative of the aliphatic diisocyanate. Examples thereof include an allophanate derivative of an aliphatic diisocyanate, a uretdione derivative of an aliphatic diisocyanate, a urea derivative of an aliphatic diisocyanate, a carbodiimide derivative of an aliphatic diisocyanate, a biuret derivative of an aliphatic diisocyanate, an oxadiazine trione derivative of an aliphatic diisocyanate, a uretonimine derivative of an aliphatic diisocyanate, and a polyol modified product of an aliphatic diisocyanate.

[0054] These other derivatives may be used alone or in combination of two or more.

[0055] As the other derivative, preferably, an allophanate derivative of an aliphatic diisocyanate is used.

[0056] The allophanate derivative of the aliphatic diisocyanate can be obtained by subjecting the above-described aliphatic diisocyanate and the above-described alcohols (preferably, the monohydric aliphatic alcohol) to a urethanization reaction, and then, subjecting the reacted product to an allophanatization reaction in the presence of a known allophanatization catalyst (e.g., bismuth octylate, tris(2-ethylhexanoic acid) bismuth, etc.). The reaction conditions in the urethanization reaction and the allophanatization reaction are not particularly limited and are appropriately set.

[0057] A content ratio of the other derivative (preferably, an allophanate derivative) is appropriately set in accordance with the purpose and the application as long as it does not damage the excellent effect of the present invention. The content ratio of the other derivative per 100 parts by mass of the total amount of the aliphatic polyisocyanate (A) is, for example, 0 part by mass or more, and for example, 50 parts by mass or less, preferably 40 parts by mass or less, more preferably 20 parts by mass or less.

[0058] Further, the aliphatic polyisocyanate (A) may contain an aliphatic polyisocyanate monomer, if necessary.

[0059] An example of the aliphatic polyisocyanate monomer includes the above-described aliphatic diisocyanate (bifunctional aliphatic polyisocyanate monomer).

[0060] These aliphatic polyisocyanate monomers may be used alone or in combination of two or more.

[0061] A content ratio of the aliphatic polyisocyanate monomer is appropriately set in accordance with the purpose and the application as long as it does not damage the excellent effect of the present invention. The content ratio of the aliphatic polyisocyanate monomer per 100 parts by mass of the total amount of the aliphatic polyisocyanate (A) is, for example, 0 part by mass or more, and for example, 50 parts by mass or less, preferably 40 parts by mass or less, more preferably 20 parts by mass or less.

[0062] Then, in the aliphatic polyisocyanate (A), a ratio of the isocyanurate derivative and/or the alcoholic modified isocyanurate derivative of the aliphatic diisocyanate, the other derivative, and the aliphatic polyisocyanate monomer is appropriately adjusted so that the average functionality of the aliphatic polyisocyanate (A) is within a range of 2.3 to 3.2 as long as it does not damage the excellent effect of the present invention.

[0063] More specifically, the ratio of the isocyanurate derivative and/or the alcoholic modified isocyanurate derivative of the aliphatic diisocyanate per 100 parts by mass of the total amount of the aliphatic polyisocyanate (A) is, for example, 50 parts by mass or more, preferably 60 parts by mass or more, more preferably 80 parts by mass or more, and for example, 100 parts by mass or less. The ratio of the other derivative and/or the aliphatic polyisocyanate monomer per 100 parts by mass of the total amount of the aliphatic polyisocyanate (A) is, for example, 0 part by mass or more, and for example, 50 parts by mass or less, preferably 40 parts by mass or less, more preferably 20 parts by mass or less.

[0064] In addition, from the viewpoint of bleeding resistance and mechanical properties, preferably, the aliphatic polyisocyanate (A) consists of an isocyanurate derivative and/or an alcoholic modified isocyanurate derivative of an aliphatic diisocyanate, more preferably, an alcoholic modified isocyanurate derivative of an aliphatic diisocyanate, further more preferably, an alcoholic modified isocyanurate derivative of a pentamethylene diisocyanate (the inclusion of an allophanate derivative (allophanate derivative without containing an isocyanurate group) and a uretdione derivative by-produced at the time of producing an isocyanurate derivative is allowed).

[0065] From the viewpoint of curability and mechanical properties, an average functionality of the aliphatic polyisocyanate (A) is 2.3 or more, preferably 2.5 or more, more preferably 2.6 or more, further more preferably 2.7 or more, and 3.2 or less, preferably 3.1 or less, more preferably 3.0 or less, and further more preferably 2.9 or less.

[0066] That average functionality of the aliphatic polyisocyanate (A) is calculated in conformity with Examples to be described later.

[0067] Further, the isocyanate group concentration of the aliphatic polyisocyanate (A) is, for example, 20.0% by mass or more, preferably 22.0% by mass or more, and for example, 30.0% by mass or less, preferably 25.0% by mass or less, more preferably 24.6% by mass or less.

[0068] The polyol (B) contains a polyoxyalkylene (carbon number of 2 to 3) polyol having an ethylene oxide content of 30% by mass or less, and/or a polytetramethylene ether glycol. When the polyol (B) contains these, a flexible polyurethane gel can be obtained.

[0069] The polyoxyalkylene (carbon number of 2 to 3) polyol is, for example, an addition polymer of an alkylene oxide having a carbon number of 2 to 3 using a low molecular weight polyol, a known low molecular weight polyamine, or the like as an initiator.

[0070] A low molecular weight polyol is, for example, a compound having 2 or more hydroxyl groups in a molecule and having a molecular weight of 50 or more and 400 or less. Examples thereof include dihydric alcohols such as ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butylene glycol, 1,3-butylene glycol, 1,2-butylene glycol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 3-methyl-1,5-pentanediol, 2,2,2-trimethylpentanediol, 3,3-dimethylolheptane, alkane (C7-20) diol, 1,3- or 1,4-cyclohexanedimethanol and mixtures thereof, 1,3- or 1,4-cyclohexanediol and mixtures thereof, hydrogenated bisphenol A, 1,4-dihydroxy-2-butene, 2,6-dimethyl-1-octen-3,8-diol, bisphenol A, diethylene glycol, triethylene glycol, and dipropylene glycol; trihydric alcohols such as glycerine, trimethylolpropane, and triisopropanolamine; and tetrahydric alcohols such as tetramethylolmethane (pentaerythritol) and diglycerine. These low molecular weight polyols may be used alone or in combination of two or more. As the low molecular weight polyol, preferably, a dihydric alcohol and a trihydric alcohol are used, more preferably, a dihydric alcohol is used.

[0071] The polyoxyalkylene (carbon number of 2 to 3) polyol is obtained as a polyoxyalkylene polyol having an average functionality in accordance with a functionality of the initiator. For example, when an initiator having a functionality of 2 is used, a polyoxyalkylene diol having an average functionality of 2 is obtained, and when an initiator having a functionality of 3 is used, a polyoxyalkylene triol having an average functionality of 3 is obtained.

[0072] Specific examples of the alkylene oxide having a carbon number of 2 to 3 include ethylene oxide and propylene oxide. An addition format of the alkylene oxide is not particularly limited, and may be either a block or a random.

[0073] In the polyoxyalkylene (carbon number of 2 to 3) polyol, from the viewpoint of bleeding resistance, an ethylene oxide content is 30% by mass or less, preferably 20% by mass or less, more preferably 10% by mass or less, further more preferably 5% by mass or less, particularly preferably 0% by mass.

[0074] In other words, examples of the polyoxyalkylene (carbon number of 2 to 3) polyol include an addition homopolymer of the propylene oxide (polyoxypropylene polyol) and an addition copolymer of the ethylene oxide and the propylene oxide (random and/or block copolymer). In addition, in the addition copolymer of the ethylene oxide and the propylene oxide, the ethylene oxide content is within the above-described range.

[0075] The ethylene oxide content can be calculated from a charging ratio in the production of the polyoxyalkylene (carbon number of 2 to 3) polyol.

[0076] These polyoxyalkylene (carbon number of 2 to 3) polyols may be used alone or in combination of two or more.

[0077] As the polyoxyalkylene (carbon number of 2 to 3) polyol, from the viewpoint of bleeding resistance, preferably, a polyoxypropylene polyol is used.

[0078] Examples of the polytetramethylene ether glycol include a ring opening polymer (crystalline polytetramethylene ether glycol) obtained by cationic polymerization of a tetrahydrofuran, and an amorphous polytetramethylene ether glycol obtained by copolymerizing the above-described dihydric alcohol with a polymerization unit such as tetrahydrofuran. The crystallinity indicates solid at normal temperature (25°C), and the amarphousness indicates liquid at normal temperature (25°C).

[0079] The amorphous polytetramethylene ether glycol can be obtained, for example, as a copolymer (tetrahydrofuran/ alkyl substituted tetrahydrofuran (mole ratio) = 15/85 to 85/ 15) of a tetrahydrofuran and an alkyl substituted tetrahydrofuran (e.g., 3-methyltetrahydrofuran etc.) and a copolymer (tetrahydrofuran/ branched glycol (mole ratio) = 15/ 85 to 85/ 15) of a tetrahydrofuran and a branched glycol (e.g., neopentyl glycol etc.).

[0080] Further, as the amorphous polytetramethylene ether glycol, a commercially available product can be used, and examples of such a commercially available product include the "PTXG" series manufactured by ASAHI KASEI FIBERS CORPORATION and the "PTG-L" series manufactured by Hodogaya Chemical Co., Ltd.

[0081] Also, a plant-derived polytetramethylene ether glycol using a tetrahydrofuran produced based on a plant-derived raw material such as furfural as a starting material can be used.

[0082] As the polytetramethylene ether glycol, from the viewpoint of mechanical properties and hardness, preferably, an amorphous polytetramethylene ether glycol is used, and from the viewpoint of bleeding resistance and low tackiness, preferably, a crystalline polytetramethylene ether glycol is used.

[0083] As the polyol (B), from the viewpoint of bleeding resistance, mechanical properties, and hardness, preferably, a polyoxypropylene glycol and a crystalline polytetramethylene ether glycol are used, more preferably, a polyoxypropylene glycol is used.

[0084] The polyol (B) may contain another polyol as long as it contains the above-described polyoxyalkylene (carbon

number of 2 to 3) polyol and/or the above-described polytetramethylene ether glycol.

[0085] Examples of the other polyol include the above-described low molecular weight polyol and a known high molecular weight polyol (excluding a polyoxyalkylene (carbon number of 2 to 3) polyol, and the above-described polytetramethylene ether glycol). The high molecular weight polyol is a compound having a molecular weight (number average molecular weight in terms of polystyrene with GPC measurement) of above 400 and having two or more hydroxyl groups. Examples thereof include polyester polyol, polycarbonate polyol, polyurethane polyol, epoxy polyol, vegetable oil polyol, polyolefin polyol, acrylic polyol, and vinyl monomer-modified polyol.

[0086] These other polyols may be used alone or in combination of two or more.

[0087] In the polyol (B), a content ratio of the other polyol is appropriately adjusted as long as it does not damage the excellent effect of the present invention.

[0088] From the viewpoint of bleeding resistance, low tackiness, mechanical properties, and hardness, the polyol (B) preferably does not contain the other polyol and consists of a polyoxyalkylene (carbon number of 2 to 3) polyol and/or a polytetramethylene ether glycol, more preferably, consists of a polyoxyalkylene (carbon number of 2 to 3) polyol.

[0089] In addition, these polyols (B) are used alone or in combination of two or more so that its average functionality and an average hydroxyl value (OH value) are within a range to be described later.

[0090] Specifically, from the viewpoint of curability, the average functionality of the polyol (B) is 2.0 or more, and from the viewpoint of mechanical properties, the average functionality of the polyol (B) is 2.3 or less, preferably 2.2 or less, more preferably 2.1 or less. From the viewpoint of bleeding resistance and low tackiness, particularly preferably, the average functionality of the polyol (B) is 2.0.

[0091] In addition, from the viewpoint of bleeding resistance and low tackiness, the average hydroxyl value (OH value) of the polyol (B) is 30 mgKOH/g or more, preferably 35 mgKOH/g or more, more preferably 37 mgKOH/g or more, further more preferably 40 mgKOH/g or more, and 70 mgKOH/g or less, preferably 65 mgKOH/g or less, more preferably 56 mgKOH/g or less.

[0092] The average functionality of the polyol (B) is calculated from the mixing formulation of the charging, and the hydroxyl value of the polyol is measured in conformity with the description of JIS K 1557-1 (2007).

[0093] In addition, from the viewpoint of curability, mechanical properties, bleeding resistance, and low tackiness, the number average molecular weight (the number average molecular weight calculated from the average functionality and the hydroxyl value) of the polyol (B) is, for example, 1600 or more, preferably 1800 or more, more preferably 2000 or more, and for example, 4300 or less, preferably 3500 or less, more preferably 3000 or less, further more preferably 2500 or less.

[0094] When the hydroxyl value and the number average molecular weight are within the above-described range, hydrophobicity can be imparted to the obtained polyurethane gel, and affinity with the plasticizer (C) can be improved to suppress bleeding.

[0095] In the polyurethane gel material, a content ratio of the aliphatic polyisocyanate (A) and the polyol (B) is adjusted so that an equivalent ratio (NCO/ hydroxyl group) of the isocyanate group in the aliphatic polyisocyanate (A) to the hydroxyl group in the polyol (B) is 0.8 to 1.2.

[0096] The plasticizer (C) has an ester group. By using the plasticizer (C) having an ester group, it is possible to improve the curability as compared with a case where a plasticizer without containing an ester group (e.g., chloroparaffin etc.) is used.

[0097] Further, when the plasticizer (C) has an ester group, the affinity for a urethane group obtained by a reaction of the aliphatic polyisocyanate (A) with the polyol (B) can be obtained.

[0098] More specifically, examples of the plasticizer (C) having an ester group include cyclohexanedicarboxylic acid esters, phthalic acid esters, isophthalic acid esters, tetrahydrophthalic acid esters, adipic acid esters, azelaic acid esters, sebacic acid esters, fumaric acid esters, maleic acid esters, trimellitic acid esters, pyromellitic acid esters, citric acid esters, itaconic acid esters, oleic acid esters, ricinoleic acid esters, stearic acid esters, other fatty acid esters, and phosphoric acid esters.

[0099] Examples of the cyclohexanedicarboxylic acid esters include dimethylcyclohexane-1,2-dicarboxylate, diethylcyclohexane-1,2-dicarboxylate, dibutylcyclohexane-1,2-dicarboxylate, di(2-ethylhexyl)cyclohexane-1,2-dicarboxylate, dioctylcyclohexane-1,2-dicarboxylate, diisodecylcyclohexane-1,2-dicarboxylate, diisononylcyclohexane-1,2-dicarboxylate, dimethylcyclohexane-1,3-dicarboxylate, diethylcyclohexane-1,3 -dicarboxylate, dibutylcyclohexane-1,3-dicarboxylate, di(3-ethylhexyl)cyclohexane-1,3-dicarboxylate, dioctylcyclohexane-1,3-dicarboxylate, diisodecylcyclohexane-1,3-dicarboxylate, diisononylcyclohexane-1,3-dicarboxylate, dimethylcyclohexane-1,4-dicarboxylate, diethylcyclohexane-1,4-dicarboxylate, dibutylcyclohexane-1,4-dicarboxylate, di(4-ethylhexyl)cyclohexane-1,4-dicarboxylate, dioctylcyclohexane-1,4-dicarboxylate, diisodecylcyclohexane-1,4-dicarboxylate, diisononylcyclohexane-1,4-dicarboxylate, 3,4-epoxy-dimethylcyclohexane-1,2-dicarboxylate, 3,4-epoxy-diethylcyclohexane-1,2-dicarboxylate, 3,4-epoxy-dibutylcyclohexane-1,2-dicarboxylate, 3,4-epoxy-di(2-ethylhexyl)cyclohexane-1,2-dicarboxylate, 4,5-epoxy-dimethylcyclohexane-1,2-dicarboxylate, 4,5-epoxy-diethylcyclohexane-1,2-dicarboxylate, 4,5-epoxy-dibutylcyclohexane-1,2-dicarboxylate, and 4,5-epoxy-di(2-ethylhexyl)cyclohexane-1,2-dicarboxylate.

[0100] Examples of the phthalic acid esters include dibutyl phthalate, isobutyl phthalate, diheptyl phthalate, di-(2-ethylhexyl) phthalate, di-n-octyl phthalate, dinonyl phthalate, diisononyl phthalate, diisodecyl phthalate, diundecyl phthalate, ditridecyl phthalate, dicyclohexyl phthalate, and diphenyl phthalate.

[0101] Examples of the isophthalic acid esters include di-(2-ethylhexyl) isophthalate and diisooctyl isophthalate.

[0102] Examples of the tetrahydrophthalic acid esters include di-(2-ethylhexyl) tetrahydrophthalate.

[0103] Examples of the adipic acid esters include di-(2-ethylhexyl) adipate, dibutoxyethyl adipate, and diisononyl adipate.

[0104] Examples of the azelaic acid esters include di-n-hexylazelate and di-(2-ethylhexyl) azelate.

[0105] Examples of the sebacic acid esters include di-n-butylsebacate.

[0106] Examples of the fumaric acid esters include di-n-butylfumarate and di-(2-ethylhexyl) fumarate.

[0107] Examples of the maleic acid esters include di-n-butylmaleate and di-(2-ethylhexyl) maleate.

[0108] Examples of the trimellitic acid esters include tri-(2-ethylhexyl) trimellitate, tri-n-octyltrimellitate, and triisooctyltrimellitate.

[0109] Examples of the pyromellitic acid esters include tetra-(2-ethylhexyl) pyromellitate and tetra-n-octylpyromellitate.

[0110] Examples of the citric acid esters include tri-n-butylcitrate and acetyltributylcitrate.

[0111] Examples of the itaconic acid esters include dimethyl itaconate, diethyl itaconate, dibutyl itaconate, and di-(2-ethylhexyl) itaconate.

[0112] Examples of the oleic acid esters include glyceryl monoolate and diethylene glycol monooleate.

[0113] Examples of the ricinoleic acid esters include glyceryl monoricinoleate and diethylene glycol monoricinoleate.

[0114] Examples of the stearic acid esters include glycerine monostearate and diethylene glycol distearate.

[0115] Examples of the other fatty acid esters include diethylene glycol dipelargonate and pentaerythritol fatty acid ester.

[0116] Examples of the phosphoric acid esters include tributoxyethyl phosphate, triphenyl phosphate, tricresyl phosphate, diphenyl decyl phosphate, and diphenyl octyl phosphate.

[0117] These plasticizers (C) having an ester group may be used alone or in combination of two or more.

[0118] As the plasticizer (C) having an ester group, from the viewpoint of curability and bleeding resistance, preferably, cyclohexanedicarboxylic acid esters, phthalic acid esters, and adipic acid esters are used, more preferably, cyclohexanedicarboxylic acid esters, adipic acid esters, and combinations of these are used, further more preferably, cyclohexanedicarboxylic acid esters are used.

[0119] A boiling point of the plasticizer (C) is, for example, 180°C or more, preferably 200°C or more, more preferably 220°C or more. The upper limit of the boiling point is about 400°C from the viewpoint of industrial availability.

[0120] In the polyurethane gel material, from the viewpoint of bleeding resistance, low tackiness, and hardness, a content ratio of the plasticizer (C) having an ester group per 100 parts by mass of the polyol component (B) is 50 parts by mass or more, preferably 80 parts by mass or more, more preferably 100 parts by mass or more, further more preferably 150 parts by mass or more, and 400 parts by mass or less, preferably 300 parts by mass or less, more preferably 250 parts by mass or less, further more preferably 200 parts by mass or less.

[0121] According to such a polyurethane gel material, it is possible to obtain the polyurethane gel which suppresses the bleeding of the plasticizer, can reduce the surface tackiness, and is excellent in curability, mechanical properties, and hardness.

[0122] When the content ratio of the plasticizer (C) is relatively large, preferably, the polyol (B) having a relatively high average hydroxyl value is used.

[0123] For example, when the content ratio of the plasticizer (C) is 300 parts by mass or more per 100 parts by mass of the polyol component (B), the average hydroxyl value of the polyol (B) is preferably 40 mgKOH/g or more, more preferably 50 mgKOH/g or more, more preferably 55 mgKOH/g or more, and 70 mgKOH/g or less.

[0124] Then, in order to obtain the polyurethane gel, first, the above-described polyurethane gel material is prepared (preparation step), then, the aliphatic polyisocyanate (A) and the polyol (B) are put into a predetermined metal mold together with the plasticizer (C) having an ester group, and preferably, the obtained mixture is subjected to a urethanization reaction (solvent-free reaction, bulk polymerization) in the absence of a solvent (reaction step).

[0125] In the urethanization reaction, for example, a known method such as a one-shot method and a prepolymer method is used, preferably, a one-shot method is used.

[0126] In the one-shot method, for example, the aliphatic polyisocyanate (A) and the polyol (B) are formulated (mixed) so that an equivalent ratio (NCO/ hydroxyl group) of the isocyanate group in the aliphatic polyisocyanate (A) to the hydroxyl group in the polyol (B) is 0.8 or more, preferably 0.9 or more, and 1.2 or less, preferably 1.1 or less, more preferably 1.05 or less, and then, the obtained mixture is subjected to a curing reaction at, for example, room temperature to 120°C, preferably at room temperature to 100°C, for, for example, from 5 minutes to 72 hours, preferably from 2 to 10 hours. The curing temperature may be a constant temperature, or may be raised or cooled in stages.

[0127] When the equivalent ratio (NCO/ hydroxyl group) of the isocyanate group in the aliphatic polyisocyanate (A) to the hydroxyl group in the polyol (B) is within the above-described range, both the flexibility and the shape-retaining properties (rigidity) of the polyurethane gel can be achieved, while the bleeding of the plasticizer (C) is suppressed.

[0128] In addition, in the above-described reaction, if necessary, a known urethanization catalyst such as amines and an organic metal compound can be, for example, added.

[0129] Examples of the amines include tertiary amines such as triethylamine, triethylenediamine, bis-(2-dimethylaminoethyl) ether, and N-methylmorpholine; quaternary ammonium salts such as tetraethylhydroxylammonium; and imidazoles such as imidazole and 2-ethyl-4-methylimidazole.

[0130] Examples of the organic metal compound include organic tin compounds such as tin acetate, tin octylate, tin oleate, tin laurate, dibutyltin diacetate, dimethyltin dilaurate, dibutyltin dilaurate, dibutyltin dimercaptide, dibutyltin maleate, dibutyltin dilaurate (dibutyltin dilaurate (IV)), dibutyltin dineodecanoate, dioctyltin dimercaptide, dioctyltin dilaurate, and dibutyltin dichloride; organic lead compounds such as lead octanoate and lead naphthenate; organic nickel compounds such as nickel naphthenate; organic cobalt compounds such as cobalt naphthenate; organic copper compounds such as copper octenate; and organic bismuth compounds such as bismuth octylate and bismuth neodecanoate.

[0131] Further, examples of the urethanization catalyst include potassium salts such as potassium carbonate, potassium acetate, and potassium octylate.

[0132] These urethanization catalysts may be used alone or in combination of two or more.

[0133] As the urethanization catalyst, preferably, an organic metal compound is used, more preferably, an organic tin compound is used, further more preferably, dibutyltin dilaurate (dibutyltin dilaurate (IV)) is used.

[0134] The timing of addition of the urethanization catalyst is not particularly limited, and may be, for example, added in advance to both or either of the aliphatic polyisocyanate (A) and the polyol (B), may be added simultaneously with the formulation thereof, and further, may be added separately after blending them.

[0135] Further, an addition ratio of the urethanization catalyst is not particularly limited, and is appropriately set in accordance with the purpose and the application.

[0136] In addition, in the above-described reaction, if necessary, a known additive such as a storage stabilizer (o-toluenesulfonamide, p-toluenesulfonamide, etc.), an anti-blocking agent, a heat-resistant stabilizer, a light-resistant stabilizer, an ultraviolet absorber, an antioxidant, a defoaming agent, a mold release agent, a pigment, a dye, a lubricant, a filler, and a hydrolysis inhibitor can be, for example, further blended at an appropriate ratio.

[0137] The timing of addition of the additive is not particularly limited, and may be, for example, added in advance to both or either of the aliphatic polyisocyanate (A) and the polyol (B), may be added simultaneously with the formulation thereof, and further, may be added separately after blending them. Further, an addition ratio of the additive is not particularly limited, and is appropriately set in accordance with the purpose and the application.

[0138] Such a polyurethane gel contains a polyurethane which is a reaction product of the aliphatic polyisocyanate (A) and the polyol (B), and the plasticizer (C), has high viscosity due to the higher order structure (three dimensional network) of the polyurethane, loses fluidity due to the inclusion of the plasticizer (C) in the polyurethane, and becomes a solid state as a whole of the system.

[0139] A shear elastic modulus at 25°C of the polyurethane gel is 1×10^3 to 1×10^7 Pa. The shear elastic modulus is measured with a solid viscoelasticity measurement device.

[0140] Such a polyurethane gel includes the plasticizer (C) having an ester group at a specific ratio in a higher order structure (three dimensional network) of the polyurethane formed by a reaction of the aliphatic polyisocyanate (A) having a specific average functionality with the polyol (B) having a specific average functionality. As a result, the plasticizer (C) is confined in the three dimensional network. As a result, the polyurethane gel can achieve both suppression of the bleeding resistance and reduction of the surface tackiness.

[0141] In other words, since the above-described polyurethane gel is obtained from the above-described polyurethane gel material, the bleeding of the plasticizer can be suppressed, the surface tackiness can be reduced, and the curability, the mechanical properties, and the hardness are excellent.

[0142] Further, according to the above-described method for producing a polyurethane gel, it is possible to obtain the polyurethane gel which suppresses the bleeding of the plasticizer, can reduce the surface tackiness, and is excellent in curability, mechanical properties, and hardness.

[0143] A size of the polyurethane gel is set in accordance with the type of the metal mold to be used, and the like, and the thickness thereof is, for example, 0.03 mm or more, preferably 0.05 mm or more, and for example, 500 mm or less, preferably 400 mm or less.

[0144] Also, the above-described polyurethane gel may be also, for example, coated on a substrate such as leather, artificial or synthetic leather, nonwoven fabric, felt, sheet, film, or the like.

[0145] Specifically, the polyurethane gel is an ultra-low hardness polyurethane elastomer, and the Asker C hardness (JIS K 7312 (1996)) thereof is, for example, 0 or more, and for example, 40 or less, preferably 30 or less, more preferably 20 or less, further more preferably 15 or less, further more preferably 12 or less, particularly preferably 10 or less.

[0146] When the Asker C hardness is within the above-described range, especially 40 or less, it can be particularly preferably used as a gel with a feel, elasticity and flexibility that is close to human skin.

[0147] Further, such a polyurethane gel can be also further used by being encapsulated in a fabric such as cotton, silk, and synthetic fibers, a natural leather, a synthetic leather, paper, a nonwoven fabric, a resin film, a flexible foam,

or the like.

[0148] The polyurethane gel can be preferably used as vibration-proof and quake-isolation members, shock absorbing members, cushioning members, surface protection members, cushioning, elbow rests, arm rests, switches, robotic components, robotic skin, manikins, members of mobility, pads, clothing components, aircraft components, cosmetics, medical devices, care and clothing materials such as diapers and floor misalignment prevention materials, wearable materials, eyewears such as frames, ear and nose pads of eyewear, earphones, headphones, grips and other sporting components, toys, playground equipment, protectors such as helmets, furniture, flexible sensors, sheets, flexible rods, non-woven fabrics, composite materials with felt, shoe soles, shoe friction prevention, actuators, pseudo-biomaterials, and the like. Among all, the polyurethane gel can be preferably used as pseudo-biomaterials.

[0149] Since the polyurethane gel of the present invention has a touch, elasticity, and flexibility close to various organs and various internal organs constituting a human body in particular, and tissues constituting them, it is preferably used as a pseudo-biomaterial or the like in a medical field, a healthcare field, or the like.

[0150] More specifically, the pseudo-biomaterial made from the above-described polyurethane gel is formed as pseudo-biological models of cartilage and joints constituting a skeletal system; muscle, skeletal muscle, smooth muscle, and cardiac muscle constituting a muscular system; heart and blood constituting a circulatory system; upper airway, lower airway, and lung constituting a respiratory system; skin, ear, and nose constituting a sensory system; oral cavity, pharynx, esophagus, stomach, small intestine, large intestine, anal canal, anal, digestive gland, liver, biliary gland, and pancreas constituting a digestive system; kidney, renal pelvis, urinary tract, urinary bladder, and urethra constituting a urinary system; testis, prostate, seminal vesicle, penis, ovary, oviduct, uterus, and vagina constituting a genital organ; hypothalamus, pituitary, thyroid, accessory thyroid, adrenal, pancreas, testis, and ovary constituting an endocrine system; and brain, spinal cord, cerebrospinal nerve, and autonomic nerve constituting a nervous system. For example, the pseudo-biomaterial is preferably used as pseudo-biological models for training in various types of medical surgeries and pseudo-biological models for training in various types of inspections (ultrasonography, CT scan, etc.), pseudo-biological models in telemedicine and medical treatment, wearable equipment and terminal equipment in the field of health care, and as exhibition samples, equipment for education, toys, and the like.

Examples

[0151] Next, the present invention is described based on Production Examples, Examples, and Comparative Examples. The present invention is however not limited by the following Examples. All designations of "part" or "parts" and "%" mean part or parts by mass and % by mass, respectively, unless otherwise particularly specified in the following description. The specific numerical values in mixing ratio (content ratio), property value, and parameter used in the following description can be replaced with upper limit values (numerical values defined as "or less" or "below") or lower limit values (numerical values defined as "or more" or "above") of corresponding numerical values in mixing ratio (content ratio), property value, and parameter described in the above-described "DESCRIPTION OF EMBODIMENTS".

[0152] The measurement methods used in the respective Production Examples, the respective Examples, and the respective Comparative Examples are described below.

1. Measurement method

<Isocyanate Group Concentration (Unit: % by mass), Conversion Rate of Isocyanate Group (Unit: % by mass)>

[0153] By using a potentiometric titrator (manufactured by KYOTO ELECTRONICS MANUFACTURING CO., LTD., model number: AT-510), the isocyanate group concentration (isocyanate group content ratio) was measured by a toluene/dibutylamine hydrochloric acid method in conformity with JIS K-1603-1 (2007), and a conversion rate of an isocyanate group of a measurement sample was calculated by the following formula.

$$\text{Conversion rate of isocyanate group} = 100 - (\text{isocyanate group concentration in reaction liquid mixture after completion of reaction} / \text{isocyanate group concentration in reaction liquid before reaction} \times 100)$$

<Isocyanate Monomer Concentration (Unit: % by mass)>

[0154] The concentration of an unreacted isocyanate monomer (pentamethylene diisocyanate monomer or hexamethylene diisocyanate monomer) was calculated by using a pentamethylene diisocyanate produced in the same manner

as in Example 1 in International Publication WO2012/121291 or a commercially available hexamethylene diisocyanate as a standard substance, being labelled with a dibenzylamine, and using a calibration curve prepared from the area values of chromatogram obtained under the following HPLC measurement conditions.

Device: Prominence (manufactured by Shimadzu Corporation)
Pumping: LC-20AT
Degasser: DGU-20A3
Autosampler: SIL-20A
Column thermostat: COT-20 A
Detector: SPD-20A
Column: SHISEIDO SILICA SG-120
Column temperature: 40°C
Eluent: n-hexane/ methanol/ 1,2-dichloroethane = 90/ 5/ 5 (volume ratio)
Flow rate: 0.2 mL/ min
Detecting method: UV 225 nm

<Viscosity (unit: mPa·s)>

[0155] The viscosity of the measurement sample was measured at 25°C in conformity with a cone plate viscometer method of JIS K5600-2-3 (2014) by using an E-type viscometer TV-30 (rotor angle: 1°34', rotor radius: 24 cm) manufactured by TOKI SANGYO CO., LTD. The number of revolutions of the cone plate at the time of measurement was sequentially changed between 100 rpm and 2.5 rpm as the viscosity increased.

<Mole Ratio of Allophanate Group to Isocyanurate Group by ^{1}H-NMR>

[0156] The ^{1}H-NMR was measured with the following device and conditions, and a content ratio (mole ratio of allophanate group/ isocyanurate group) of the allophanate group to 1 mol of the isocyanurate group in the aliphatic polyisocyanate was calculated by the following formula. As a reference of chemical shift ppm, a tetramethylsilane (0 ppm) in D^{6}-DMSO solvent was used.

Device: JNM-AL400 (manufactured by JEOL Ltd.)
Conditions: measurement frequency: 400 MHz, solvent: D^{6}-DMSO, solute concentration: 5% by mass
Assigned peak (6H) of proton of isocyanurate group (methylene group (CH_2 group) directly bonded to isocyanurate group): 3.8 ppm
Assigned peak (1H) of proton of allophanate group (NH group in allophanate group): 8.3 to 8.7 ppm
Allophanate group/ isocyanurate group (mole ratio) = integrated value of assigned peak of proton of allophanate group/ (integrated value of assigned peak of proton of isocyanurate group/ 6)

<Average Number of Isocyanate Group (Average Functionality)>

[0157] An average number of the isocyanate group of the aliphatic polyisocyanate was calculated from the isocyanate group concentration, the solid content concentration (NV), and a number average molecular weight of gel permeation chromatography measured by the following device and conditions according to the following formula.

$$\text{Average number of isocyanate group} = A/B \times C/42.02$$

(wherein A represents the isocyanate group concentration, B represents the solid content concentration, and C represents a number average molecular weight.)

Device: HLC-8220GPC (manufactured by TOSOH CORPORATION)
Column: series connection of TSKgelG1000HXL, TSKgelG2000HXL, and TSKgelG3000HXL (manufactured by TOSOH CORPORATION)
Detector: differential refractometer
Measurement conditions
Injection volume :100 μm
Eluent: tetrahydrofuran

Flow rate: 0.8 mL/ min
Temperature: 40°C
Calibration curve: standard polyethylene oxide in a rage of 106 to 22450 (manufactured by TOSOH CORPORATION, trade name: TSK standard polyethylene oxide)

<Average Number of Hydroxyl Group (Average Functionality)>

[0158] A hydroxyl value was defined as the number of mg of potassium hydroxide corresponding to a hydroxyl group in 1 g of a polyoxyalkylene polyol. The hydroxyl value of the polyol was measured in conformity with "hydroxyl value" of Section 6.4 of JIS K1557 (2007).

2. Materials

(1) Aliphatic Polyisocyanate (A)

Preparation Example 1 (Isocyanate (a-1) (Alcoholic Modified Isocyanurate Derivative of PDI))

[0159] A four-neck flask equipped with a thermometer, a stirring device, a reflux tube, and a nitrogen introducing tube, was charged with 500 parts by mass of pentamethylene diisocyanate produced in the same manner as in Example 1 in the specification of International Publication WO2012/121291 (hereinafter, referred to as PDI), 6.9 parts by mass of isobutyl alcohol, 0.3 parts by mass of 2,6-di(tert-butyl)-4-methylphenol, and 0.3 parts by mass of tris(tridecyl) phosphite to be reacted at 80°C for 2 hours.

[0160] Then, 0.05 parts by mass of N-(2-hydroxypropyl)-N,N,N-trimethylammonium-2-ethylhexanoate was blended as an isocyanuration catalyst. The isocyanate group concentration was measured, and the reaction was continued until its concentration reached 48.3% by mass (that is, conversion rate of 10% by mass). When a predetermined conversion rate (conversion rate of 10% by mass) was reached after 20 minutes, 0.12 parts by mass of o-toluenesulfonamide was added thereto. The obtained reaction liquid mixture was passed through a thin film distillation device (temperature: 150°C, vacuum degree: 0.093 kPa) to remove unreacted pentamethylene diisocyanate monomer, and further, 0.02 parts by mass of o-toluenesulfonamide and 0.003 parts by mass of benzoyl chloride were added to 100 parts by mass of the obtained residue to obtain an alcoholic modified isocyanurate derivative of PDI. This was referred to as an isocyanate (a-1).

[0161] In the isocyanate (a-1), the average number of the isocyanate group was 2.8, the isocyanate monomer concentration was 0.4% by mass, the isocyanate group concentration was 23.4% by mass, and the viscosity at 25°C was 950 mPa·s.

[0162] Further, the mole ratio of the allophanate group to the isocyanurate group by ^{1}H-NMR measurement was an allophanate group/ isocyanurate group = 33.0/ 100.

Preparation Example 2 (Isocyanate (a-2) (Alcoholic Modified Isocyanurate Derivative of PDI))

[0163] A four-neck flask equipped with a thermometer, a stirring device, a reflux tube, and a nitrogen introducing tube was charged with 500 parts by mass of PDI, 0.5 parts by mass of isobutyl alcohol, 0.3 parts by mass of 2,6-di(tert-butyl)-4-methylphenol, and 0.3 parts by mass of tris(tridecyl) phosphite to be reacted at 80°C for 2 hours.

[0164] Then, 0.05 parts by mass of N-(2-hydroxypropyl)-N,N,N-trimethylammonium-2-ethylhexanoate was blended as an isocyanuration catalyst. The isocyanate group concentration was measured, and the reaction was continued until its concentration reached 48.9% by mass (that is, conversion rate of 10% by mass). When a predetermined conversion rate (conversion rate of 10% by mass) was reached after 50 minutes, 0.12 parts by mass of o-toluenesulfonamide was added thereto. The obtained reaction liquid mixture was passed through a thin film distillation device (temperature: 150°C, vacuum degree: 0.093 kPa) to remove unreacted pentamethylene diisocyanate monomer, and further, 0.02 parts by mass of o-toluenesulfonamide and 0.003 parts by mass of benzoyl chloride were added to 100 parts by mass of the obtained residue to obtain an alcoholic modified isocyanurate derivative of PDI. This was referred to as an isocyanate (a-2).

[0165] In the isocyanate (a-2), the average number of the isocyanate group was 3.1, the isocyanate monomer concentration was 0.5% by mass, the isocyanate group concentration was 24.7% by mass, and the viscosity at 25°C was 2000 mPa·s.

[0166] Further, the mole ratio of the allophanate group to the isocyanurate group by ^{1}H-NMR measurement was an allophanate group/ isocyanurate group = 7.4/ 100.

Preparation Example 3 (Isocyanate (a-3) (Isocyanurate Derivative of PDI))

[0167] A four-neck flask equipped with a thermometer, a stirring device, a reflux tube, and a nitrogen introducing tube

was charged with 500 parts by mass of PDI, 0.3 parts by mass of 2,6-di(tert-butyl)-4-methylphenol, and 0.3 parts by mass of tris(tridecyl) phosphite to be heated to 80°C. Then, 0.05 parts by mass of N-(2-hydroxypropyl)-N,N,N-trimethylammonium-2-ethylhexanoate was blended as an isocyanuration catalyst. The isocyanate group concentration was measured, and the reaction was continued until its concentration reached 49.0% by mass (that is, conversion rate of 10% by mass). When a predetermined conversion rate (conversion rate of 10% by mass) was reached after 50 minutes, 0.12 parts by mass of o-toluenesulfonamide was added thereto. The obtained reaction liquid mixture was passed through a thin film distillation device (temperature: 150°C, vacuum degree: 0.093 kPa) to remove unreacted pentamethylene diisocyanate monomer, and further, 0.02 parts by mass of o-toluenesulfonamide and 0.003 parts by mass of benzoyl chloride were added to 100 parts by mass of the obtained residue to obtain an isocyanurate derivative of PDI. This was referred to as an isocyanate (a-3).

[0168] In the isocyanate (a-3), the average number of the isocyanate group was 3.2, the isocyanate monomer concentration was 0.5% by mass, the isocyanate group concentration was 24.9% by mass, and the viscosity at 25°C was 2800 mPa·s.

[0169] Further, the mole ratio of the allophanate group to the isocyanurate group by ^{1}H-NMR measurement was an allophanate group/ isocyanurate group = 0/ 100.

Preparation Example 4 (Isocyanate (a-4) (Alcoholic Modified Isocyanurate Derivative of PDI))

[0170] A four-neck flask equipped with a thermometer, a stirring device, a reflux tube, and a nitrogen introducing tube was charged with 500 parts by mass of PDI, 0.5 parts by mass of isobutyl alcohol, 0.3 parts by mass of 2,6-di(tert-butyl)-4-methylphenol, and 0.3 parts by mass of tris(tridecyl) phosphite to be reacted at 80°C for 2 hours.

[0171] Then, 0.05 parts by mass of N-(2-hydroxypropyl)-N,N,N-trimethylammonium-2-ethylhexanoate was blended as an isocyanuration catalyst. The isocyanate group concentration was measured, and the reaction was continued until its concentration reached 40.3% by mass (that is, conversion rate of 26% by mass). When a predetermined conversion rate (conversion rate of 26% by mass) was reached after 130 minutes, 0.12 parts by mass of o-toluenesulfonamide was added thereto. The obtained reaction liquid mixture was passed through a thin film distillation device (temperature: 150°C, vacuum degree: 0.093 kPa) to remove unreacted pentamethylene diisocyanate monomer, and further, 0.02 parts by mass of o-toluenesulfonamide and 0.003 parts by mass of benzoyl chloride were added to 100 parts by mass of the obtained residue to obtain an alcoholic modified isocyanurate derivative of PDI. This was referred to as an isocyanate (a-4).

[0172] In the isocyanate (a-4), the average number of the isocyanate group was 3.8, the isocyanate monomer concentration was 0.5% by mass, the isocyanate group concentration was 23.1% by mass, and the viscosity at 25°C was 9000 mPa·s.

[0173] Further, the mole ratio of the allophanate group to the isocyanurate group by ^{1}H-NMR measurement was an allophanate group/ isocyanurate group = 5.0/ 100.

Preparation Example 5 (Isocyanate (a-5) (Alophanate Derivative of PDI))

[0174] In a reactor equipped with a thermometer, a stirring device, a nitrogen introducing tube, and a cooling tube, 1500 parts by mass of PDI, 24 parts by mass of isobutanol, 0.3 parts by mass of 2,6-di(t-butyl)-4-methylphenol, and 0.3 parts by mass of tris(tridecyl) phosphite were charged under a nitrogen atmosphere to be subjected to a urethanization reaction at 85°C for 3 hours.

[0175] Then, 0.02 parts by mass of tris(2-ethylhexanoic acid) bismuth was added as an allophanatization catalyst, and the obtained mixture was reacted until the isocyanate group concentration reached a calculated value (46.7% by mass, that is, a conversion rate of 10% by mass), and then, 0.02 parts by mass of o-toluenesulfonamide was added thereto.

[0176] Thereafter, the obtained reaction liquid was passed through a thin film distillation device (vacuum degree of 0.093 KPa, temperature of 150°C) to remove unreacted pentamethylene diisocyanate, and further, 0.02 parts by mass of o-toluenesulfonamide was added to 100 parts by mass of the obtained residue to obtain an allophanate derivative of PDI. This was referred to as an isocyanate (a-5).

[0177] In the isocyanate (a-5), the average number of the isocyanate group was 2.0, the isocyanate group concentration was 20.4% by mass, the viscosity at 25°C was 24 mPa·s, and the isocyanate monomer concentration was 0.2% by mass.

[0178] Further, the mole ratio of the allophanate group to the isocyanurate group by ^{1}H-NMR measurement was an allophanate group/ isocyanurate group = 100/ 0.

Preparation Example 6 (Isocyanate (a-6) (Alcoholic Modified Isocyanurate Derivative of HDI))

[0179] An alcoholic modified isocyanurate derivative of HDI was obtained in the same manner as in Preparation Example 1, except that PDI was changed to a hexamethylene diisocyanate (manufactured by Mitsui Chemicals, Inc., trade name: Takenate 700 (hereinafter, referred to as HDI)). This was referred to as an isocyanate (a-6).

[0180] In the isocyanate (a-6), the average number of the isocyanate group was 2.9, the isocyanate monomer concentration was 0.5% by mass, the isocyanate group concentration was 22.1% by mass, and the viscosity at 25°C was 840 mPa·s.

[0181] Further, the mole ratio of the allophanate group to the isocyanurate group by ^{1}H-NMR measurement was an allophanate group/ isocyanurate group = 34.3/ 100.

[0182] Preparation Example 7 (Isocyanate (a-7) (Polyol Derivative of PDI (TMP Modified Product))

[0183] A four-neck flask equipped with a stirring device, a thermometer, a reflux tube, and a nitrogen introducing tube was charged with 200 parts by mass of PDI to be heated to 95°C under a nitrogen atmosphere with stirring. Next, 21.1 parts by mass of trimethylolpropane (hereinafter, referred to as TMP) was charged into a dropping funnel to be heated with a ribbon heater.

[0184] The melted TMP was added dropwise over a period of about 60 minutes. Thereafter, the urethanization reaction was continued for about 3 hours until the isocyanate group concentration reached a calculated value. The obtained reaction liquid was passed through a thin film distillation device (vacuum degree of 50 Pa, temperature of 130°C) to remove unreacted PDI, thereby obtaining a polyol derivative of PDI (TMP modified product). This was referred to as an isocyanate (a-7).

[0185] In the isocyanate (a-7), the average number of the isocyanate group was 3.7, the isocyanate group concentration was 13.8% by mass, and the viscosity at 25°C was 450 mPa·s.

(2) Polyol (B)

Preparation Example 1 (Polyol (b-1))

[0186] A polyoxyalkylene polyol (polyether polyol obtained by subjecting propylene glycol to addition polymerization of propylene oxide, number average molecular weight (Mn) = 2000, average functionality of 2, hydroxyl value of 56 mgKOH/g, ethylene oxide concentration in total oxyalkylene = 0% by mass) was referred to as a polyol (b-1).

[0187] The polyol (b-1) was a polyoxypropylene glycol (PPG).

Preparation Example 2 (Polyol (b-2))

[0188] A polyoxyalkylene polyol (polyether polyol obtained by subjecting propylene glycol to addition polymerization of propylene oxide, number average molecular weight (Mn) = 1000, average functionality of 2, hydroxyl value of 112 mgKOH/g, ethylene oxide concentration in total oxyalkylene = 0% by mass) was referred to as a polyol (b-2).

[0189] The polyol (b-2) was a polyoxypropylene glycol (PPG).

Preparation Example 2-1 (Polyol (b-2-1))

[0190] The polyol (b-1) having a number average molecular weight of 2000 and the polyol (b-2) having a number average molecular weight of 1000 were mixed so as to have 1: 1 (b-1: b-2 (mass ratio)), and as a mixture, a polyol (b-2-1) was obtained. The polyol (b-2-1) had a number average molecular weight of about 1300 (1335), an average functionality of 2, a hydroxyl value of 84 mgKOH/g, and the ethylene oxide concentration in the total oxyalkylene of 0% by mass.

[0191] The polyol (b-2-1) was a polyoxypropylene glycol (PPG).

Preparation Example 2-2 (Polyol (b-2-2))

[0192] The polyol (b-1) having a number average molecular weight of 2000 and the polyol (b-2) having a number average molecular weight of 1000 were mixed so as to have 4: 1 (b-1: b-2 (mass ratio)), and as a mixture, a polyol (b-2-2) was obtained. The polyol (b-2-2) had a number average molecular weight of about 1700 (1674), an average functionality of 2, a hydroxyl value of 67 mgKOH/g, and the ethylene oxide concentration in the total oxyalkylene of 0% by mass.

[0193] The polyol (b-2-2) was a polyoxypropylene glycol (PPG).

Preparation Example 3 (Polyol (b-3))

[0194] A polyoxyalkylene polyol (polyether polyol obtained by subjecting propylene glycol to addition polymerization of propylene oxide, number average molecular weight (Mn) = 3000, average functionality of 2, hydroxyl value of 37 mgKOH/g, ethylene oxide concentration in total oxyalkylene = 0% by mass) was referred to as a polyol (b-3).

[0195] The polyol (b-3) was a polyoxypropylene glycol (PPG).

Preparation Example 4 (Polyol (b-4))

[0196] A polyoxyalkylene polyol (polyether polyol obtained by subjecting propylene glycol to addition polymerization of propylene oxide, number average molecular weight (Mn) = 4000, average functionality of 2, hydroxyl value of 28 mgKOH/g, ethylene oxide concentration in total oxyalkylene = 0% by mass) was referred to as a polyol (b-4).

[0197] The polyol (b-4) was a polyoxypropylene glycol (PPG).

Preparation Example 5 (Polyol (b-5))

[0198] A polyoxyalkylene polyol (polyether polyol obtained by subjecting glycerine to addition polymerization of propylene oxide, number average molecular weight (Mn) = 3000, average functionality of 3, hydroxyl value of 56 mgKOH/g, ethylene oxide concentration in total oxyalkylene = 0% by mass) was referred to as a polyol (b-5).

[0199] The polyol (b-5) was a polypropylene triol (PPT).

Preparation Example 6 (Polyol (b-6))

[0200] A polyoxyalkylene polyol (polyether polyol obtained by subjecting glycerine to addition polymerization of propylene oxide and next, to addition polymerization of ethylene oxide, number average molecular weight (Mn) = 2000, average functionality of 2, hydroxyl value of 56 mgKOH/g, ethylene oxide concentration in total oxyalkylene = 20% by mass) was referred to as a polyol (b-6).

[0201] The polyol (b-6) was an ethylene oxide (EO)-propylene oxide (PO) copolymer.

Preparation Example 7 (Polyol (b-7))

[0202] A polyoxyalkylene polyol (polyether polyol obtained by subjecting glycerine to addition polymerization of propylene oxide and next, to addition polymerization of ethylene oxide, number average molecular weight (Mn) = 2000, average functionality of 2, hydroxyl value of 56 mgKOH/g, ethylene oxide concentration in total oxyalkylene = 40% by mass) was referred to as a polyol (b-7).

[0203] The polyol (b-7) was an ethylene oxide (EO)-propylene oxide (PO) copolymer.

Preparation Example 8 (Polyol (b-8))

[0204] A polytetramethylene ether glycol having a number average molecular weight of 2000 (PTMEG, manufactured by Hodogaya Chemical Co., Ltd., trade name: PTG-2000SN, hydroxyl value of 56 mgKOH/g, average functionality of 2) was referred to as a polyol (b-8).

Preparation Example 9 (Polyol (b-9))

[0205] A polytetramethylene ether glycol having a number average molecular weight of 1000 (PTMEG, manufactured by Hodogaya Chemical Co., Ltd., trade name: PTG-1000, hydroxyl value of 112 mgKOH/g, average functionality of 2) was referred to as a polyol (b-9).

Preparation Example 10 (Polyol (b-10))

[0206] An amorphous polytetramethylene ether glycol having a number average molecular weight of 1800 (manufactured by ASAHI KASEI FIBERS CORPORATION, trade name: PTXG, hydroxyl value of 60 mgKOH/g, average functionality of 2, copolymer of tetrahydrofuran and neopentyl glycol) was referred to as a polyol (b-10).

(3) Plasticizer (c)

Preparation Example 11 (Plasticizer (c-1))

[0207] A diisononylcyclohexane-1,2-dicarboxylate (manufactured by BASF SE, trade name: Hexamol DINCH, boiling point of 394°C) was referred to as a plasticizer (c-1).

Preparation Example 12 (Plasticizer (c-2))

[0208] A diisononyl adipate (manufactured by Mitsubishi Chemical Corporation, trade name: DINA, boiling point of

250°C) was referred to as a plasticizer (c-2).

Preparation Example 13 (Plasticizer (c-3))

[0209] A di-(2-ethylhexyl) phthalate (manufactured by Mitsubishi Chemical Corporation, trade name: DOP, boiling point of 386°C) was referred to as a plasticizer (c-3).

Preparation Example 14 (Plasticizer (c-4))

[0210] A chloroparaffin (manufactured by Sigma-Aldrich Co. LLC, trade name: Chloroparaffin) was referred to as a plasticizer (c-4).

(4) Catalyst (d)

[0211] Manufactured by TOKYO CHEMICAL INDUSTRY CO., LTD., reagent, dibutyltin dilaurate

(5) Antifoaming Agent (e)

[0212] Manufactured by BYK Japan KK, trade name: BYK-088

3. Production of Polyurethane Gel

Example 1

[0213] The isocyanate (a-1), the polyol (b-1), and the plasticizer (c-1) were prepared at the mass ratio shown in Table 1 to obtain a polyurethane gel material (preparation step).

[0214] Then, 100 parts by mass of the polyol (b-1) adjusted at 25°C, 17.93 parts by mass of the polyisocyanate (a-1) (equivalent ratio of isocyanate group to hydroxyl group (NCO/ hydroxyl group = 1.0)), 200 parts by weight of the plasticizer (c-1), 0.03 parts by weight of the dibutyltin dilaurate (d) of the catalyst, and 0.2 parts by weight of the defoaming agent (e) were put into a plastic container, and the mixture was stirred and mixed for one minute under stirring at 7000 rpm by using a three-one motor (manufactured by SHINTO Scientific Co., Ltd., trade name: HEIDOM FBL3000).

[0215] Thereafter, the liquid mixture was immediately defoamed under a reduced pressure, and after removing the foam of the liquid mixture, it was poured into the following metal mold which was previously coated with Teflon (registered trademark) and heated to 80°C without contamination of bubbles. Then, the liquid mixture was allowed to react at 80°C for 2 hours to obtain a urethane gel.

- Sheet metal mold having a thickness of 2 mm
- Square block metal mold having a size of 5 cm × 5 cm × height of 15 mm
- Columnar metal mold having a diameter of 29 mm × height of 13 mm

[0216] This polyurethane gel was left to stand in a room at 23°C with relative humidity of 55% for seven days and then, subjected to various property measurement.

Examples 2 to 17 and Comparative Examples 1 to 12

[0217] A polyurethane gel was obtained in the same manner as in Example 1, except that the formulation was changed to those shown in Tables 1 to 4.

4. Evaluation

<Curability of Polyurethane Gel>

[0218] A liquid mixture of a polyurethane gel material was poured into a block metal mold, and the mixture was reacted at 80°C for 2 hours. Then, the flowability of the polyurethane gel material was confirmed, and the curability of the polyurethane gel was evaluated. Criteria for evaluation are as follows.

[0219] Bad: the polyurethane gel material has flowability and cannot retain its shape after demolding.

[0220] Excellent: the polyurethane gel material has flowability and can retain its shape after demolding.

<Mechanical Properties of Polyurethane Gel (Elongation at Break (EL) (unit: %)>

[0221] A polyurethane gel prepared with a 2 mm-sheet metal mold was punched into a No. 3 test piece shape to prepare a measurement sample. The measurement sample was subjected to a tensile test by using a tensile compressive tester (manufactured by INTESCO co., ltd., Model 205N) in conformity with JIS K-6400 (2012) to calculate the elongation at break.

<Bleeding Resistance of Polyurethane Gel>

[0222] A polyurethane gel obtained with a columnar metal mold was punched into a columnar test piece to prepare a measurement sample, and the weight thereof was measured (W1).

[0223] After the upper and the lower surfaces of the sample were sandwiched between filter papers (manufactured by Advantec Tokyo Kaisha, Ltd., FILTER PAPER No. 5C) and treated in an oven at 80°C for five days, they were left to stand in a room at 23°C with relative humidity of 55 % for one day, and then, the surface was further thoroughly wiped off with the filter paper to measure the weight thereof again (W2).

[0224] Bleeding resistance was evaluated by a weight change before and after treatment (W: W = (W1-W2)/W1 × 100 (unit: %)).

<Low Tackiness of Polyurethane Gel>

[0225] A stainless steel plate having a thickness of 1 mm× 4 cm× 4 cm (material: JIS G 4305 SUS304, surface finish BA, surface roughness: JIS B0601, difference Ra = 50± 25 nm) was placed on the polyurethane gel obtained with the block metal mold to be then left to stand in a room at 23°C with relative humidity of 55% for one day. Thereafter, the stress (kgf/ 16 cm^2) required when the stainless steel plate was removed with a push-pull gauge was measured.

<Asker C Hardness of Polyurethane Gel>

[0226] The Asker C hardness of the polyurethane gel obtained with the block metal mold was measured by a type C hardness test of JIS K 7312 (1996).

[Table 1]

[0227]

Table 1

No.				Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comparative Ex. 1	Comparative Ex. 2	Comparative Ex. 3
Mixing Formulation (parts by mass)	Polyisocyanate (A)	Preparation Ex. 1 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-1	100	-	-	60	-	-	30	-
		Preparation Ex. 2 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-2	-	100	-	-	-	-	-	-
		Preparation Ex. 3 (Isocyanurate Derivative of PDI)	a-3	-	-	100	-	-	-	-	-
		Preparation Ex. 4 (Alcoholic Modified Isocvanurate Derivative of PDI)	a-4	-	-	-	-	-	100	-	-
		Preparation Ex. 5 (Allophanate Derivative of PDI)	a-5	-	-	-	40	-	-	70	-
		Preparation Ex. 6 (Alcoholic Modified Isocyanurate Derivative of HDI)	a-6	-	-	-	-	100	-	-	-
		Preparation Ex. 7 (Polyol Derivative of PDI)	a-7	-	-	-	-	-	-	-	100
		Average Functionality		2.8	3.1	3.2	2.5	2.9	3.8	2.2	3.7
		Preparation Ex. 1 (PPG: Mn2000)	b-1	100	100	100	100	100	100	100	100

(continued)

No.				Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comparative Ex. 1	Comparative Ex. 2	Comparative Ex. 3
	Polyol (B)	Preparation Ex. 2-1 (PPG: Mn1300)	b-2-1	-	-	-	-	-	-	-	-
		Preparation Ex. 2-2 (PPG: Mn1700)	b-2-2	-	-	-	-	-	-	-	-
		Preparation Ex. 3 (PPG: Mn3000)	b-3	-	-	-	-	-	-	-	-
		Preparation Ex. 4 (PPG: Mn4000)	b-4	-	-	-	-	-	-	-	-
		Preparation Ex. 5 (PPT: Mn3000)	b-5	-	-	-	-	-	-	-	-
		Preparation Ex. 6 (EOPO: Mn2000)	b-6	-	-	-	-	-	-	-	-
		Preparation Ex. 7 (EOPO: Mn2000)	b-7	-	-	-	-	-	-	-	-
		Preparation Ex. 8 (PTMEG: Mn2000)	b-8	-	-	-	-	-	-	-	-
		Preparation Ex. 9 (PTMEG: Mn1000)	b-9	-	-	-	-	-	-	-	-
		Preparation Ex. 10 (Amorphous PTMEG: Mn1800)	b-10	-	-	-	-	-	-	-	-
		Average Functionality		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
		Average Hydroxyl Value (mgKOH/g)		56	56	56	56	56	56	56	56
		EO Content (% by mass)		0	0	0	0	0	0	0	0

(continued)

No.			Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comparative Ex. 1	Comparative Ex. 2	Comparative Ex. 3
Plasticizer (c) (parts by mass per 100 parts by mass of polyol)	Diisononylcyclohexane-1,2-dicarboxylate (DINCH)	c-1	200	200	200	200	200	200	200	200
	Diisononyl Adipate (DINA)	c-2	-	-	-	-	-	-	-	-
	Di-(2-ethylhexyl) phthalate (DOP)	c-3	-	-	-	-	-	-	-	-
	Chloroparaffin	c-4	-	-	-	-	-	-	-	-
Evaluation	Curability		Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Bad	Excellent
	Elongation at Break (%)		190	118	102	233	185	78	-	54
	Bleeding Resistance (weight loss rate: %)		0.6	0.3	0.2	0.9	0.7	0.2	-	0.8
	Low Tackiness (tensile load value: kaf/16 cm^2)		1.1	0.9	0.8	1.3	1.2	0.7	-	1.3
	Asker C Hardness		7	19	28	<1	8	30	-	14

[Table 2]

[0228]

Table 2

No.				Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11
Mixing Formulation (parts by mass)	Polyisocyanate (A)	Preparation Ex. 1 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-1	100	100	100	100	100	100
		Preparation Ex. 2 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-2	-	-	-	-	-	-
		Preparation Ex. 3 (Isocyanurate Derivative of PDI)	a-3	-	-	-	-	-	-
		Preparation Ex. 4 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-4	-	-	-	-	-	-
		Preparation Ex. 5 (Allophanate Derivative of PDI)	a-5	-	-	-	-	-	-
		Preparation Ex. 6 (Alcoholic Modified Isocyanurate Derivative of HDI)	a-6	-	-	-	-	-	-
		Preparation Ex. 7 (Polyol Derivative of PDI)	a-7	-	-	-	-	-	-
		Average Functionality		2.8	2.8	2.8	2.8	2.8	2.8
		Preparation Ex. 1 (PPG: Mn2000)	b-1	-	-	-	-	90	-
		Preparation Ex. 2-1 (PPG: Mn1300)	b-2-1	-	-	-	-	-	-
		Preparation Ex. 2-2 (PPG: Mn1700)	b-2-2	100	-	-	-	-	-
		Preparation Ex. 3 (PPG: Mn3000)	b-3	-	100	-	-	-	-
		Preparation Ex. 4 (PPG: Mn4000)	b-4	-	-	-	-	-	-

(continued)

No.				Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11
	Polyol (B)	Preparation Ex. 5 (PPT: Mn3000)	b-5	-	-	-	-	10	-
		Preparation Ex. 6 (EOPO: Mn2000)	b-6	-	-	-	100	-	-
		Preparation Ex. 7 (EOPO: Mn2000)	b-7	-	-	-	-	-	-
		Preparation Ex. 8 (PTMEG: Mn2000)	b-8	-	-	100	-	-	-
		Preparation Ex. 9 (PTMEG: Mn1000)	b-9	-	-	-	-	-	-
		Preparation Ex. 10 (Amorphous PTMEG: Mn1800)	b-10	-	-	-	-	-	100
		Average Functionality		2.0	2.0	2.0	2.0	2.1	2.0
		Average Hydroxyl Value (mgKOH/g)		67	37	56	56	56	60
		EO Content (% by mass)		0	0	0	20	0	0
Plasticizer (c) (parts by mass per 100 parts by mass of polyol)		Diisono nylcyclohexane-1,2-dicarboxylate (DINCH)	c-1	200	200	200	200	200	200
		Diisononyl Adipate (DINA)	c-2	-	-	-	-	-	-
		Di-(2-ethylhexyl) phthalate (DOP)	c-3	-	-	-	-	-	-
		Chloroparaffin	c-4	-	-	-	-	-	-
Evaluation		Curability		Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
		Elongation at Break (%)		173	284	160	186	178	175
		Bleeding Resistance (weight loss rate: %)		2.4	0.3	0.4	1.5	0.6	0.6
		Low Tackiness (tensile load value: kgf/16 cm^2)		1.1	1.2	1.0	0.9	1.0	1.1
		Asker C Hardness		20	2	37	18	10	30

[Table 3]

[0229]

Table 3

No.				Comparative Ex. 4	Comparative Ex. 5	Comparative Ex. 6	Comparative Ex. 7	Comparative Ex. 8	Comparative Ex. 9
Mixing Formulation (parts by mass)	Polyisocyanate (A)	Preparation Ex. 1 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-1	100	100	100	100	100	100
		Preparation Ex. 2 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-2	-	-	-	-	-	-
		Preparation Ex. 3 (Isocyanurate Derivative of PDI)	a-3	-	-	-	-	-	-
		Preparation Ex. 4 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-4	-	-	-	-	-	-
		Preparation Ex. 5 (Allophanate Derivative of PDI)	a-5	-	-	-	-	-	-
		Preparation Ex. 6 (Alcoholic Modified Isocyanurate Derivative of HDI)	a-6	-	-	-	-	-	-
		Preparation Ex. 7 Derivative of PDI)	a-7	-	-	-	-	-	-
		Average Functionality		2.8	2.8	2.8	2.8	2.8	2.8
		Preparation Ex. 1 (PPG: Mn2000)	b-1	-	-	-	50	-	-

(continued)

No.				Comparative Ex. 4	Comparative Ex. 5	Comparative Ex. 6	Comparative Ex. 7	Comparative Ex. 8	Comparative Ex. 9
	Polyol (B)	Preparation Ex. 2-1 (PPG: Mn1300)	b-2-1	100	-	-	-	-	-
		Preparation Ex. 2-2 (PPG: Mn1700)	b-2-2	-	-	-	-	-	-
		Preparation Ex. 3 (PPG: Mn3000)	b-3	-	-	-	-	-	-
		Preparation Ex. 4 (PPG: Mn4000)	b-4	-	100	-	-	-	-
		Preparation Ex. 5 (PPT: Mn3000)	b-5	-	-	100	50	-	-
		Preparation Ex. 6 (EOPO: Mn2000)	b-6	-	-	-	-	-	-
		Preparation Ex. 7 (EOPO: Mn2000)	b-7	-	-	-	-	-	100
		Preparation Ex. 8 (PTMEG: Mn2000)	b-8	-	-	-	-	-	-
		Preparation Ex. 9 (PTMEG: Mn1000)	b-9	-	-	-	-	100	-
		Preparation Ex. 10 (Amorphous PTMEG: Mn1800)	b-10	-	-	-	-	-	-
		Average Functionality		2.0	2.0	3	2.5	2.0	2.0
		Average Hydroxyl Value (mgKOH/g)		84	28	56	56	112	56
		EO Content (% by mass)		0	0	0	0	0	40

(continued)

No.			Comparative Ex. 4	Comparative Ex. 5	Comparative Ex. 6	Comparative Ex. 7	Comparative Ex. 8	Comparative Ex. 9
Plasticizer (c) (parts by mass per 100 parts by mass of polyol)	Diisononylcyclohexane-1,2-dicarboxylate DINCH)	c-1	200	200	200	200	200	200
	Diisononyl Adipate (DINA)	c-2	-	-	-	-	-	-
	Di-(2-ethylhexyl)phthalate (DOP)	c-3	-	-	-	-	-	-
	Chloroparaffin	c-4	-	-	-	-	-	-
Evaluation	Curability		Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
	Elongation at Break (%)		104	301	36	45	170	165
	Bleeding Resistance (weight loss rate: %)		5.1	0.1	0.2	0.3	4.8	4.9
	Low Tackiness (tensile load value: kgf/16 cm^2)		0.9	1.9	0.8	0.9	0.9	0.9
	Asker C Hardness		30	<1	34	20	43	10

[Table 4]

[0230]

Table 4

No.				Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Comparative Ex. 10	Comparative Ex. 11	Comparative Ex. 12
	Polyisocyanate (A)	Preparation Ex. 1 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-1	100	100	100	100	100	100	100	100	100
		Preparation Ex. 2 (Alcoholic Modified Isocyanurate Derivative of PDI)	a-2	-	-	-	-	-	-	-	-	-
		Preparation Ex. 3 (Isocyanurate Derivative of PDI)	a-3	-	-	-	-	-	-	-	-	-
		Preparation Ex. 4 (Alcoholic Modified Isocyanurate Derivative of PDI	a-4	-	-	-	-	-	-	-	-	-
		Preparation Ex. 5 (Allophanate Derivative of PDI)	a-5	-	-	-	-	-	-	-	-	-
		Preparation Ex. 6 (Alcoholic Modified Isocyanurate Derivative of HDI)	a-6	-	-	-	-	-	-	-	-	-
		Preparation Ex. 7 (Polyol Derivative of PDI)	a-7	-	-	-	-	-	-	-	-	-
		Average Functionality		2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
		Preparation Ex. 1 (PPG: Mn2000)	b-1	100	100	100	100	-	100	100	100	100

(continued)

No.				Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Comparative Ex. 10	Comparative Ex. 11	Comparative Ex. 12
Mixing Formulation (parts by mass)	Polyol (B)	Preparation Ex. 2-1 (PPG: Mn1300)	b-2-1	-	-	-	-	-	-	-	-	-
		Preparation Ex. 2-2 (PPG: Mn1700)	b-2-2	-	-	-	-	100	-	-	-	-
		Preparation Ex. 3 (PPG: Mn3000)	b-3	-	-	-	-	-	-	-	-	-
		Preparation Ex. 4 (PPG: Mn4000)	b-4	-	-	-	-	-	-	-	-	-
		Preparation Ex. 5 (PPT: Mn3000)	b-5	-	-	-	-	-	-	-	-	-
		Preparation Ex. 6 (EOPO: Mn2000)	b-6	-	-	-	-	-	-	-	-	-
		Preparation Ex. 7 (EOPO: Mn2000)	b-7	-	-	-	-	-	-	-	-	-
		Preparation Ex. 8 (PTMEG: Mn2000)	b-8	-	-	-	-	-	-	-	-	-
		Preparation Ex. 9 (PTMEG: Mn1000)	b-9	-	-	-	-	-	-	-	-	-
		Preparation Ex. 10 (Amorphous PTMEG: Mn1800)	b-10	-	-	-	-	-	-	-	-	-
		Average Functionality		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
		Average Hydroxyl Value (mgKOH/g)		56	56	56	56	62	56	56	56	56
		EO Content (% by mass)		0	0	0	0	0	0	0	0	0

(continued)

No.			Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Comparative Ex. 10	Comparative Ex. 11	Comparative Ex. 12
Plasticizer (c) (parts by mass per 100 parts by mass of polyol)	Diisononylcyclohexane-1,2-dicarboxylate (DINCH)	c-1	-	400	50	-	400	100	10	450	-
	Diisononyl Adipate (DINA)	c-2	200	-	-	-	-	100	-	-	-
	Di-(2-ethylhexyl)phthalate (DOP)	c-3	-	-	-	200	-	-	-	-	-
	Chloroparaffin	c-4	-	-	-	-	-	-	-	-	200
Evaluation	Curability		Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Bad
	Elongation at Break (%)		196	198	173	183	185	193	236	152	-
	Bleeding Resistance (weight loss rate: %)		0.4	2.5	0.1	1.8	2.8	0.5	0.0	3.3	-
	Low Tackiness (tensile load value: kgf/16 cm^2)		1.1	0.3	1.5	1.0	1.1	1.1	2.0	0.2	-
	Asker C Hardness		9	<1	38	10	<1	8	52	<1	-

[0231] While the illustrative embodiments of the present invention are provided in the above description, such is for illustrative purpose only and it is not to be construed as limiting the scope of the present invention. Modification and variation of the present invention that will be obvious to those skilled in the art is to be covered by the following claims.

INDUSTRIAL APPLICATION

[0232] The polyurethane gel material, the polyurethane gel, the pseudo-biomaterial, and the method for producing a polyurethane gel of the present invention are, for example, preferably used in the field of pseudo-biomaterials such as a medical field and a healthcare field.

Claims

1. A polyurethane gel material comprising:

an aliphatic polyisocyanate (A) having an average functionality of 2.3 or more and 3.2 or less,
a polyol (B) having an average functionality of 2.0 or more and 2.3 or less, and
a plasticizer (C) having an ester group, wherein
the aliphatic polyisocyanate (A) contains an isocyanurate derivative of an aliphatic diisocyanate and/or an alcoholic modified isocyanurate derivative of an aliphatic diisocyanate,
the polyol (B) contains a polyoxyalkylene (carbon number of 2 to 3) polyol having an ethylene oxide content of 30% by mass or less, and/or a polytetramethylene ether glycol,
the polyol (B) has an average hydroxyl value of 30 mgKOH/g or more and 70 mgKOH/g or less, and
a ratio of the plasticizer (C) per 100 parts by mass of the polyol component (B) is 50 parts by mass or more and 400 parts by mass or less.

2. The polyurethane gel material according to claim 1, wherein
the polyol (B) has an average functionality of 2.0.

3. The polyurethane gel material according to claim 1, wherein
the polyol (B) has an average hydroxyl value of 37 mgKOH/g or more and 56 mgKOH/g or less.

4. The polyurethane gel material according to claim 1, wherein
the aliphatic polyisocyanate (A) has an average functionality of 2.3 or more and 3.0 or less.

5. The polyurethane gel material according to claim 1, wherein
the aliphatic diisocyanate includes a pentamethylene diisocyanate and/or a hexamethylene diisocyanate.

6. The polyurethane gel material according to claim 1, wherein
a ratio of the plasticizer (C) per 100 parts by mass of the polyol component (B) is 100 parts by mass or more and 200 parts by mass or less.

7. The polyurethane gel material according to claim 1, wherein
the plasticizer (C) is cyclohexanedicarboxylic acid esters and/or adipic acid esters.

8. A polyurethane gel being a reaction product of the polyurethane gel material according to claim 1.

9. The polyurethane gel according to claim 8, wherein
in the polyurethane gel material,
an equivalent ratio (NCO/ hydroxyl group) of an isocyanate group in an aliphatic polyisocyanate (A) to a hydroxyl group in a polyol (B) is 0.8 or more and 1.2 or less.

10. A pseudo-biomaterial comprising the polyurethane gel according to claim 8.

11. A method for producing a polyurethane gel comprising:

a preparation step of preparing the polyurethane gel material according to claim 1 and
a reaction step of reacting and curing the polyurethane gel material to obtain a polyurethane gel, wherein

in the reaction step,
an equivalent ratio (NCO/ hydroxyl group) of an isocyanate group in an aliphatic polyisocyanate (A) to a hydroxyl group in a polyol (B) is 0.8 or more and 1.2 or less.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/014590

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C08G18/73(2006.01)i, C08G18/08(2006.01)i, C08G18/48(2006.01)i, C08G18/79(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. C08G18/73, C08G18/08, C08G18/48, C08G18/79

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAplus/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2017/010422 A1 (MITSUI CHEMICALS, INC.) 19 January 2017, entire text & US 2018/0208720 A1, entire text & EP 3321086 A1 & CN 107848285 A	1-11
A	JP 2013-067757 A (DIC CORPORATION) 18 April 2013, entire text (Family: none)	1-11
A	WO 2016/190131 A1 (BANDO CHEMICAL INDUSTRIES, LTD.) 01 December 2016, entire text & US 2018/0171139 A1, entire text & EP 3305823 A1 & CN 107614558 A & KR 10-2018-0011790 A	1-11
P, A	JP 2018-090662 A (MITSUI CHEMICALS, INC.) 14 June 2018, entire text (Family: none)	1-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 June 2019 (25.06.2019)	02 July 2019 (02.07.2019)

Name and mailing address of the ISA/	Authorized officer
Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2011079985 A **[0007]**
- WO 2017010422 A **[0007]**
- WO 2012121291 A **[0154]**
- WO 2012L21291 A **[0159]**

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 June 2016 (09.06.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/090081 A1

(51) International Patent Classification:
A61K 8/87 (2006.01) *C08L 75/04* (2006.01)
C08L 47/00 (2006.01)

(21) International Application Number:
PCT/US2015/063604

(22) International Filing Date:
3 December 2015 (03.12.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/087,332 4 December 2014 (04.12.2014) US

(71) Applicant: **LUBRIZOL ADVANCED MATERIALS, INC.** [US/US]; 9911, Brecksville Road, Cleveland, Ohio 44141-3247 (US).

(72) Inventors: **PACZKOWSKI, Mark A.**; 9911 Brecksville Road, Cleveland, Ohio 44141-3247 (US). **MCMAHON, Mallory L.**; 9911 Brecksville Road, Cleveland, Ohio 44141-3247 (US). **WU, Anchuu**; 9911 Brecksville Road, Cleveland, Ohio 44141-3247 (US). **TAMAMI, Mana**; 9911 Brecksville Road, Cleveland, Ohio 44141-3247 (US). **JOHNSON, II, Jay W.**; 9911 Brecksville Road, Cleveland, Ohio 44141-3247 (US).

(74) Agents: **DEMAS, Christopher P.** et al.; 29400, Lakeland Blvd., Wickliffe, Ohio 44092-2298 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2016/090081 A1

(54) **Title**: VISCOSITY MODIFICATION OF ORGANIC PHASE CONTAINING COMPOSITIONS

(57) **Abstract**: The disclosed technology relates to structurant polymers based on polyure- thane/polyurea chemistry, which efficiently thicken or gel (i.e., provide structure to) oils and oil mixtures. The disclosed technology further relates to structurant polymers based on polyurethane/polyurea chemistry that are oil soluble or oil dispersible and that provide beneficial properties, such as, for example, desirable clarity and/or feel. In addition, the technology relates to cosmetically and/or household acceptable formu- la- tions containing an oil as well as a structurant polymer based on polyurethane/poly- urea chemistry.

TITLE

VISCOSITY MODIFICATION OF ORGANIC PHASE CONTAINING COMPOSITIONS

BACKGROUND OF THE INVENTION

[0001] The disclosed technology relates to structurant polymers based on polyurethane/polyurea chemistry, which efficiently thicken or gel (i.e., provide structure to) oils and oil mixtures. The disclosed technology further relates to structurant polymers based on polyurethane/polyurea chemistry that are oil soluble or oil dispersible and that provide beneficial properties, such as, for example, desirable clarity and/or feel. In addition, the technology relates to cosmetically and/or household acceptable formulations containing an oil as well as a structurant polymer based on polyurethane/polyurea chemistry.

[0002] In the personal care industry, organic phase materials, i.e., oils, emollients, fragrances etc., are used in lotions, crèmes and other products to replenish the oils lost from a substrate, such as skin or hair, during cleansing in order to keep the substrate hydrated, and to improve visual appearance and sensory perception. Most oils and emollients used in the personal care industry are low viscosity fluids which, if used alone, are difficult to handle due to their low viscosity and low surface tension. In addition, various combinations of oils and emollients are often used to provide a pleasant sensory experience that would be otherwise difficult to obtain from single or simple mixture of oils/emollients due to the heavy or tacky feeling of many of the oils and emollients.

[0003] A good deal of effort has been dedicated to the development of thickeners and sensory modifiers for such oil systems but there are large gaps in the current technologies. For example, with respect to thickening of oils, US 2010/0190648, published Jul. 29, 2010 to Croda International, teaches a structured oil system of an oil and a structurant oligomer including urethane and/or urea linkages. The structurant oligomer is limited to those derived from dimer or trimer fatty acids.

[0004] However, oils and emollients, and even fragrances used in the personal care industry span the range of polarities. Current oil thickeners on the market work very well with low polarity oils such as isohexadecane and mineral oil or with very polar oils and solvents, but there are fewer that work with medium polar oils and

emollients or span a large range of oil polarities. In addition, it is much more difficult finding thickener systems that work across oil types and mixtures and leave a highly clear system. The availability of one thickener system would not address the varying oil types.

[0005] In addition, characterization of the polarity of oils, emollients and fragrances is a difficult process since many of those used are not a single molecule but, especially in natural oils, are mixtures of molecules with various but similar structures, which may contain polar groups not found in the main chemical species. Depending on the thickening mechanism, these lower concentration species can have a pronounced effect on the thickening ability of a thickener.

[0006] There are several different mechanisms by which liquids can be thickened: these include hydrodynamic volume, microgels, fibrils and associative molecules or combinations of these. The challenge in commercial formulations is to find materials that will thicken or gel the liquid in the most efficient and lowest cost manner. In all cases, the material used to thicken or gel the oil should be easily soluble or dispersible in the oil. Since oils possess a wide range of polarities, it is difficult to find a single system that will work for all oils. Furthermore, the rheological response that one needs or wants must be factored in the selection of the mechanism since interactions can lead to unpleasant results. Current commercial oil thickeners and gellants use a variety of chemistries which result in a complex understanding of where certain technologies can and cannot be used.

[0007] Accordingly, there is a need for new solutions to the problem of thickening formulations containing an organic phase.

SUMMARY OF THE INVENTION

[0008] The disclosed technology provides structurant polymers based on polyurethane/polyurea chemistry to thicken or gel an organic phase and mixtures of organic phase materials, such as oils and oil mixtures. The disclosed technology further provides structurant polymers based on polyurethane/polyurea chemistry that are soluble or dispersible in an organic phase and that provide beneficial properties, such as, for example, desirable clarity and/or feel. In addition, the technology provides cosmetically and/or household acceptable formulations containing an organic phase and a structurant polymer based on polyurethane/polyurea chemistry.

[0009] In an embodiment, the technology includes an organic phase composition. The organic phase composition can include A) from about 0.01 to about 10 wt.% of a structurant polymer, and B) at least one organic phase. In an embodiment, the organic phase can be present as a majority of the composition. As used herein, "majority" means more than 50 wt%, or more than 60 wt%, or even 70 or 80 wt%, and in an embodiment, from about 50 to 99.5 wt%.

[0010] One aspect of the present technology includes a structurant polymer. The structurant polymer can include i) hard segments, and ii) soft segments. The hard segments of the structurant polymer can be derived from 1) at least one linear non-branched aliphatic diisocyanate, or 2) at least one linear non-branched aliphatic diisocyanate in combination with at least one chain extending compound. The soft segment of the structurant polymer can have an average molecular weight of between about 500 and 6000 and can be derived from at least one hydrophobic oligomer. In one embodiment, the average molecular weight between respective diisocyanates on the structurant polymer backbone can be from between about 500 to about 2000.

[0011] In an embodiment, at least one hydrophobic oligomer can be at least one polyol compound, polyamine compound, or mixtures thereof. In a particular embodiment, the hydrophobic oligomer can be chosen from at least one of a hydrogenated polybutadiene (HPBD), polytetrahydrofuran (pTHF), polypropylene glycol (PPG), polyester, polycaprolactone, polycarbonate, polycastor oil, fatty acid/alcohol adduct, or mixtures thereof. In further embodiments, the hydrophobic oligomer can be in the form of an adduct with a lactone, diacid, or mixture thereof. In embodiments, the hydrophobic oligomer can be modified with an alcohol, amine, anhydride, or mixture thereof. In one embodiment, the hydrophobic oligomer is modified with no more than 2 mole% of a diamine.

[0012] In an embodiment, the structurant polymer can be a polyurethane. In another embodiment, the structurant polymer can be a polyurea. In a further embodiment, the structurant polymer can be a mixed polyurethane/polyurea.

[0013] In an aspect of the organic phase compositions of the present technology there can be employed an organic phase. In an embodiment, the organic phase can be derived from an animal oil, vegetable oil, mineral oil, synthetic oil, or mixture thereof. In a further embodiment, the organic phase can be hydrogenated.

[0014] In an embodiment of the organic phase compositions of the present technology, the ratio of the total hydrogen bonding donor sites to the total hydrogen bonding acceptor sites in the organic phase composition can be about 1 or greater. In a further embodiment, the ΔHSP (defined below) between the oil and the polymer can be less than about 4.

[0015] The present technology also include a method of thickening an organic phase composition. In an embodiment, the method include adding to an organic phase up to about 10 wt.% of a structurant polymer as herein described.

DETAILED DESCRIPTION OF THE INVENTION

[0016] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0017] Without limitation, the present technology includes a structurant polymer, as well as a composition containing the structurant polymer in an organic phase. The structurant polymer provides at least one of thickening/gelling or clarity to the organic phase composition, as well as improved sensorial properties.

Structurant Polymer

[0018] The structurant polymer can be a polyurethane, polyurea, or a mixed polyurethane/polyurea polymer.

[0019] As a polyurethane, the structurant polymer can have a number average molecular weight ("Mn") of from about 7,000 to about 40,000, or from about 8,000 to about 32,000, or from about 9,000 to about 25,000. In some embodiments, the structurant polymer can have an Mn of about 8,000 or 10,000 to about 20,000 or 30,000.

[0020] As a polyurea, or mixed polyurethane/polyurea, the structurant polymer can have a number average molecular weight ("Mn") of from about 7,000 to about 40,000, or from about 8,000 to about 32,000, or from about 9,000 to about 25,000. In some embodiments, the structurant polymer can have an Mn of about 8,000 or 10,000 to about 30,000.

[0021] The structurant polymer can contain (i) hard segments, including diisocyanates and chain extenders, and (ii) soft segments of hydrophobic oligomers.

The Soft Segments

[0022] The soft segments of the structurant polymer can be derived from at least one hydrophobic oligomer (that is, a single hydrophobic oligomers or mixture of two or more different hydrophobic oligomers). The average molecular weight of the at least one hydrophobic oligomer employed in the structurant polymer, and thus, the soft segments of the structurant polymer can be less than about 6,000, such as, for example, less than 5,000, or less than 3,000, or less than about 2,500, or even less than about 2,000. In some embodiments, the average molecular weight of the hydrophobic oligomers and thus, the soft segments in the structurant polymer can be between about 250 or 500 and about 6,000, or 3,000, or between about 750 and about 4,500, or from about 500 to about 3,000. In further embodiments, the molecular weight of the hydrophobic oligomers and thus, the soft segments can be, on average, less than about 2,000, or less than about 1,500, or even less than about 1,250 or 1,000. In some embodiments, the average molecular weight of the hydrophobic oligomers and thus, the soft segments in the structurant polymer can be between about 500 and about 2,000, or between about 500 and about 1,500, or between about 750 and about 1,250, or from about 250 to about 1,000. By average molecular weight, it is meant the sum of the molecular weights of the hydrophobic oligomers/soft segments divided by the total number of hydrophobic oligomers/soft segments.

[0023] The hydrophobic oligomers in the soft segment of the structurant polymer can be polyols, polyamines, or mixtures thereof.

[0024] An example polyol hydrophobic oligomer used in synthesizing the polymer can be, for example, a diol of a conjugated diolefin monomer; polyether polyols; polyesters; polycaprolactones; polycarbonates; polycastor oils; fatty acid/alcohols adducts, or mixtures thereof.

[0025] Diols of conjugated olefin monomers that can be used can include hydrogenated polybutadienediols, and hydrogenated polyisoprene diol. Hydrogenated polybutadiene ("HPBD") polyols are sold by Nippon Soda Co., Ltd under the trade name Nisso-PB™ and Krasol™ polyols sold by Cray Valley USA, LLC. In an embodiment, the hydrophobic oligomer is a hydrogenated polybutadiene.

[0026] Suitable polyether polyols include polyether polyols derived from a diol or polyol having a total of from 2 to 15 carbon atoms, in some embodiments an alkyl

diol or glycol which is reacted with an ether comprising an alkylene oxide having from 2 to 6 carbon atoms, typically ethylene oxide or propylene oxide or mixtures thereof. For example, hydroxy functional polyether can be produced by first reacting propylene glycol with propylene oxide followed by subsequent reaction with ethylene oxide. Primary hydroxy groups resulting from ethylene oxide are more reactive than secondary hydroxy groups and thus are preferred. Useful commercial polyether polyols include poly(ethylene glycol) comprising ethylene oxide reacted with ethylene glycol, poly(propylene glycol) comprising propylene oxide reacted with propylene glycol, poly(tetramethylene ether glycol) comprising water reacted with tetrahydrofuran which can also be described as polymerized tetrahydrofuran or pTHF, and which is commonly referred to as PTMEG. In some embodiments, the polyether intermediate includes PTMEG. Copolyethers can also be utilized in the described compositions. Typical copolyethers include the reaction product of THF and ethylene oxide or THF and propylene oxide. These are available from BASF as PolyTHF® B, a block copolymer, and PolyTHF® R, a random copolymer. In an embodiment the hydrophobic oligomer is polytetrahydrofuran. In another embodiment, the hydrophobic oligomer is polypropylene glycol. The various polyether polyols generally have a number average molecular weight (Mn) as determined by assay of the terminal functional groups which is an average molecular weight greater than about 700, such as from about 700 to about 10,000, from about 1,000 to about 5,000, or from about 1,000 to about 2,500. In some embodiments, the polyether polyols include a blend of two or more different molecular weight polyethers, such as a blend of 2,000 Mn and 1,000 Mn PTMEG.

[0027] Suitable polyesters can include linear polyesters having a number average molecular weight (Mn) of from about 500 to about 10,000, from about 700 to about 5,000, or from about 700 to about 4,000, and generally have an acid number less than 1.3 or less than 0.5. The molecular weight is determined by assay of the terminal functional groups and is related to the number average molecular weight. The polyesters may be produced by (1) an esterification reaction of one or more glycols with one or more dicarboxylic acids or anhydrides or (2) by transesterification reaction, i.e., the reaction of one or more glycols with esters of dicarboxylic acids. Mole ratios generally in excess of more than one mole of glycol to acid are preferred so as to

obtain linear chains having a preponderance of terminal hydroxy groups. Suitable polyesters also include various lactones such as polycaprolactone typically made from ε-caprolactone and a bifunctional initiator such as diethylene glycol. The dicarboxylic acids of the desired polyester can be aliphatic, cycloaliphatic, aromatic, or combinations thereof. Suitable dicarboxylic acids which may be used alone or in mixtures generally have a total of from 4 to 15 carbon atoms and include: succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, dodecanedioic, isophthalic, terephthalic, cyclohexane dicarboxylic, and the like. Anhydrides of the above dicarboxylic acids such as phthalic anhydride, tetrahydrophthalic anhydride, or the like, can also be used. Adipic acid is a preferred acid. The glycols which are reacted to form a desirable polyester intermediate can be aliphatic, aromatic, or combinations thereof, including any of the glycols described above in the chain extender section, and have a total of from 2 to 20 or from 2 to 12 carbon atoms. Suitable examples include ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol, 1,4-cyclohexanedimethanol, decamethylene glycol, dodecamethylene glycol, and mixtures thereof.

[0028] Polycaprolactones useful in the technology described herein can include polyester diols derived from caprolactone monomers. The polycaprolactone polyester polyols are terminated by primary hydroxy groups. Suitable polycaprolactone polyester polyols may be made from ε-caprolactone and a bifunctional initiator such as diethylene glycol, 1,4-butanediol, or any of the other glycols and/or diols listed herein. In some embodiments, the polycaprolactone polyester polyols are linear polyester diols derived from caprolactone monomers. Useful examples include CAPA™ 2202A, a 2,000 number average molecular weight (Mn) linear polyester diol, and CAPA™ 2302A, a 3,000 Mn linear polyester diol, both of which are commercially available from Perstorp Polyols Inc. These materials may also be described as polymers of 2-oxepanone and 1,4-butanediol. The polycaprolactone polyester polyols may be prepared from 2-oxepanone and a diol, where the diol may be 1,4-butanediol, diethylene glycol, monoethylene glycol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol, or any combination thereof. In some embodiments, the diol used to prepare the polycaprolactone polyester polyol is linear. In some embodiments, the polycaprolactone polyester polyol is prepared from 1,4-butanediol. In some embodiments, the

polycaprolactone polyester polyol has a number average molecular weight from 500 to 10,000, or from 500 to 5,000, or from 1,000 or even 2,000 to 4,000 or even 3,000.

[0029] Suitable polycarbonates include those prepared by reacting a glycol with a carbonate. U.S. Patent No. 4,131,731 is hereby incorporated by reference for its disclosure of hydroxy terminated polycarbonates and their preparation. Such polycarbonates are linear and have terminal hydroxy groups with essential exclusion of other terminal groups. The essential reactants are glycols and carbonates. Suitable glycols are selected from cycloaliphatic and aliphatic diols containing 4 to 40, and or even 4 to 12 carbon atoms, and from polyoxyalkylene glycols containing 2 to 20 alkoxy groups per molecule with each alkoxy group containing 2 to 4 carbon atoms. Suitable diols include aliphatic diols containing 4 to 12 carbon atoms such as 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-hexanediol, 1,10-decanediol, hydrogenated dilinoleylglycol, hydrogenated dioleylglycol, 3-methyl-1,5-pentanediol; and cycloaliphatic diols such as 1,3-cyclohexanediol, 1,4-dimethylolcyclohexane, 1,4-cyclohexanediol, 1,3-dimethylolcyclohexane, 1,4-endomethylene-2-hydroxy-5-hydroxymethyl cyclohexane, and polyalkylene glycols. The diols used in the reaction may be a single diol or a mixture of diols depending on the properties desired in the finished product. Polycarbonate intermediates which are hydroxy terminated are generally those known to the art and in the literature. Suitable carbonates are selected from alkylene carbonates composed of a 5 to 7 member ring. Suitable carbonates for use herein include ethylene carbonate, trimethylene carbonate, tetramethylene carbonate, 1,2-propylene carbonate, 1,2-butylene carbonate, 2,3-butylene carbonate, 1,2-ethylene carbonate, 1,3-pentylene carbonate, 1,4-pentylene carbonate, 2,3-pentylene carbonate, and 2,4-pentylene carbonate. Also, suitable herein are dialkylcarbonates, cycloaliphatic carbonates, and diarylcarbonates. The dialkylcarbonates can contain 2 to 5 carbon atoms in each alkyl group and specific examples thereof are diethylcarbonate and dipropylcarbonate. Cycloaliphatic carbonates, especially dicycloaliphatic carbonates, can contain 4 to 7 carbon atoms in each cyclic structure, and there can be one or two of such structures. When one group is cycloaliphatic, the other can be either alkyl or aryl.

On the other hand, if one group is aryl, the other can be alkyl or cycloaliphatic. Examples of suitable diarylcarbonates, which can contain 6 to 20 carbon atoms in each aryl group, are diphenylcarbonate, ditolylcarbonate, and dinaphthylcarbonate.

[0030] Polycastor oils may also be employed as the hydrophobic oligomer. Polycastor oil is polymerized castor oil. Unsaturated bonds (C=C) derived from ricinoleic acid in the castor oil molecules are radically polymerized using organic peroxides or the like as an initiator, thereby forming polycastor oil. Polycastor oil has a structure with more branched portions than castor oil, and the number of hydroxy groups in such a fat and oil molecule is larger than that of castor oil. That is to say, polycastor oil has more hydroxy groups that may function as origins of polymerization, and has a structure with more branched portions. Polycastor oils (for example, those available from Vertellus™) can have functionalities of 2 and higher.

[0031] The hydrophobic oligomers may also be employed as adducts. Suitable adducts can include, for example, adducts with a lactone, diacid or mixtures thereof.

[0032] In one embodiment the hydrophobic oligomer can be a dimer diol (for example, Pripol™ 2030 available from Croda™) with a lactone, diacid or mixture thereof.

The Hard Segments

[0033] The hard segments of the structurant polymer can be derived from at least one diisocyanate. Diisocyanates suitable for use in preparing the polymer can include linear, non-branched aliphatic diisocyanates of from about 2 to about 36 carbon atoms, or about 3 to 33 carbon atoms, or even about 4 or 5 to about 27 or 30 carbon atoms. Such diisocyanates can include, but not be limited to, for example, diisocyanatomethane, hexamethylene diisocyanate (HDI), 1,10-decane diisocyanate, 1,4-butane diisocyanate (BDI), 1,12-dodecane diisocyanate, and the like. In some embodiments, the structurant polymer is prepared with a diisocyanate component that includes HDI. In some embodiments, the structurant polymer is prepared with a diisocyanate component that consists essentially of HDI. In some embodiments, the structurant polymer is prepared with a diisocyanate component that consists of HDI.

[0034] In some embodiments, the diisocyanate component is essentially free of, or even completely free of, diisocyanates having aromatic or cyclic moieties.

[0035] In some embodiments, the diisocyanate component can include other diisocyanates in addition to the linear, non-branched aliphatic diisocyanates, such as, for example, branched diisocyanates, cyclic diisocyanates, aromatic diisocyanates, or mixtures thereof. Branched or cyclic aliphatic diisocyanates were found not to influence intermolecular hydrogen bonding and therefore polymers made exclusively with these diisocyanates did not exhibit thickened oil systems. However, branched or cyclic diisocyanates could be used up to about 50 mole%, or for example, up to about 40 mole%, or up to about 20 or about 30 mole% along with linear unbranched diiocyanates to control the rheological response of the subsequent polymer. In an embodiment, branched or cyclic diisocyanates can be used from about 0.1 to about 50 mole%, or from about 0.5 to about 25 mole%, or from about 1 to about 5 or 10 mole%.

[0036] In an embodiment, the hard segment of the structurant polymer can be prepared from a single diisocyanate, and in other embodiments, the hard segment of the structurant polymer can be prepared from a combination of at least two or more diisocyanates.

[0037] In addition to the diisocyanate, the hard segment can be derived from at least one chain extending compound. Chain extenders can include short chain (i.e., less than 250 molecular weight) polyols, polyamines, and combination thereof.

[0038] Suitable chain extending polyol compounds can include, for example lower aliphatic or short chain glycols having from 2 to 20, or 2 to 12, or 2 to 10 carbon atoms. Suitable examples include ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,4-butanediol (BDO), 1,6-hexanediol (HDO), 1,3-butanediol, 1,5-pentanediol, neopentylglycol, 1,4-cyclohexanedimethanol (CHDM), 2,2-bis[4-(2-hydroxyethoxy) phenyl]propane (HEPP), hexamethylenediol, heptanediol, nonanediol, dodecanediol, 3-methyl-1,5-pentanediol, and hydroxyethyl resorcinol (HER), and the like, as well as mixtures thereof. A particular chain extending diol suitable for the organic phase compositions can include the dimer diols available from Croda™ as Pripol™, and particularly, Pripol 2030.

[0039] Suitable chain extending polyamine compounds can include lower aliphatic or short chain diamines having from 2 to 20, or 2 to 12, or 2 to 10 carbon atoms. Suitable examples include primary amines such as ethylenediamine, propylenediamine, butanediamine, hexamethylenediamine, and the like, as well as mixtures

thereof. Other example polyamine chain extending compound can include secondary amines, such as dimethyl diamine or diphenyl diamine. The chain extender can also include a mixed primary and secondary amines, such as, for example those commercially available as Duomeens™ from AkzoNobel™.

[0040] In some embodiments, the chain extender used to prepare the structurant polymer includes a cyclic chain extender. Suitable examples include CHDM, HEPP, HER, and combinations thereof. In some embodiments, the chain extender used to prepare the polymer includes an aromatic cyclic chain extender, for example HEPP, HER, or a combination thereof. In some embodiments, the chain extender used to prepare the polymer includes an aliphatic cyclic chain extender, for example CHDM. In some embodiments, the chain extender used to prepare the polymer is substantially free of, or even completely free of aromatic chain extenders, for example aromatic cyclic chain extenders. In some embodiments, the chain extender used to prepare the polymer is substantially free of, or even completely free of polysiloxanes. In some embodiments, the chain extender used to prepare the polymer include a linear aliphatic chain extender, which can be branched or non-branched. In one embodiment, the chain extender can be a linear non-branched aliphatic chain extender.

[0041] In some embodiments, the chain extender component includes 1,4-butanediol, 2-ethyl-1,3-hexanediol, 2,2,4-trimethyl pentane-1,3-diol, 1,6-hexanediol, 1,4-cyclohexane dimethylol, 1,3-propanediol, 3-methyl-1,5-pentanediol or combinations thereof. In some embodiments, the chain extender component includes 1,4-butanediol, 3-methyl-1,5-pentanediol or combinations thereof. In some embodiments, the chain extender component includes 1,4-butanediol. Other chain extenders include amine alcohols such as ethanolamine, propanolamine and the like.

[0042] In an embodiment, the hard segment of the structurant polymer can be prepared from a single diisocyanate and a single chain extending compound, and in other embodiments, the hard segment of the structurant polymer can be prepared from a single diisocyanate and a combination of at least two or more chain extending compounds. In an embodiment, the hard segment of the structurant polymer can be prepared from a at least two or more diisocyanates and a single chain extending compound, and in other embodiments, the hard segment of the structurant polymer can be prepared from

at least two or more diisocyanates and a combination of at least two or more chain extending compounds.

Other Optional Components of the Structurant Polymer

[0043] The structurant polymer may be the simple reaction product of the variously chosen diisocyanates, chain extending compounds, and hydrophobic oligomers. However, the structurant polymer may also contain functional groups or substituents reacted onto the polymer backbone. For example, short chain diols or diamines, triols etc. may be reacted onto the structurant polymer to create increased branching. In addition, the polymer may be terminated, or capped, with the addition of a mono-functional reactant, such as, for example, a monofunctional alcohol, amine, anhydride, or mixture thereof. The addition of functional groups or other substituents along the polymer backbone, as well as the termination of the polymer may be done by well known methods in the art. In a particular embodiment, the polymer can be capped with an alkylamine. Other alcohols considered are C_1-C_{60} alkyl alcohols, cholesterol, tocopherol and other alcohols.

[0044] One issue that may arise with thickened cosmetic compositions can be the presence of "orange peel" on the inside surface of the container. Orange peel is known in the coating industry and is produced by three factors: high viscosity, poor flow and surface energy mismatch. The structurant polymer may be modified to reduce the presence of such orange peel by reducing the surface tension of the polymer. In an embodiment, a flow improving reactant may be reacted either into the backbone of the structurant polymer or to the ends of the structurant polymer. The flow improving reactant may be, for example, a silicone containing compound or a fluorine containing compound, such as, for example, a reactive silicone di-hydroxy polymer that may be reacted into the structurant backbone (such a dihydroxy-poly(dimethylsiloxane) (e.g. Aldrich)), or a mono-hydroxy silicone (such as poly(dimethylsiloxane) mono-hydroxy (e.g. Aldrich)) that may be reacted onto the chain ends or a fluorine containing polyols such as Polyfox PF-6320 (Omnova). Such flow improvers may also be added simply in admixture with the structurant polymer however, reacting these moieties into the backbone improves clarity of the polymer in oil. Some example flow improvers can include, but not be limited to, polyether modified

siloxanes, such as BYK™-349 from Atlanta; phosphate esters of tridecyl alcohol ethoxylate, such as Dexter™ OC-70 from Dexter Chemicals; ethoxylated non-ionic wetters, such as Dynol™ 604 from Air Products; alkyl ammonium chloride flourosurfactants, such as Chemguard™ S103A from Chemguard; anionic flourosurfactants, such as Capstone™ FS63 and FS64 from DuPont; ?????, such as Additol™ VXL-4930 from Prospector; polyether siloxane copolymers, such as TegoWet™ 500 from Evonik; polysilicone-16 (and) trideceth-5, such as SilSoft Spread™ SEL from Momentive; dimethicone PEG-7 isostearate, such as SilSense™ DW-18 Silicone, or dimethicone PEG-8 phosphate, such as SilSense™ PE-100 Silicone, or PEG-7 amodimethicone, such as SilSense™ A-21 Silicone, all from Noveon; flourosurfactant diols, such as PolyFox™ 636 or 6520 from Omnova; poly(dimethylsiloxane)-mono; poly(dimethylsiloxane)hydroxyl terminated; or fluoroaliphatic surfactants, such as Masurf™ FS-3240 from Pilot.

Organic phase Compositions

[0045] The inventors have found that an organic phase can be thickened or gelled by adding to the organic phase a structurant polymer specifically formulated to the organic phase. The formulating of the structurant polymer can be achieved, for example, by taking into account 1) the constituent parts of the organic phase, such as the various triglycerides, esters, waxes, etc., that might be in the organic phase, and 2) preparing a structurant polymer having constituent parts (e.g., the hydrophobic oligomer, the diisocyanate, and the other optional components that might be in the structurant polymer) that synergistically interact with the constituent parts of the organic phase.

[0046] The Organic Phase

[0047] The organic phase is generally a hydrocarbon, such as an oil, but may include emollients, fragrances and the like. In essence, the organic phase is any organic material in which a structurant polymer is miscible.

[0048] Non-limiting examples of an organic phase include mineral oils; petrolatums; vegetable oils (including nut oils); hydrogenated vegetable oils; essential oils; algae oils; fish oils; fatty alcohols; fatty acids; fatty acid and fatty alcohol esters;

alkoxylated fatty alcohols; alkoxylated fatty acid esters; benzoate esters; Guerbet esters; alkyl ether derivatives of polyethylene glycols, such as, for example methoxypolyethylene glycol (MPEG); and polyalkylene glycols; lanolin and lanolin derivatives; waxes; and the like, as well as mixtures thereof. The organic phase can be utilized in an amount of greater than about 75 wt. % by weight of the total composition in one aspect, greater than 80 wt. % in another aspect, or greater than 85 or 90 wt. % in a further aspect.

[0049] Mineral oils and petrolatums include cosmetic, USP and NF grades and are commercially available from Penreco under the Drakeol™ and Penreco™ trade names.

[0050] Exemplary vegetable oils suitable as an organic phase can include but are not limited to peanut oil, sesame oil, avocado oil, coconut oil, cocoa butter, almond oil, safflower oil, corn oil, cotton seed oil, castor oil, olive oil, jojoba oil, palm oil, palm kernel oil, soybean oil, wheat germ oil, linseed oil, sunflower seed oil; and the mono-, di-, and triglycerides thereof, and hydrogenated derivatives thereof; and mixtures thereof. Exemplary mono-, di- and triglycerides are, for example, caprylic triglyceride, capric triglyceride, caprylic/capric triglyceride, and caprylic/capric/lauric triglyceride, caprylic/capric/stearic triglyceride, and caprylic/capric/linoleic triglyceride.

[0051] Ethoxylated mono- and diglycerides of the foregoing vegetable oils are also contemplated, such as, for example, PEG-8 Caprylic/Capric Glycerides.

[0052] Essential oils can be employed as an organic phase and can encompass oils having an aromatic essence. Essential oils include, but are not limited to peppermint oil, cedar oil, castor oil, clove oil, geranium oil, lemongrass oil, linseed oil, mint oil, thyme oil, rosemary oil, cornmint oil (Mentha arvensis), garlic oil, anise oil, basil oil, camphor oil, citronella oil, eucalyptus oil, fennel oil, ginger oil, grapefruit oil, lemon oil, lime oil, mandarin oil, orange oil, pine needle oil, pepper oil, rose oil, tangerine oil, tea tree oil, tea seed oil, mineral oil and fish oil.

[0053] Suitable fatty alcohol an organic phase include but are not limited to fatty alcohols containing 8 to 50 carbon atoms. Exemplary fatty alcohols include capryl alcohol, pelargonic alcohol, capric alcohol, lauryl alcohol, myristyl alcohol, cetyl al-

cohol, isocetyl alcohol, stearyl alcohol, isostearyl alcohol, cetearyl alcohol, oleyl alcohol, ricinoleyl alcohol, arachidyl alcohol, icocenyl alcohol, behenyl alcohol, and mixtures thereof.

[0054] Suitable fatty acids as the organic phase include but are not limited to fatty acids containing 10 to 50 carbon atoms. Exemplary fatty acids are selected from capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, arachidic acid, behenic acid, and mixtures thereof.

[0055] Suitable fatty acid and fatty alcohol ester organic phases include but are not limited to hexyl laurate, decyl oleate, isopropyl stearate, isopropyl isostearate, butyl stearate, octyl stearate, ethylhexyl stearate, cetyl stearate, myristyl myristate, octyldodecyl stearoylstearate, octylhydroxystearate, diisopropyl adipate, isopropyl myristate, isopropyl palmitate, ethyl hexyl palmitate, isodecyl oleate, isodecyl neopentanoate, diisopropyl sebacate, isostearyl lactate, isostearyl hydroxy stearate, diisostearyl fumarate, lauryl lactate, diethyl hexyl maleate, PPG-14 butyl ether and PPG-2 myristyl ether propionate, ethylhexyl octanoate, cetearyl octanoate, cetearyl ethylhexanoate, and mixtures thereof.

[0056] Alkoxylated fatty alcohols are ethers formed from the reaction of a fatty alcohol with an alkylene oxide, generally ethylene oxide or propylene oxide. Suitable ethoxylated fatty alcohols are adducts of fatty alcohols and polyethylene oxide. In one aspect the ethoxylated fatty alcohols can be represented by the formula R--$(OCH_2CH_2)_n$--OH wherein R represents the linear or branched aliphatic residue of the parent fatty alcohol and n represents the number of molecules of ethylene oxide. In another aspect, R is derived from a fatty alcohol containing 8 to 40 carbon atoms. In one aspect n is an integer ranging from 2 to 100, 3 to 80 in another aspect, and 3 to 50 in a further aspect. In a still further aspect, R is derived from a fatty alcohol organic phase set forth above. Exemplary ethoxylated fatty alcohols can include but are not limited to capryl alcohol ethoxylate, lauryl alcohol ethoxylate, myristyl alcohol ethoxylate, cetyl alcohol ethoxylate, stearyl alcohol ethoxylate, cetearyl alcohol ethoxylate oleyl alcohol ethoxylate, and, behenyl alcohol ethoxylate, wherein the number of ethylene oxide units in each of the foregoing ethoxylates can range from 2 and above in one aspect, and from 2 to about 150 in another aspect. It is to be

recognized that the propoxylated adducts of the foregoing fatty alcohols and ethoxylated/propoxylated adducts of the foregoing fatty alcohols are also contemplated. More specific examples of alkoxylated alcohols are beheneth 5-30 (the 5-30 meaning the number of repeating ethylene oxide or propylene oxide units), Ceteareth 2-100, Ceteth 1-45, Cetoleth 24-25, Choleth 10-24, Coceth 3-10, C9-11 Pareth 3-8, C11-15 pareth 5-40, C11-21 Pareth 3-10, C12-13 Pareth 3-15, Deceth 4-6, Dodoxynol 5-12, Glycereth 7-26, Isoceteth 10-30, Isodeceth 4-6, Isolaureth 3-6, Isosteareth 3-50, Laneth 5-75, Laureth 1-40, Nonoxynol 1-120, Nonoxynol 5-150, Octoxynol 3-70, Oleth 2-50, Steareth 2-100, Trideceth 2-10, and so on.

[0057] Alkoxylated fatty acids are formed when a fatty acid is reacted with an alkylene oxide or with a pre-formed polymeric ether. The resulting product may be a monoester, diester, or mixture thereof. Suitable ethoxylated fatty acid ester organic phases suitable for use are products of the addition of ethylene oxide to fatty acids. The product is a polyethylene oxide ester of a fatty acid. In one aspect, the ethoxylated fatty acid esters can be represented by the formula R--C(O)O(CH_2CH_2O)$_n$--H, wherein R represents the linear or branched aliphatic residue of a fatty acid and n represents the number of molecules of ethylene oxide. In another aspect, n is an integer ranging from 2 to 50, 3 to 25 in another aspect, and 3 to 10 in a further aspect. In still another aspect, R is derived from a fatty acid containing 8 to 30 carbon atoms. In a still further aspect, R and the C(O)O- group is derived from a fatty acid organic phase material set forth above. It is to be recognized that propoxylated and ethoxylated/propoxylated products of the foregoing fatty acids are also contemplated. Exemplary alkoxylated fatty acid esters include but are not limited to capric acid ethoxylate, lauric acid ethoxylate, myristic acid ethoxylate, stearic acid ethoxylate, oleic acid ethoxylate, coconut fatty acid ethoxylate, and polyethylene glycol 400 propoxylated monolaurate, wherein the number of ethylene oxide units in each of the foregoing ethoxylates can range from 2 and above in one aspect, and from 2 to about 50 in another aspect. More specific examples of ethoxylated fatty acids are PEG-8 distearate (the 8 meaning the number of repeating ethylene oxide units), PEG-8 behenate, PEG-8 caprate, PEG-8 caprylate, PEG-8 caprylate/caprate, PEG cocoates (PEG without a number designation meaning that the number of ethylene oxide units ranges from 2 to 50), PEG-15 dicocoate, PEG-2 diisononanoate, PEG-8 diisostearate,

PEG-dilaurates, PEG-dioleates PEG-distearates, PEG Ditallates, PEG-isostearates, PEG-jojoba acids, PEG-laurates, PEG-linolenates, PEG-myristates, PEG-oleates, PEG-palmitates, PEG-ricinoleates, PEG-stearates, PEG-tallates, and the like.

[0058] Benzoate ester organic phases are selected from but not limited to C_{12} to C_{15} alkyl benzoate, isostearyl benzoate, octyl dodecyl benzoate, stearyl benzoate, dipropylene glycol dibenzoate, methyl gluceth-20 benzoate, castor oil benzoate, cetyl ricinoleate benzoate, ethylhexyl hydroxystearate benzoate, dimethicone PEG/PPG-20/23 benzoate, and dimethicone PEG-8 benzoate.

[0059] Guerbet ester organic phase materials are formed from the esterification reaction of a Guerbet alcohol with a carboxylic acid. Guerbet ester organic phase materials are commercially available from Noveon, Inc. as G-20, G-36, G-38, and G-66.

[0060] Lanolin and lanolin derivatives are selected from lanolin, lanolin wax, lanolin oil, lanolin alcohols, lanolin fatty acids, alkoxylated lanolin, isopropyl lanolate, acetylated lanolin alcohols, and combinations thereof. Lanolin and lanolin derivatives are commercially available from Noveon, Inc. under the following trade names Lanolin LP 108 USP, Lanolin USP AAA, Acetulan™, Ceralan™, Lanocerin™, Lanogel™ (product designations 21 and 41), Lanogene™, Modulan™, Ohlan™, Solulan™ (product designations 16, 75, L-575, 98, and C-24), Vilvanolin™ (product desginations C, CAB, L-101, and P).

[0061] Waxes include those derived from plant, animal/insect, mineral, petroleum and synthetic sources. Synthetically modified natural (plant and animal/insect) waxes are also contemplated. Exemplary plant derived waxes include but are not limited to bayberry wax, candelilla wax, hydrolyzed candelilla wax, carnauba wax, ethoxylated carnauba wax (e.g., PEG-12 carnauba wax), hydrolyzed carnauba wax, carnauba acid wax, hydrogenated castor wax, esparto wax, hydrogenated Japan wax, hydrogenated jojoba oil, jojoba oil esters, sulfurized jojoba oil, ouricury wax, palm kernel wax, and hydrogenated rice bran wax. Exemplary animal/insect derived waxes include but are not limited to beeswax, oxidized beeswax, ethoxylated beeswax (e.g., PEG-6 beeswax, PEG-8 beeswax, PEG-12 beeswax, PEG-20 beeswax), dimethicone copolyol beeswax esters and dimethiconol beeswax ester (e.g. Bis-Hydroxyethoxypropyl Di-

methicone Beeswax Esters, Dimethicone PEG-8 Beeswax, and Dimethiconol Beeswax available from Noveon, Inc. under the Ultrabee™ trademark), Chinese wax, shellac wax, spermaceti wax, mink wax, and lanolin wax. Exemplary mineral waxes include but are not limited to ceresin waxes, montan wax, montan acid wax, and ozocerite. Exemplary petroleum waxes include paraffin waxes, such as isododecane and isohexadecane, microcrystalline waxes, and oxidized microcrystalline waxes. Exemplary synthetic waxes include synthetic beeswax, synthetic candelilla wax, synthetic carnauba wax, synthetic Japan wax, synthetic jojoba oil, polyolefin waxes (e.g., polyethylene wax), ethylene glycol diesters or triesters of fatty acids containing 18 to 40 carbon atoms. Mixtures of two or more of the forgoing waxes and classes of waxes are also contemplated.

[0062] In some embodiments, the organic phase material can be an emollient such as dioctyl/dicapryl ether.

[0063] In some embodiments, the organic phase material can be an organic sunscreen.

[0064] The organic phase material can also be a fragrance, whether naturally derived or synthetically derived.

[0065] In some embodiments, the oil comprises, consists essentially of, or consists of a mineral oil. In other embodiments, the oil comprises, consists essentially of, or consists of a vegetable oil.

[0066] In some embodiments, the organic phase material can be any of the common oils employed in cosmetic formulations, such as, for example, castor oil, cocoglycerides (di, tri), caprylic/capric triglyceride, coconut oil, sweet almond oil, sunflower oil, isopropyl palmitate, cetearyl ethylhexanoate, ethylhexyl stearate, jojoba oil, isododecane, mineral oil, isohexadecane, dioctyl/dicapryl ether, or mixtures thereof.

[0067] It will be recognized by those of skill in the art that the various organic phase materials mentioned above may be considered in various categories. Thus, the exemplary descriptions of the various organic phase materials is not meant as a single definition of any one specific organic phase material. There are many more organic phase materials not referenced herein, but nonetheless would be expected to be suitable as an organic phase hereunder when employing the formulating principles set

forth herein. In addition, the organic phase materials may be used alone or in combination with other organic phase materials.

[0068] Clarity

[0069] A starting point for determining the appropriate structurant polymer for a chosen organic phase material can be to determine the desired clarity of the composition. To achieve a clear composition for a given organic phase, hydrophobic oligomers that are soluble in the chosen organic phase can be employed as a constituent part of the structurant polymer. The determination of solubility of hydrophobic oligomers in the organic phase can be achieved empirically, for example, by measuring the clarity of the solution. Clarity can be measured by several methods. One example method for measuring clarity can encompass employing a reflectance probe (such as a Brinkman PC950 colorimeter) to measure the average light transmission of the sample, and comparing the average transmission to the transmission of a standard filtered neat oil. Another method can include visually comparing the sample to a scale of samples having varying clarity. For example, a number of standard samples can be prepared with varying amounts of scattering in the oil of interest. The standard samples can be graded from 1 (poor) to 5 (excellent) and the reference sample can subsequently be graded in comparison to the standard samples.

[0070] In addition, a method of determining the solubility of hydrophobic oligomers in the organic phase can be to compare the Hansen Solubility Parameters ("HSP") of the hydrophobic oligomers with the HSP of the chosen organic phase. The HSP includes a dispersive parameter "δD," a polar parameter "δP," and a hydrogen bonding parameter "δH." The comparison between the different parameters of the organic phase and the hydrophobic oligomers can be designated as the ΔHSP_{o-p}, and can be calculated according to Formula I:

Formula I

$$\Delta HSP_{o-p}=\sqrt{\{4(\delta D_o-\delta D_p)^2+(\delta P_o-\delta P_p)^2+(\delta H_o-\delta H_p)^2\}}$$

where the respective δD, δP and δH parameters encompass both single values and the average of the parameters for all materials in the respective mixtures.

[0071] In some cases the HSP of the organic phase and/or hydrophobic oligomers can be extracted from the literature, and in others the HSP can be estimated from software developed by S. Abbott, C. Hansen and H. Yamamoto (www.hansen-solubility.com). The smaller the ΔHSP_{o-p}, the more likely the hydrophobic oligomers will be soluble in the chosen organic phase, and thereby the clearer the composition is likely to be. For a clear composition, the ΔHSP_{o-p} can be less 4, or less than 2, and in some cases 1 or less or 0.5 or less. If clarity is not a required property of the composition, the ΔHSP_{o-p} can also be 4 or greater. However, if the ΔHSP_{o-p} is too high (> 8), then the polymer will be minimally soluble in the oil and therefore will not thicken.

[0072] In another embodiment, solubilty of the polymer can be deduced from the solubility of the oligomer simply by measuring the solubility of the oligomer. Solubility of the oligomer can be found, for example, by dissolving up to 50 wt % of the oligomer of interest in 50 wt% oil of interest and heating the mixture to 80°C for 12-16 hours in an oven with intermittent stirring. After allowing the sample to cool to room temperature, the solubility can be assessed qualitatively. If the solution is completely clear, the oligomer can be considered to be completely soluble. If the solution is cloudy or separated, the process can be repeated with a reduced amount of the oligomer concentration (for example, in steps of 5 wt%) until a clear solution is obtained. The oligomer solubility is reported as the highest concentration that gave a clear solution.

[0073] Thickening/Gelling

[0074] To achieve a thickened or gelled composition, it has been found that the distance between diisocyanate moieties along the structurant polymer backbone can have an effect on the thickening or gelling efficiency of the polymer within the chosen organic phase. In general, the closer the diisocyanates moieties are spaced relative to neighboring diisocyanates along the polymer backbone, the better the thickening efficiency of the polymer in the organic phase. The largest contributor to the spacing of the diisocyanate moieties on the polymer backbone can be the hydrophobic oligomer. Thus, the hydrophobic oligomers in the polymer can be chosen by molecular weight to minimize the spacing between diisocyanate moieties. In an embodiment of the technology, the molecular weight of the hydrophobic oligomers can be,

on average, less than about 2,000, or less than about 1,500, or less than 1,250, or even less than about 1,000. In some embodiments, the average molecular weight of the oligomers in the polymer can be between about 500 and about 2,000, or about 500 to about 1,500, or between about 750 and about 1,250, or from about 250 to about 1,000. By average molecular weight, it is meant is the sum of the molecular weights of the oligomers divided by the total number of oligomers.

[0075] In an embodiment, the polymer can optionally contain chain extending components. Chain extending components are generally short chain compounds, such as, for example, short chain diols or short chain diamines. The use of such chain extending compounds can serve to intermittently replace the oligomers along the polymer backbone. Where the chain extending component replaces the oligomer, the respective diisocyanate moieties will necessarily be closer together. Thus, the use of chain extending components can be employed to affect the thickening efficiency of the polymer in a particular organic phase. As a result, the use of chain extending components can allow for higher molecular weight oligomers in the polymer backbone. In such cases that a chain extending component is employed in the polymer, the average molecular weight of the oligomers can be on average, less than about 6,000, such as, for example, less than 4,500, or less than about 3,000, or less than about 2,500, or even less than about 2,000. In some embodiments, the average molecular weight of the oligomers in the polymer can be between about 500 and about 3,000, or between about 750 and about 2,500, or from about 250 to about 2,000.

[0076] In addition to controlling the molecular weight of the oligomer, the ratio of the hydrogen bonding donors (H_d) to hydrogen bonding acceptors (H_a) in the polymer/organic phase can be controlled. In particular, the ratio of H_d/H_a can be 1 or greater, or greater than 1. The H_d and H_a of the system can be determined by inventorying the constituent parts of both the organic phase and the polymer, and taking the summation of the total H_d and H_a between the two. Where the H_d/H_a is less than 1, or 1 or less. H_d can be increased by adding more polymer to the system.

[0077] For example, consider a theoretical polyurethane prepared from a di-functional oligomer of about 1,500 molecular weight, and a diisocyanate, which provides a polymer of about 15,000 molecular weight. Each oligomer is di-functional and

therefore has 2 hydrogen bonding acceptors. Likewise, each diisocyanate is di-functional and has 2 hydrogen bond donors. Based on the stoichiometry to achieve a 15,000 molecular weight polymer, the polymer will have an oligomer/diisocyanate ratio of about 10/11. Thus, the total H_d for the polymer will be about 22, that is, 11 diisocyanates having 2 donors each. By comparison, if the oligomer was replaced with a lower molecular weight oligomer (for example, 1,000) then, at the same polymer molecular weight (~15,000), the number of donor sites would be larger (2 x 16 = 32).

[0078] For most solvents (e.g., oil or emollient), the H_d/H_a is generally nearly zero since such materials are generally based on esters of fatty acids. For example, for isopropyl palmitate ("IPP"), H_d is 0 and H_a is 2, such that H_d/H_a is 0 for each IPP molecule. On a molecule-to-molecule basis, the theoretical polymer to IPP will provide an H_d/H_a ratio of about 11 excess donors (i.e., 22 from the polymer and 2 from the IPP for 22/2=11). Since the molecular weight of the IPP is about 50 times less than the polymer and the polymer concentration in solution is much less than the IPP (say 5 wt%), the effective H_d/H_a would be approximately 10^{-2} and it would not be expected that the polymer would thicken at this concentration unless some driving force, such as phase separation occurred.

[0079] The total concentration of polymer in the organic phase can be up to 10 wt%, or up to 8 wt%, or up to 6 wt%. In some embodiments, the total concentration of polymer in the organic phase can be from about 0.1 to about 10 wt%, or from about 0.1 or 0.5 to about 5 or 6 wt%, and even from about 1 to about 3 or 4 wt%.

[0080] In the case of adding an amine, whether as the hydrophobic oligomer or as a chain extending compound, urea linkages can be formed rather than urethane linkages. The use of urea linkages in the structurant polymers should be done with caution since ureas are more polar moieties than urethanes and can reduce the clarity and solubility of the polymer in the organic phase. However, judicious use of urea can also increase the efficiency and produce a higher gel strength in the oil formulation as such urea linkages increase the number of H_d in the composition.

[0081] The rheology of the compositions can be determined by measuring the storage modulus (G') and loss modulus (G") of a sample, which are commonly reported in Pascals (Pa). G' describes the elastic or solid-like properties of a sample. The higher

the G' value, the more elastic or solid-like the sample will be. G" describes the viscous or fluid-like properties of the sample. The higher the G", the more fluid-like the sample will be. Where G' is greater than G", the sample will behave in a more elastic or solid-like manner, and where G" is greater than G', the sample will behave in a more fluid-like or viscous manner. Both G' and G" can be determined by employing standard rheometric techniques.

Other Additives

[0082] The organic phase compositions can additionally contain other additives, or the organic phase compositions can be employed in a fully formulated composition alongside other additives. Other additives can include, for example, additives commonly found in personal care, home care, health care, and/or institutional and industrial care compositions.

[0083] The term "personal care products" as used herein includes, without being limited thereto, cosmetics, toiletries, cosmeceuticals, beauty aids, insect repellents, personal hygiene and cleansing products applied to the body, including the skin, hair, scalp, and nails of humans and animals.

[0084] The term "home care products" as used herein includes, without being limited thereto, products employed in a domestic household for surface cleaning or maintaining sanitary conditions, such as in the kitchen and bathroom (e.g., hard surface cleaners, hand and automatic dish care, toilet bowl cleaners and disinfectants), and laundry products for fabric care and cleaning (e.g., detergents, fabric conditioners, pre-treatment stain removers), and the like.

[0085] The term "health care products" as used herein includes, without being limited thereto, pharmaceuticals (controlled release pharmaceuticals), pharmacosmetics, oral care (mouth and teeth) products, such as oral suspensions, mouthwashes, toothpastes, dentifrices, and the like, and over-the-counter products and appliances (topical and transdermal), such as patches, plasters and the like, externally applied to the body, including the skin, scalp, nails and mucous membranes of humans and animals, for ameliorating a health-related or medical condition, for generally maintaining hygiene or well-being, and the like.

[0086] The term "institutional and industrial care" ("I&I") as used herein includes, without being limited thereto, products employed for surface cleaning or maintaining sanitary conditions in institutional and industrial environments, textile treatments (e.g., textile conditioners, carpet and upholstery cleaners), automobile care (e.g., hand and automatic car wash detergents, tire shines, leather conditioners, liquid car polishes, plastic polishes and conditioners), paints and coatings, and the like.

[0087] For example, the oil compositions can include, Pharmaceutical and Cosmeceutical acitves; Opacifying/Pearlescent Materials; Opacifiers; Particulates; Botanicals; Preservatives; Auxiliary Rheology Modifier; Chelating Agents; Auxiliary Solvents and Diluents; Fragrances; Surfactants; silicone fluids (e.g., volatile silicone oils and non-volatile silicone oils); Organic and Inorganic UV Filters, and Emollients; among others.

[0088] Pharmaceutical and Cosmeceutical Actives

[0089] The organic phase compositions can be formulated with a pharmaceutical and/or a cosmeceutical active to deliver a desired effect. Examples of such active ingredients include, but are not limited to, caffeine, vitamin C, vitamin D, vitamin E, anti-stretch mark compounds, astringents (e.g., alum, oatmeal, yarrow, witch hazel, bayberry, and isoinvinvepropyl alcohol), draining compounds, depilatories (e.g., calcium and sodium hydroxide, calcium or sodium thioglycolate, or mixtures thereof), hair growth promoting compounds (e.g., monoxidil), skin and hair nourishing compounds, skin and hair protecting compounds, self-tanning compounds (e.g., mono- or polycarbonyl compounds such as, for example, isatin, alloxan, ninhydrin, glyceraldehyde, mesotartaric aldehyde, glutaraldehyde, erythrulose, tyrosine, tyrosine esters, and dihydroxyacetone), UV absorbers (e.g., ethylhexyl methoxy cinnamate, octinoxate, octisalate, oxybenzone), skin lighteners (e.g., kojic acid, hydroquinone, arbutin, fruital, vegetal or plant extracts, such as lemon peel extract, chamomile, green tea, paper mulberry extract, and the like, ascorbyl acid derivatives, such as ascorbyl palmitate, ascorbyl stearate, magnesium ascorbyl phosphate, and the like), lip plumping compounds, anti-aging, anti-cellulite, and anti-acne compounds (e.g., acidic agents such as alpha-hydroxy acids (ANAs), beta-hydroxy acids (BHAs), alpha amino-acids, alpha-keto acids (AKAs), acetic acid, azelaic acid, and mixtures thereof), anti-in-

flammatory compounds (e.g., aspirin, ibuprofen, and naproxen), analgesics (e.g., acetaminophen), antioxidant compounds, antiperspirant compounds (e.g., aluminum halides, aluminum hydroxyhalides, aluminum sulfate, zirconium (zirconyl) oxyhalides, zirconium (zirconyl)hydroxyhalides, and mixtures or complexes thereof), deodorant compounds (e.g., 2-amino-2-methyl-1-propanol (AMP), ammonium phenolsulfonate; benzalkonium chloride; benzethonium chloride, bromochlorophene, cetyltrimethylammonium bromide, cetyl pyridinium chloride, chlorophyllin-copper complex, chlorothymol, chloroxylenol, cloflucarban, dequalinium chloride, dichlorophene, dichloro-m-xylenol, disodium dihydroxyethyl sulfosuccinylundecylenate, domiphen bromide, hexachlorophene, lauryl pyridinium chloride, methylbenzethonium chloride, phenol, sodium bicarbonate, sodium phenolsulfonate, triclocarban, triclosan, zinc phenolsulfonate, zinc ricinoleate, and mixtures thereof); and suitable mixtures of any of the above.

[0090] Opacifying/Pearlescent Materials

[0091] Some formulations are often opacified by deliberately incorporating pearlescent materials therein to achieve a cosmetically attractive pearl-like appearance, known as pearlescence. An opacifier often is included in a composition to mask an undesirable aesthetic property, such as to improve the color of a composition that is darkened due to the presence of a particular ingredient, or to mask the presence of particulate matter in the composition. Opacifiers also are included in compositions to improve the aesthetics and consumer acceptance of an otherwise esthetically unpleasing composition. For example, an opacifier can impart a pearlescent appearance to a clear composition, thereby communicating an appearance of creaminess, mildness and body to the consumer. Persons skilled in the art are aware of problems faced by formulators in consistently preparing a stable pearlescent formulation. A detailed discussion is found in the article "Opacifiers and pearling agents in shampoos" by Hunting, Cosmetic and Toiletries, Vol. 96, pages 65-78 (July 1981), incorporated herein by reference.

[0092] The opacifying or pearlescent material includes ethylene glycol monostearate, ethylene glycol distearate, polyethylene glycol distearate, stearic alcohol, bismuth oxychloride coated mica, mica coated metal oxides (e.g., titanium dioxide,

chromium oxide, iron oxides), myristyl myristate, guanine, glitter (polyester or metallic), and mixtures thereof. Other pearlescent materials can be found in U.S. Pat. No. 4,654,207, U.S. Pat. No. 5,019,376, and U.S. Pat. No. 5,384,114, which are herein incorporated by reference.

[0093] An opacifier can be selected from a number of different chemical classes including inorganic compounds, e.g., various aluminum and magnesium salts, and organic compounds, like fatty alcohols, fatty esters and various polymers and copolymers. A representative listing of opacifiers is found in the CTFA Cosmetic Ingredient Handbook, J. Nikitakis, ed., The Cosmetic, Toiletry and Fragrance Association, Inc., Washington, D.C., 1988, at page 75.

[0094] In one aspect, the amount of the pearlescent material can be used in amounts ranging from about 0.05% to about 10% by weight, and from about 0.1% to about 3% by weight in another aspect, based upon the total weight of the organic phase composition.

[0095] Particulates

[0096] Numerous other substantially insoluble compounds and components which require stabilization and/or suspension can be utilized in the organic phase compositions. Examples of such other insoluble compounds include pigments, exfoliants, and anti-dandruff agents.

[0097] Exemplary pigments are metal compounds or semi-metallic compounds and may be used in ionic, nonionic or oxidized form. The pigments can be in this form either individually or in a mixture or as individual mixed oxides or mixtures thereof, including mixtures of mixed oxides and pure oxides. Examples are the titanium oxides (e.g., TiO_2), zinc oxides (e.g., ZnO), aluminum oxides (for example, Al_2O_3), iron oxides (for example, Fe_2O_3), manganese oxides (e.g., MnO), silicon oxides (e.g., SiO_2), silicates, cerium oxide, zirconium oxides (e.g., ZrO_2), barium sulfate ($BaSO_4$), and mixtures thereof.

[0098] Numerous cosmetically useful particulate exfoliating agents are known in the art, and the selection and amount is determined by the exfoliating effect desired from the use of the composition, as recognized by those skilled in the cosmetic arts. Useful exfoliating agents include, but are not limited to, natural abrasives, inorganic

abrasives, synthetic polymers, and the like, and mixtures thereof. Representative exfoliants include, but are not limited to, ground or powdered pumice, stone, zeolites, nut shells (e.g., almond, pecan, walnut, coconut, and the like), nut meals (e.g., almond, and the like), fruit pits (e.g., apricot, avocado, olive, peach, and the like), hulls, seed and kernel (e.g., oat bran, corn meal, rice bran, grape seed, kiwi seed, wheat, jojoba seed, loofah seed, rose hip seed, and the like), plant matter (e.g., tea tree leaves, corn cob, fruit fibers, seaweed, loofah sponge, microcrystalline cellulose, and the like), bivalve shells (oyster shell, and the like), calcium carbonate, dicalcium pyrophosphate, chalk, silica, kaolin clay, silicic acid, aluminum oxide, stannic oxide, sea salt (e.g., Dead Sea salt), talc, sugars (e.g., table, brown, and the like), polyethylene, polystyrene, microcrystalline polyamides (nylons), microcrystalline polyesters, polycarbonates, and stainless steel fibers. The foregoing exfoliants can be used in the form of granules, powders, flours, and fibers.

[0099] Any suitable anti-dandruff agent can be employed in the organic phase compositions. Exemplary anti-dandruff agents include, but are not limited to, sulfur, zinc pyrithione, zinc omadine, miconazole nitrate, selenium sulfide, piroctone olamine, N,N-bis(2-hydroxyethyl)undecenamide, cade oil, pine tar, Allium cepa extract Picea abies extract, and Undecyleneth-6, and the like, and mixtures thereof.

[0100] Other particulates suitable for use in the present compositions include clay, swellable clay, laponite, gas bubbles, liposomes, microsponges, cosmetic beads and flakes. Cosmetic beads, flakes and capsules can be included in a composition for aesthetic appearance or can function as micro- and macro-encapsulants for the delivery of benefit agents to the skin and hair. Exemplary bead components include, but are not limited to, agar beads, alginate beads, jojoba beads, gelatin beads, Styrofoam™ beads, polyacrylate, polymethylmethacrylate (PMMA), polyethylene beads, Unispheres™ and Unipearls™ cosmetic beads (Induchem USA, Inc., New York, N.Y.), Lipocapsule™, Liposphere™, and Lipopearl™ microcapsules (Lipo Technologies Inc., Vandalia, Ohio), and Confetti II™ dermal delivery flakes (United-Guardian, Inc., Hauppauge, N.Y.).

[0101] In one aspect, the amount of particulate component can range from about 0.1% to about 10% by weight based on the total weight of the composition.

[0102] Botanicals

[0103] Optionally, the organic phase compositions can be formulated with botanical material extracts. Extracted botanical materials can include any water soluble or oil soluble material extracted from a particular plant, fruit, nut, or seed. In one aspect, the botanical actives are present in an amount ranging from about 0.1% to about 10% by weight, from about 0.5% to about 8% by weight in another aspect, and from about 1% to about 5% by weight in a further aspect, based of the total weight of the composition.

[0104] Suitable botanical agents can include, for example, extracts from Echinacea (e.g., sp. angustifolia, purpurea, pallida), yucca glauca, willow herb, basil leaves, Turkish oregano, carrot root, grapefruit, fennel seed, rosemary, tumeric, thyme, blueberry, bell pepper, blackberry, spirulina, black currant fruit, tea leaves, such as for, example, Chinese tea, black tea (e.g., var. Flowery Orange Pekoe, Golden Flowery Orange Pekoe, Fine Tippy Golden Flowery Orange Pekoe), green tea (e.g., var. Japanese, Green Darjeeling), oolong tea, coffee seed, dandelion root, date palm fruit, gingko leaf, green tea, hawthorn berry, licorice, sage, strawberry, sweet pea, tomato, vanilla fruit, comfrey, arnica, centella asiatica, cornflower, horse chestnut, ivy, magnolia, oat, pansy, skullcap, seabuckthorn, white nettle, and witch hazel. Botanical extracts include, for example, chlorogenic acid, glutathione, glycrrhizin, neohesperidin, quercetin, rutin, morin, myricetin, absinthe, and chamomile.

[0105] Preservatives

[0106] In one aspect, any preservative suitable for use in personal care, home care, health care, and institutional and industrial care products, can be used in the organic phase compositions. Suitable preservatives include polymethoxy bicyclic oxazolidine, methyl paraben, propyl paraben, ethyl paraben, butyl paraben, benzyltriazole, DMDM hydantoin (also known as 1,3-dimethyl-5,5-dimethyl hydantoin), imidazolidinyl urea, phenoxyethanol, phenoxyethylparaben, methylisothiazolinone, methylchloroisothiazolinone, benzoisothiazolinone, triclosan, and suitable polyquaternium compounds disclosed above (e.g., Polyquaternium-1).

[0107] In another aspect, acid based preservatives are useful in the organic phase compositions. Any acid based preservative that is useful in personal care, home care, health care, and institutional and industrial care products can be used in the organic

phase compositions. In one aspect the acid preservative is a carboxylic acid compound represented by the formula: $R^{53}C(O)OH$, wherein R^{53} represents hydrogen, a saturated and unsaturated hydrocarbyl group containing 1 to 8 carbon atoms or C_6 to C_{10} aryl. In another aspect, R^{53} is selected from a hydrogen, a C_1 to C_8 alkyl group, a C_2 to C_8 alkenyl group, or phenyl. Exemplary acids are, but are not limited to, formic acid, acetic acid, propionic acid, sorbic acid, caprylic acid, and benzoic acid, and mixtures thereof.

[0108] The preservatives typically comprise from about 0.01% to about 3.0% by weight in one aspect, from about 0.1% to about 1% by weight in another aspect, and from about 0.3% to about 1% by weight in a further aspect, of the total weight of the personal care organic phase compositions.

[0109] Auxiliary Rheology Modifiers

[0110] In another aspect, the organic phase compositions can be formulated with one or more rheology modifiers and thickeners. Suitable rheology modifiers and thickeners can include, for example, silica and waxes.

[0111] Emulsifiers

[0112] Emulsifiers when employed in the organic phase compositions include, but are not limited to, the C_{12}-C_{22} fatty alcohols, C_{12}-C_{22} alkoxylated alcohols, C_{12}-C_{22} fatty acids, C_{12}-C_{22} alkoxylated fatty acids (the alkoxylates each having 10 to 80 units of ethylene oxide, propylene oxide, and combinations of ethylene oxide/propylene oxide present in the molecule), C_8-C_{22} APGs, ethoxylated sterols (wherein the number of ethylene oxide units ranges from 2 to about 150), partial esters of polyglycerols, esters and partial esters of polyols having 2 to 6 carbon atoms, partial esters of polyglycerols, and organosiloxanes, and combinations thereof.

[0113] The C_8-C_{22} alkyl APG emulsifiers are prepared by reacting glucose or an oligosaccharide with primary fatty alcohols having 8 to 22 carbon atoms, and comprise a glucosidically bonded C_8-C_{16} alkyl group on an oligoglucoside residue whose average degree of oligomerization is 1 to 2. In addition to the APGs described as surfactants above, APGs are available under the trademark Plantacare™ (Cognis Corporation, Cincinnati, Ohio). Exemplary alkyl glucosides and oligoglycosides are selected from octyl glucoside, decyl glucoside, lauryl glucoside, palmityl glucoside,

isostearyl glucoside, stearyl glucoside, arachidyl glucoside and behenyl glucoside, and mixtures thereof.

[0114] Emulsifiers based on the esters and partial esters of polyols having 2 to 6 carbon atoms are condensed with linear saturated and unsaturated fatty acids having 12 to 30 carbon atoms are, for example, the monoesters and diesters of glycerol or ethylene glycol or the monoesters of propylene glycol with saturated and unsaturated C_{12}-C_{30} fatty acids.

[0115] Exemplary fatty alcohols and fatty acids, as well as their alkoxylates, the partial esters of polyglycerols, as well as the organosiloxanes are described above.

[0116] Chelating Agents

[0117] Chelating agents can be employed to stabilize the personal care, home care, health care, and institutional care organic phase compositions against the deleterious effects of metal ions. When utilized, suitable chelating agents include EDTA (ethylene diamine tetraacetic acid) and salts thereof such as disodium EDTA, citric acid and salts thereof, cyclodextrins, and the like, and mixtures thereof. Such suitable chelators typically comprise about 0.001 wt. % to about 3 wt. %, preferably about 0.01 wt. % to about 2 wt. %, and more preferably about 0.01 wt. % to about 1 wt. % of the total weight of the personal care organic phase compositions.

[0118] Auxiliary Solvents and Diluents

[0119] The personal care, home care, health care, and institutional care compositions of the organic phase compositions in combination with one or more of the foregoing active ingredients and/or with the one or more additives and/or adjuvants, conventionally or popularly included in personal care, health care, home care, and institutional care products discussed above can be prepared as water-free or water-based formulations, and formulations containing water-miscible auxiliary solvents and/or diluents, but are not limited thereto. Useful solvents commonly employed are typically liquids, such as water (deionized, distilled or purified), alcohols, fatty alcohols, polyols, and the like, and mixtures thereof. Non-aqueous or hydrophobic auxiliary solvents are commonly employed in substantially water-free products, such as nail lacquers, aerosol propellant sprays, or for specific functions, such as removal of oily soils, sebum, make-up, or for dissolving dyes, fragrances, and the like, or are incorporated in the oily phase of an emulsion. Non-limiting examples of auxiliary solvents,

other than water, include linear and branched alcohols, such as ethanol, propanol, isopropanol, hexanol, and the like; aromatic alcohols, such as benzyl alcohol, cyclohexanol, and the like; saturated C_{12} to C_{30} fatty alcohol, such as lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, behenyl alcohol, and the like. Non-limiting examples of polyols include polyhydroxy alcohols, such as glycerin, propylene glycol, butylene glycol, hexylene glycol, C_2 to C_4 alkoxylated alcohols and C_2 to C_4 alkoxylated polyols, such as ethoxylated, propoxylated, and butoxylated ethers of alcohols, diols, and polyols having about 2 to about 30 carbon atoms and 1 to about 40 alkoxy units, polypropylene glycol, polybutylene glycol, and the like. Non-limiting examples of non-aqueous auxiliary solvents or diluents include silicones, and silicone derivatives, such as cyclomethicone, and the like, ketones such as acetone and methylethyl ketone; natural and synthetic oils and waxes, such as vegetable oils, plant oils, animal oils, essential oils, mineral oils, C_7 to C_{40} isoparaffins, alkyl carboxylic esters, such as ethyl acetate, amyl acetate, ethyl lactate, and the like, jojoba oil, shark liver oil, and the like. Some of the foregoing non-aqueous auxiliary solvents or diluents may also be conditioners and emulsifiers.

[0120] Scents and Fragrances

[0121] The organic phase composition may be formulated with scents and fragrances. The range of the natural odorants includes, in addition to readily volatile, also moderately and only slightly volatile components. The synthetic odorants embrace representatives from practically all classes of odorant substances. The following list comprises examples of known odorants which may be employed with the organic phase compositions, without being limited thereto:

natural products such as tree moss absolute, basil oil, tropical fruit oils (such as bergamot oil, mandarin oil, etc.), mastix absolute, myrtle oil, palmarosa oil, patchouli oil, petitgrain oil, wormwood oil, lavender oil, rose oil, jasmine oil, ylang-ylang oil, etc.; alcohols: farnesol, geraniol, linalool, nerol, phenylethyl alcohol, rhodinol, cinnamic alcohol, (Z)-hex-3-en-1-ol, menthol, a-terpineol, etc.; aldehydes such as citral, alpha-hexyl cinnamaldehyde, Lilial, methylionone, verbenone, nootkatone, geranylacetone, etc.; esters such as allyl phenoxyacetate, benzyl salicylate, cinnamyl propionate, citronellyl acetate, decyl acetate, dimethylbenzylcarbinyl acetate, dime-

thylbenzylcarbinyl butyrate, ethyl acetoacetate, cis-3-hexenyl isobutyrate, cis-3-hexenyl salicylate, linalyl acetate, methyl dihydrojasmonate, styralyl propionate, vetiveryl acetate, benzyl acetate, geranyl acetate, etc.; lactones such as gamma-undecalactone, delta-decalactone, pentadecanolide, 12-oxahexadecanolide, etc.; acetals such as Viridine (phenylacetaldehyde dimethylacetal), etc.; and other components often used in perfumery such as indole, p-mentha-8-thiol-3-one, methyleugenol, eugenol, anethol, etc.

[0122] Surfactants

[0123] Suitable surfactants that can be employed with the organic phase compositions can include anionic, cationic, amphoteric, and nonionic surfactants, as well as mixtures thereof. Such compositions are useful in personal care cleansing compositions that contain various components such as substantially insoluble materials requiring suspension or stabilization (e.g., a silicone, an oily material, a pearlescent material, aesthetic and cosmeceutical beads and particles, gaseous bubbles, exfoliants, and the like).

[0124] The anionic surfactant can be any of the anionic surfactants known or previously used in the art of aqueous surfactant compositions. Suitable anionic surfactants include but are not limited to alkyl sulfates, alkyl ether sulfates, alkyl sulphonates, alkaryl sulfonates, .alpha.-olefin-sulphonates, alkylamide sulphonates, alkarylpolyether sulphates, alkylamidoether sulphates, alkyl monoglyceryl ether sulfates, alkyl monoglyceride sulfates, alkyl monoglyceride sulfonates, alkyl succinates, alkyl sulfosuccinates, alkyl sulfosuccinamates, alkyl ether sulphosuccinates, alkyl amidosulfosuccinates; alkyl sulphoacetates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, alkyl amidoethercarboxylates, N-alkylamino acids, N-acyl amino acids, alkyl peptides, N-acyl taurates, alkyl isethionates, carboxylate salts wherein the acyl group is derived from fatty acids; and the alkali metal, alkaline earth metal, ammonium, amine, and triethanolamine salts thereof.

[0125] In one aspect, the cation moiety of the forgoing salts is selected from sodium, potassium, magnesium, ammonium, mono-, di- and triethanolamine salts, and mono-, di-, and tri-isopropylamine salts. The alkyl and acyl groups of the foregoing surfactants contain from about 6 to about 24 carbon atoms in one aspect, from 8 to 22 carbon atoms in another aspect and from about 12 to 18 carbon atoms in a further

aspect and may be unsaturated. The aryl groups in the surfactants are selected from phenyl or benzyl. The ether containing surfactants set forth above can contain from 1 to 10 ethylene oxide and/or propylene oxide units per surfactant molecule in one aspect, and from 1 to 3 ethylene oxide units per surfactant molecule in another aspect.

[0126] Examples of suitable anionic surfactants include sodium, potassium, lithium, magnesium, and ammonium salts of laureth sulfate, trideceth sulfate, myreth sulfate, C_{12}-C_{13} pareth sulfate, C_{12}-C_{14} pareth sulfate, and C_{12}-C_{15} pareth sulfate, ethoxylated with 1, 2, and 3 moles of ethylene oxide; sodium, potassium, lithium, magnesium, ammonium, and triethanolamine lauryl sulfate, coco sulfate, tridecyl sulfate, myritstyl sulfate, cetyl sulfate, cetearyl sulfate, stearyl sulfate, oleyl sulfate, and tallow sulfate, disodium lauryl sulfosuccinate, disodium laureth sulfosuccinate, sodium cocoyl isethionate, sodium C_{12}-C_{14} olefin sulfonate, sodium laureth-6 carboxylate, sodium methyl cocoyl taurate, sodium cocoyl glycinate, sodium myristyl sarcocinate, sodium dodecylbenzene sulfonate, sodium cocoyl sarcosinate, sodium cocoyl glutamate, potassium myristoyl glutamate, triethanolamine monolauryl phosphate, and fatty acid soaps, including the sodium, potassium, ammonium, and triethanolamine salts of a saturated and unsaturated fatty acids containing from about 8 to about 22 carbon atoms.

[0127] Suitable classes of cationic surfactants include but are not limited to alkyl amines, alkyl imidazolines, ethoxylated amines, quaternary compounds, and quaternized esters. In addition, alkyl amine oxides can function as a cationic surfactant at a low pH.

[0128] Alkylamine surfactants can be salts of primary, secondary and tertiary fatty C_{12}-C_{22} alkylamines, substituted or unsubstituted, and substances sometimes referred to as "amidoamines." Non-limiting examples of alkylamines and salts thereof include dimethyl cocamine, dimethyl palmitamine, dioctylamine, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated stearylamine, dihydroxy ethyl stearylamine, arachidylbehenylamine, dimethyl lauramine, stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride, and amodimethicone (INCI name for a silicone polymer and blocked with amino functional groups, such as aminoethylamino propylsiloxane).

[0129] Non-limiting examples of amidoamines and salts thereof include stearamido propyl dimethyl amine, stearamidopropyl dimethylamine citrate, palmitamidopropyl diethylamine, and cocamidopropyl dimethylamine lactate.

[0130] Non-limiting examples of alkyl imidazoline surfactants include alkyl hydroxyethyl imidazoline, such as stearyl hydroxyethyl imidazoline, coco hydroxyethyl imidazoline, ethyl hydroxymethyl oleyl oxazoline, and the like.

[0131] Non-limiting examples of ethoxylated amines include PEG-cocopolyamine, PEG-15 tallow amine, quaternium-52, and the like.

[0132] Exemplary quaternary ammonium surfactants include, but are not limited to cetyl trimethylammonium chloride, cetylpyridinium chloride, dicetyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dieicosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, behenyl trimethyl ammonium chloride, benzalkonium chloride, benzethonium chloride, and di(coconutalkyl)dimethyl ammonium chloride, ditallowedimethyl ammonium chloride, di(hydrogenated tallow)dimethyl ammonium chloride, di(hydrogenated tallow)dimethyl ammonium acetate, ditallowedimethyl ammonium methyl sulfate, ditallow dipropyl ammonium phosphate, and ditallow dimethyl ammonium nitrate.

[0133] At low pH, amine oxides can protonate and behave similarly to N-alkyl amines. Examples include, but are not limited to, dimethyl-dodecylamine oxide, oleyldi(2-hydroxyethyl)amine oxide, dimethyltetradecylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, dimethylhexadecylamine oxide, behenamine oxide, cocamine oxide, decyltetradecylamine oxide, dihydroxyethyl C_{12-15} alkoxypropylamine oxide, dihydroxyethyl cocamine oxide, dihydroxyethyl lauramine oxide, dihydroxyethyl stearamine oxide, dihydroxyethyl tallowamine oxide, hydrogenated palm kernel amine oxide, hydrogenated tallowamine oxide, hydroxyethyl hydroxypropyl C_{12}-C_{15} alkoxypropylamine oxide, lauramine oxide, myristamine oxide, cetylamine oxide, oleamidopropylamine oxide, oleamine oxide, palmitamine oxide, PEG-3 lauramine oxide, dimethyl lauramine oxide, potassium trisphosphonomethylamine oxide, soyamidopropylamine oxide, cocamidopropylamine oxide, stearamine oxide, tallowamine oxide, and mixtures thereof.

[0134] Amphoteric or zwitterionic surfactants are molecules that contain acidic and basic moieties and have the capacity of behaving either as an acid or a base. Suitable surfactants can be any of the amphoteric surfactants known or previously used in the art of surfactant compositions. Exemplary amphoteric surfactant classes include but are not limited to amino acids (e.g., N-alkyl amino acids and N-acyl amino acids), betaines, sultaines, and alkyl amphocarboxylates.

[0135] The amino acid surfactants can be derived from the alkylation and acylation of α-amino acids such as, for example, alanine, arginine, aspartic acid, glutamic acid, glycine, isoleucine, leucine, lysine, phenylalanine, serine, tyrosine, and valine. Representative N-acyl amino acid surfactants are, but not limited to the mono- and di-carboxylate salts (e.g., sodium, potassium, ammonium and TEA) of N-acylated glutamic acid, for example, sodium cocoyl glutamate, sodium lauroyl glutamate, sodium myristoyl glutamate, sodium palmitoyl glutamate, sodium stearoyl glutamate, disodium cocoyl glutamate, disodium stearoyl glutamate, potassium cocoyl glutamate, potassium lauroyl glutamate, and potassium myristoyl glutamate; the carboxylate salts (e.g., sodium, potassium, ammonium and TEA) of N-acylated alanine, for example, sodium cocoyl alaninate, and TEA lauroyl alaninate; the carboxylate salts (e.g., sodium, potassium, ammonium and TEA) of N-acylated glycine, for example, sodium cocoyl glycinate, and potassium cocoyl glycinate; the carboxylate salts (e.g., sodium, potassium, ammonium and TEA) of N-acylated sarcosine, for example, sodium lauroyl sarcosinate, sodium cocoyl sarcosinate, sodium myristoyl sarcosinate, sodium oleoyl sarcosinate, and ammonium lauroyl sarcosinate; and mixtures of the foregoing surfactants.

[0136] Examples of suitable betaines include, but are not limited to, lauryl betaine, coco betaine, oleyl betaine, cocohexadecyl dimethylbetaine, lauryl amidopropyl betaine, cocoamidopropyl betaine, and cocamidopropyl hydroxysultaine.

[0137] Exemplary alkylamphocarboxylates include, but are not limited to, sodium cocoamphoacetate, sodium lauroamphoacetate, sodium capryloamphoacetate, disodium cocoamphodiacetate, disodium lauroamphodiacetate, disodium caprylamphodiacetate, disodium capryloamphodiacetate, disodium cocoamphodipropionate, disodium lauroamphodipropionate, disodium caprylamphodipropionate, and disodium capryloamphodipropionate.

[0138] The nonionic surfactant can be any of the nonionic surfactants known or previously used in the art of surfactant compositions. Suitable nonionic surfactants include, but are not limited to, aliphatic (C_6-C_{18}) primary or secondary linear or branched chain acids, alcohols or phenols; alkyl ethoxylates; alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy moieties); block alkylene oxide condensates of alkyl phenols; alkylene oxide condensates of alkanols; and ethylene oxide/propylene oxide block copolymers. Other suitable nonionic surfactants include mono- or dialkyl alkanolamides; alkyl polyglucosides (APGs); sorbitan fatty acid esters; polyoxyethylene sorbitan fatty acid esters; polyoxyethylene sorbitol esters; polyoxyethylene acids, and polyoxyethylene alcohols. Other examples of suitable nonionic surfactants include coco mono- or diethanolamide, coco glucoside, decyl diglucoside, lauryl diglucoside, coco diglucoside, polysorbate 20, 40, 60, and 80, ethoxylated linear alcohols, cetearyl alcohol, lanolin alcohol, stearic acid, glyceryl stearate, PEG-100 stearate, laureth 7, and oleth 20.

[0139] In another embodiment, non-ionic surfactants include, but are not limited to, alkoxylated methyl glucosides such as, for example, methyl gluceth-10, methyl gluceth-20, PPG-10 methyl glucose ether, and PPG-20 methyl glucose ether, available from Lubrizol Advanced Materials, Inc., under the trade names, Glucam™ E10, Glucam™ E20, Glucam™ P10, and Glucam™ P20, respectively; and hydrophobically modified alkoxylated methyl glucosides, such as PEG 120 methyl glucose dioleate, PEG-120 methyl glucose trioleate, and PEG-20 methyl glucose sesquistearate, available from Lubrizol Advanced Materials, Inc., under the trade names, Glucamate™ DOE-120, Glucamate™ LT, and Glucamate™ SSE-20, respectively, are also suitable. Other exemplary hydrophobically modified alkoxylated methyl glucosides are disclosed in U.S. Pat. Nos. 6,573,375 and 6,727,357, the disclosures of which are hereby incorporated by reference in their entirety.

[0140] Other surfactants which can be utilized are set forth in more detail in WO 99/21530, U.S. Pat. No. 3,929,678, U.S. Pat. No. 4,565,647, U.S. Pat. No. 5,720,964, and U.S. Pat. No. 5,858,948. In addition, suitable surfactants are also described in McCutcheon's Emulsifiers and Detergents (North American and International Editions, by Schwartz, Perry and Berch) which is hereby fully incorporated by reference.

[0141] While the amounts of the surfactant utilized can vary widely depending on a desired application, the amounts which are often utilized generally range from about 1% to about 80% by weight in one aspect, from about 3% to about 65% weight in another aspect, from about 5% to about 30% by weight in still another aspect, from about 6% to about 20% by weight in a further aspect, and from about 8% to about 16% by weight, based upon the total weight of the personal care, home care, health care, and institutional and industrial care composition in which it is included.

[0142] Light Screening Agents

[0143] Light screening agents are advantageously selected from UV-A, UV-B, UV-C and/or broadband filters. Examples of UV-B or broad spectrum screening agents, i.e. substances having absorption maximums between about 290 and 340 nm, may be organic or inorganic compounds. Organic UV-B or broadband screening agents are e.g. acrylates such as 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (octocrylene, PARSOL™ 340), ethyl 2-cyano-3,3-diphenylacrylate and the like; camphor derivatives such as 4-methyl benzylidene camphor (PARSOL™ 5000), 3-benzylidene camphor, camphor benzalkonium methosulfate, polyacrylamidomethyl benzylidene camphor, sulfo benzylidene camphor, sulphomethyl benzylidene camphor, terephthalidene dicamphor sulfonic acid and the like; Cinnamate derivatives such as ethylhexyl methoxycinnamate (PARSOL™ MCX), ethoxyethyl methoxycinnamate, diethanolamine methoxycinnamate (PARSOL™ Hydro), isoamyl methoxycinnamate and the like as well as cinnamic acid derivatives bond to siloxanes; p-aminobenzoic acid derivatives, such as p-aminobenzoic acid, 2-ethylhexyl p-dimethylaminobenzoate, N-oxypropylenated ethyl p-aminobenzoate, glyceryl p-aminobenzoate; benzophenones such as benzophenone-3, benzophenone-4, 2,2',4,4'-tetrahydroxy-benzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone and the like; esters of benzalmalonic acid such as di-(2-ethylhexyl) 4-methoxybenzalmalonate; esters of 2-(4-ethoxy-anilinomethylene)propandioic acid such as 2-(4-ethoxy anilinomethylene) propandioic acid diethyl ester as described in the European Patent Publication EP 0895 776; organosiloxane compounds containing benzmalonate groups as described in the European Patent Publications EP 0358584 B1, EP 0538431 B1 and EP 0709080 A1 such as polysilicone-15 (PARSOL™ SLX); drometrizole trisiloxane (Mexoryl XL); imidazole derivatives such as e.g. 2-phenyl benzimidazole sulfonic acid and its

salts (PARSOL™ HS). Salts of 2-phenyl benzimidazole sulfonic acid are e.g. alkali salts such as sodium- or potassium salts, ammonium salts, morpholine salts, salts of primary, sec. and tert. amines like monoethanol amine salts, diethanol amine salts and the like; salicylate derivatives such as isopropylbenzyl salicylate, benzyl salicylate, butyl salicylate, ethylhexyl salicylate (PARSOL™ EHS, NEO Heliopan OS), isooctyl salicylate or homomethyl salicylate (homosalate, PARSOL™ HMS, NEO Heliopan OS) and the like; triazine derivatives such as ethylhexyl triazone (Uvinul T-150), diethylhexyl butamido triazone (Uvasorb HEB); Encapsulated UV-filters such as encapsulated ethylhexyl methoxycinnamate (Eusolex UV-pearls) or microcapsules loaded with UV-filters as e.g. disclosed in EP 1471995 and the like. Inorganic compounds are pigments such as microparticulated TiO_2, ZnO and the like. The term "microparticulated" refers to a particle size from about 5 nm to about 200 nm, particularly from about 15 nm to about 100 nm. The TiO_2 particles may also be coated by metal oxides such as e.g. aluminum or zirconium oxides or by organic coatings such as e.g. polyols, methicone, aluminum stearate, alkyl silane. Such coatings are well known in the art.

[0144] Examples of broad spectrum or UV-A screening agents i.e. substances having absorption maximums between about 320 and 400 nm may be organic or inorganic compounds e.g. dibenzoylmethane derivatives such as 4-tertbutyl-4'-methoxydibenzoyl-methane (PARSOL™ 1789), dimethoxydibenzoylmethane, isopropyldibenzoylmethane and the like; benzotriazole derivatives such as 2,2'-methylene-bis-(6-(2H-benzotriazole-2-yl)-4-(1,1,3,3,-tetramethylbuty- l)-phenol (TINOSORB M) and the like; bis-ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb S) and the like; phenylene-1,4-bis-benzimidazolsulfonic acids or salts such as 2,2-(1,4-phenylene)bis-(1H-benzimidazol-4,6-disulfonic acid) (Neoheliopan AP); amino substituted hydroxybenzophenones such as 2-(4-Diethylamino-2-hydroxy-benzoyl)-benzoic acid hexylester (Uvinul A plus) as described in the European Patent Publication EP 1046391; Ionic UV-A filters as described in the International Patent Publication WO2005080341 A1; Pigments such as microparticulated ZnO or TiO_2 and the like. The term "microparticulated" refers to a particle size from about 5 nm to about 200 nm, particularly from about 15 nm to about 100 nm. The particles may also be coated by other metal oxides such as e.g. aluminum or zirconium oxides or by

organic coatings such as e.g. polyols, methicone, aluminum stearate, alkyl silane. Such coatings are well known in the art.

[0145] As dibenzoylmethane derivatives have limited photostability it may be desirable to photostabilize these UV-A screening agents. Thus, the term "conventional UV-A screening agent" also refers to dibenzoylmethane derivatives such as e.g. PARSOL ™ 1789 stabilized by, e.g. 3,3-Diphenylacrylate derivatives as described in the European Patent Publications EP 0 514 491 B1 and EP 0 780 119 A1; Benzylidene camphor derivatives as described in the U.S. Pat. No. 5,605,680; Organosiloxanes containing benzmalonate groups as described in the European Patent Publications EP 0358584 B1, EP 0538431 B1 and EP 0709080 A1.

Silicone Fluids

[0146] Volatile silicone oils include cyclic and linear polydimethylsiloxanes, low molecular weight organo-functional silicones, and the like. Cyclic volatile silicones (cyclomethicones) typically contain about 3 to about 7 silicon atoms, alternating with oxygen atoms, in a cyclic ring structure. Each silicon atom is typically substituted with two alkyl groups, such as, for example, methyl groups. Volatile linear polydimethylsiloxanes (dimethicones) typically contain about 2 to about 9 silicon atoms, alternating with oxygen atoms in a linear arrangement. Each silicon atom is also substituted with two alkyl groups (the terminal silicon atoms are substituted with three alkyl groups), such as, for example, methyl groups. The linear volatile silicones typically have viscosities of less than about 5 cP at 25 °C., while the cyclic volatile silicones typically have viscosities of less than about 10 cP at 25 °C. "Volatile" means that the silicone has a measurable vapor pressure, or a vapor pressure of at least 2 mm of Hg at 20 °C. Non-volatile silicones have a vapor pressure of less than 2 mm Hg at 20 °C. A description of volatile silicones is found in Todd and Byers, Volatile Silicone Fluids for Cosmetics, Cosmetics and Toiletries, Vol. 91, pp. 29-32, 1976, and in Kasprzak, Volatile Silicones, Soap/Cosmetics/Chemical Specialties, pp. 40-43, December 1986, each incorporated herein by reference.

[0147] Exemplary volatile cyclomethicones are D4 cyclomethicone (octamethylcyclotetrasiloxane), D5 cyclomethicone (decamethylcyclopentasiloxane), D6 cyclomethicone, and blends thereof (e.g., D4/D5 and D5/D6). Volatile cyclomethicones

and cyclomethicone blends are commercially available from G.E. Silicones as SF1173, SF1202, SF1256, and SF1258, Dow Corning Corporation as Dow Corning™ 244, 245, 246, 345, and 1401 Fluids. Blends of volatile cyclomethicones and volatile linear dimethicones are also contemplated.

[0148] Exemplary volatile linear dimethicones include hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane and blends thereof. Volatile linear dimethicones and dimethicone blends are commercially available from Dow Corning Corporation as Dow Corning 200™ Fluid (e.g., product designations 0.65 CST, 1 CST, 1.5 CST, and 2 CST) and Dow Corning™ 2-1184 Fluid.

[0149] Exemplary volatile low molecular weight organo-functional silicones include phenyl trimethicone, caprylyl trimethicone, caprylyl methicone, and hexyl methicone, and blends thereof. Low molecular weight organo-functional silicones are commercially available from Clariant under the trade name Silcare™ 41M10, Slicare™ 31M60, Silcare™ 41M10, and Silcare™ 41M15.

[0150] The non-volatile silicone oils useful as organic phases can be linear and typically have viscosities from about 10 cP to about 100,000 cP at 25 °C. They typically contain above about 10 dialkyl/diaryl or monoalkyl/monoaryl substituted silicon atoms, alternating with oxygen atoms in a linear arrangement. They include polyalkylsiloxane, polyarylsiloxane, and polyalkylarylsiloxane polymers. Exemplary non-volatile silicone oils include the polydimethylsiloxanes (dimethicones), polydiethylsiloxanes, polymethylphenylsiloxanes, and the like. In one aspect, the non-volatile silicone oil is selected from a non-volatile polydimethylsiloxane having a viscosity range from about 10 cP to about 100,000 cP at 25 °C. Non-volatile dimethicones are commercially available from Dow Corning Corporation as Dow Corning 200™ Fluid (product designations 10 CST through 10,000 CST).

Uses and Compositions

[0151] The structurant polymers can be employed in any organic phase composition, and the organic phase compositions containing said structurant polymers can be utilized in any personal care, home care, health care, and institutional and industrial care composition requiring rheology, sensory and/or aesthetic property modification.

In a given composition or application, the structurant polymers or organic phase compositions containing the structurant polymer can, but need not, serve more than one function, such as a thickener, stabilizer, emulsifier, film former, deposition aid, emollient, and the like.

[0152] The personal care, home care, health care, and institutional and industrial care organic phase compositions can be packaged and dispensed from containers such as jars, tubes, sprays, wipes, roll-ons, sticks and the like, without limitation. There is no limitation as to the form of the product in which these compositions can be incorporated, so long as the purpose for which the product is used is achieved. For example, personal and health care products containing the organic phase compositions can be applied to the skin, hair, scalp, and nails, without limitation in the form of gels, sprays (liquid or foams), emulsions (creams, lotions, pastes), liquids (rinses, shampoos), bars, ointments, suppositories, and the like. The organic phase compositions can be employed, for example, in oil compositions, water-in-oil emulsions, oil-in-water emulsions, oil-in-oil emulsions, oil-in-silicon emulsions, and in silicone-in-oil emulsions.

[0153] In one personal care aspect, the organic phase compositions are suitable for preparation of personal care (cosmetics, toiletries, cosmeceuticals), including, without limitation, hair care products (shampoos, combination shampoos, such as "two-in-one" conditioning shampoos), pre-shampoo treatments and serums, post-shampoo rinses, setting and style maintenance agents (including setting aids, such as gels and sprays, grooming aids such as pomades, conditioners, perms, relaxers, hair smoothing products, hair oils and the like), skin care products (facial, body, hands, scalp and feet), such as creams, lotions, body oils, and cleansing products, antiacne products, antiaging products (exfoliant, keratolytic, anticellulite, antiwrinkle, and the like), skin protectants (sun care products, such as sunscreens, sunblock, barrier creams, oils, silicones and the like), skin color products (whiteners, lighteners, sunless tanning accelerators and the like), hair colorants (hair dyes, hair color rinses, highlighters, bleaches and the like), pigmented skin colorants (face and body make-ups, foundation creams, mascara, rouge, lip products, and the like) bath and shower products (body cleansers, body wash, shower gel, liquid soap, soap bars, syndet bars,

conditioning liquid bath oil, bubble bath, bath powders, and the like), nail care products (polishes, polish removers, strengtheners, lengtheners, hardeners, cuticle removers, softness, and the like), pharmaceutical creams, ointments, and other medicated types of skin care products.

[0154] Toiletries and beauty aids containing the organic phase compositions can include, without limitation, hair-removal products (shaving creams and lotions, epilators, after-shaving skin conditioner, and the like), hair growth promoting products, deodorants and antiperspirants, oral care products (mouth, teeth, gums), such as mouth wash, dentifrice, such as toothpaste, tooth powder, tooth polishes, tooth whiteners, breath fresheners, denture adhesives, and the like; facial and body hair bleach and the like. Other beauty aids that can contain the organic phase compositions include, without limitation, sunless tanning applications containing artificial tanning accelerators, such as dihydroxyacetone (DHA), tyrosine, tyrosine esters and the like: skin depigmenting, whitening and lightening, formulations containing such active ingredients as kojic acid, hydroquinone, arbutin, fruital, vegetable or plant extracts, (lemon peel extract, chamomile, green tea, paper mulberry extract, and the like), ascorbyl acid derivatives ascorbyl palmitate, ascorbyl stearate, magnesium ascorbyl phosphate and the like).

[0155] The organic phase compositions can be suitable for dermal cleansing products containing particulates, insoluble benefit agents, microabrasives, and abrasives and combinations thereof. Dermal cleansing products include shampoos, body washes, shower gels, bath gels, masks and skin cleansers.

[0156] The amount of each chemical component described is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated. However, unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade.

[0157] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can

migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by mixing the components described above.

[0158] The invention herein is useful for thickening an oil composition, improving clarity of the oil composition, or both, which may be better understood with reference to the following examples.

EXAMPLES

[0159] In the following examples, viscosity was measured on a TA Instrument rheometer (AR 1000, AR 2000, or HR-2) in flow mode using a 4 cm stainless steel 2° cone and measuring at 20°C. Shear rates were captured from 1 to 1000 s^{-1} but reported only at 1 s^{-1}.

[0160] Moduli (G' and G") are shown to highlight the samples that are gels vs. liquids and values are obtained from a stress sweep (at 0.01% strain) of the sample using the same TA Instrument rheometer. Reported values were at a stress of approximately 0.01 Pa. Clarity is reported as either a visual observation, or as an average transmission as measured on a Brinkman PC950 colorimeter.

Example 1

[0161] Sample Polymer 1 ("SP1") - To a 500 ml reaction kettle outfitted with an overhead stirrer and a nitrogen port and a Dean Stark trap, 200 ml of toluene, 0.01207 moles of 1-hexadecanol, 0.03614 moles of a hydrogenated polybutadiene having a number average molecular weight ("Mn") of about 1500 (Nisso PB™ GI-1000) were added with stirring (350 rpm) and the solution was heated to reflux to remove any residual water through the toluene-water azeotrope. After water removal, the solution was cooled to 70 °C and 0.04219 moles of hexamethylene diisocyanate was added and stirred for 10 min. Three drops (~30 microliters) of a bismuth carboxylate catalyst (K-Kat™ 348 from King Industries) was added and an exotherm was immediately noticed. The reaction was allowed to run for 2 hours or until all of the isocyanate was reacted (by FTIR; peak at 2270 cm-1). After solvent removal in vacuum, the structurant polymer was collected. Mn=14K; polydispersity ("PDI") = 2.4.

[0162] The ΔHSP_{o-p} between SP1 and sunflower oil or mineral oil was calculated using the Y-MB method as described in "Hansen Solubility Parameters: A User's Handbook", C. M. Hansen, CRC Press:Boca Raton, Fl, 2007. The ΔHSP_{o-p} for the sunflower oil mixture was 3.6 $(J/cm^3)^{1/2}$, which gave a visually clear composition. The ΔHSP_{o-p} of the mineral oil mixture was about 4.7 $(J/cm^3)^{1/2}$, which gave a hazy composition.

[0163] SP1 was further tested for its thickening efficiency by heating the structurant polymer in sunflower oil between 70-90 °C for 24 hours, cooling the mixture and allowing the mixture to equilibrate over a period of several days to a week. The viscosity (at 1 sec^{-1}) of the mixture was found to be proportional to the concentration of the thickener as shown in Table 1 below.

Table 1

Wt.% SP1	Viscosity (Pa·s @ $1s^{-1}$)
0	0
.5	0.2
1.2	0.75
2.5	2.75
4.0	6.25
4.5	9.8
5	11.92

[0164] At 5 wt.% loading, SP1 improved the viscosity of various different oils as shown in Table 2 below.

Table 2

Organic phase	Viscosity with No Structurant Polymer (Pa·s @ $1s^{-1}$)	Viscosity with 5 wt.% SP1 (Pa·s @ $1s^{-1}$)
Capric/Caprylic Triglyceride	**0.03**	**3.04**

Sunflower Oil	**0.06**	**11.92**
Cetearyl Ehtylhexanoate	**0.01**	**0.95**
Octyl/Ethylhexyl Stea-rate	**0.02**	**2.53**
Dioctyl Ether	**0.002**	**1.72**
Mineral Oil	**0.02**	**18.04**
Isohexadecane	**0.004**	**11.66**
Isododecane	**0.004**	**10.27**
Jojoba Oil	**0.05**	**9.22**
Safflower Oil	**0.05**	**13.44**
C_{12-15} alkyl benzoate	**0.01**	**2.13**

[0165] The rheology of SP1 at 5 wt.% was found to be thixotropic with a recovery time of from minutes to days, depending on the polarity of the oil.

[0166] Stoichiometric variants of SP1 were prepared changing the level of 1-hexadecanol to alter the Mn of the resultant structurant polymer. Table 3 below shows the resulting structurant polymers SP2 to SP5 and the corresponding molecular weights with clarity at 5 wt.% in sunflower oil.

Table 3

Sample	Actual Mn	Actual Mw	PDI	Relative Clarity*
SP2	6,293	10,535	1.674	0.18
SP3	13,992	33,694	2.408	0.93
SP4	18,262	53,967	2.955	1.00
SP5	21,051	70,139	3.332	0.90

*Measured employing a Brinkman PC950 colorimeter (highest clarity=1.00)

[0167] The influence of molecular weight and polydispersity on rheology was also tested by blending the various structurant polymers into sunflower oil. The results are shown in Table 4 below.

Table 4

Blend Sample	Structurant Polymer				Calculated Mn	Relative Clarity	Storage Modulus G' (Pa)	Loss Modulus G" (Pa)
	SP2	SP3	SP4	SP5				
1	1				6,293	0.18	0.1	1.2
2		1			13,992	0.93	27.2	18.4
3			1		18,262	1.00	1.2	3.6
4				1	21,051	0.90	0.9	3.3
5	1	1	1	1	14,900	0.74	17.7	8.3
6	1			1	13,672	0.25	4.7	4.5
7	1	1			10,143	0.20	5.3	4.8
8	1		1		12,278	0.15	6.4	5.1
9	1			1	13,672	0.28	5.8	4.8
10		1		1	17,522	0.90	2.5	5.2

Example 2

[0168] Comparative Sample Polymer 1 ("CSP1") - To a 500 ml reaction kettle outfitted with an overhead stirrer and a nitrogen port and a Dean Stark trap, 200 ml of toluene, 0.0121 moles of 1-hexadecanol, 0.0361 moles of a hydrogenated polybutadiene having an Mn of about 2,100 (Nisso PB™ GI-2000) were added with stirring (350 rpm) and the solution was heated to reflux to remove any residual water through the toluene-water azeotrope. After water removal, the solution was cooled to 70 °C and 0.0.0422 moles of hexamethylene diisocyanate was added and stirred for 10 min. Three drops (~30 microliters) of a bismuth carboxylate catalyst (K-Kat™ 348 from King Industries) is added and an exotherm was immediately noticed. The reaction was allowed to run for 2 hours until all of the isocyanate was reacted (by FTIR; peak at 2,270 cm^{-1}). After solvent removal in vacuum, the polymer was collected. Mn=17K; PDI = 6.5.

[0169] The ΔHSP_{o-p} between CSP1 and sunflower oil or mineral oil was calculated using the Y-MB method as described in "Hansen Solubility Parameters: A User's Handbook", C. M. Hansen, CRC Press: Boca Raton, FL, 2007. The ΔHSP_{o-p} for the sunflower oil mixture was 1.9 $(J/cm^3)^{1/2}$, which gave a clear composition. The

ΔHSP_{o-p} of the mineral oil mixture was about 3.5 $(J/cm^3)^{1/2}$, which gave a clear but slightly hazy composition.

[0170] CSP1 was further tested for its thickening efficiency by heating the structurant polymer in sunflower oil between 70-90 °C for 24 hours, cooling the mixture and allowing the mixture to equilibrate over a period of several days to a week. The viscosity (at 1 sec^{-1}) of the mixture was found to be unchanged from baseline.

Example 3

[0171] Sample Polymer 6 – The procedure for preparing CSP1 was followed except that 0.0361 moles of the hydrogenated polybutadiene was added and the polymerization reaction was allowed to run for 1 hour before 0.0121 moles of 1-hexadecylamine was added. After addition of the chain extender, the reaction was allowed to run for 1 additional hour until all of the isocyanate was reacted (by FTIR; peak at 2,270 cm-1). After solvent removal in vacuum, the polymer was collected. Mn=19K; PDI = 3.5.

[0172] The ΔHSP_{o-p} between SP6 and sunflower oil or mineral oil was calculated using the Y-MB method as described in "Hansen Solubility Parameters: A User's Handbook", C. M. Hansen, CRC Press: Boca Raton, FL, 2007. The ΔHSP_{o-p} for the sunflower oil mixture was 2.01 $(J/cm^3)^{1/2}$, which gave a clear composition. The ΔHSP_{o-p} of the mineral oil mixture was about 3.8 $(J/cm^3)^{1/2}$, which gave a clear but slightly hazy composition.

[0173] SP6 was further tested for its thickening efficiency by heating the structurant polymer in sunflower oil between 70-90 °C for 24 hours, cooling the mixture and allowing the mixture to equilibrate over a period of one week before measuring viscosity. The viscosity (at 1 sec^{-1}) of the mixture was found to thicken the sunflower oil to 1 Pa·s from around 0.06 Pa·s at 20 °C (as shown in table 2).

Example 4

[0174] Sample Polymer 7 - To a 500 ml reaction kettle outfitted with an overhead stirrer and a nitrogen port and a Dean Stark trap, 200 ml of toluene, 0.0036 moles of a hydrogenated polybutadiene having an Mn of about 2,100 (Nisso PB™ GI-2000) and 0.0325 moles of a dimer diol (Pripol™ 2030*) were added with stirring (350 rpm) and the solution was heated to reflux to remove any residual water through the toluene-water azeotrope. After water removal, the solution was cooled to 70 °C and

0.0422 moles of hexamethylene diisocyanate was added and stirred for 10 min. Three drops (~30 microliters) of a bismuth carboxylate catalyst (K-Kat™ 348 from King Industries) was added and an exotherm was immediately noticed. The reaction was allowed to run for 1 hour before 0.0.0121 moles of a 1-octadecylalcohol was added, and the reaction was allowed to continue for an additional 1 hour until all of the isocyanate was reacted (by FTIR; peak at 2,270 cm-1). After solvent removal in vacuum, the polymer was collected. Mn=25K; PDI = 2.3.

*a dimer having an average hydroxy group number of between 204-212 with a structure of a roughly C36 diol coupled at the 9,10 position

[0175] The solid polymer (5 wt%) is added to sunflower oil and heated to 75 °C until all of the solid was homogeneously mixed into solution which was highly translucent but not clear. Upon cooling, the solution gelled and became more turbid. The viscosity (at 1 sec^{-1}) of the mixture was found to be proportional to the concentration of the thickener as shown in Table 5 below.

Table 5

Wt.% SP7	Viscosity (Pa.s @ 1s^{-1})
0	0.06
0.75	1
1.25	10
2.5	45
5	233

Example 5

[0176] Sample Polymer 8 - To a 500 ml reaction kettle outfitted with an overhead stirrer and a nitrogen port was added 0.1054 mole of dimer diol (Pripol 2030*) and 0.105 mole of ε-caprolactone (Sigma Aldrich) and mixed thoroughly at 300 rpm with a Teflon paddle stirring blade. 30 ppm of a bismuth carboxylate catalyst (K-Kat™ 348 from King Industries) was then added and the entire solution was heated to 125 °C. The reaction of the caprolactone with the dimer diol was followed by FTIR (carbonyl band shifts from 1,725 cm-1 to 1,735 cm-1). The reaction was allowed to continue until all of the caprolactone was consumed to give a low viscosity water

white liquid. At this point the solution was cooled to room temperature and 0.0130 mole of a hydrogenated polybutadiene having an Mn of about 2100 (Nisso PB™ GI-2000) in 200 ml of toluene was added with constant stirring followed by 0.143 moles of hexamethylene diisocyanate. The reaction mixture was heated to 70 °C and the consumption of isocyanate was monitored (by FTIR; peak at 2,270 cm-1). The reaction was allowed to run for 1 hour (isocyanate concentration reached a minimum) and then 0.0484 moles of 1-octadecylalcohol was added and the reaction was allowed to run for 1 additional hour until all of the isocyanate was reacted (by FTIR; peak at 2,270 cm-1). After solvent removal in vacuum, the polymer was collected. Mn=24,000; PDI = 2.2.

*a dimer having an average hydroxy group number of between 204-212 with a structure of a roughly C36 diol coupled at the 9,10 position

[0177] 5 wt.% of SP8 was dissolved in caprylic capric triglyceride at 75 °C and cooled to room temperature to produce a translucent viscous gel viscosity of 1.7 Pa·s at (1 sec^{-1} and 20 °C).

Example 6

Sample Polymer 9 - To a 500 ml reaction kettle outfitted with an overhead stirrer and a nitrogen port and 200 ml of toluene, 0.0067 moles of a hydrogenated polybutadiene having an Mn of about 3300 (Cray Valley HLBH-3000) and 0.0325 moles of a dimer diol (Pripol™ 2030) were added with stirring (350 rpm) and heated to 70°C. Then, 0.0422 moles of hexamethylene diisocyanate was added and stirred for 10 min. Three drops (~30 microliters) of a bismuth carboxylate catalyst (K-Kat™ 348 from King Industries) was added and an exotherm was immediately noticed. The reaction was allowed to run for 1 hour before 0.0079 moles of a 1-octadecylalcohol was added, and the reaction was allowed to continue for an additional 1 hour until all of the isocyanate was reacted (by FTIR; peak at 2,270 cm-1). After solvent removal in vacuum, the polymer was collected. Mn= 25,000; PDI=2.8. This polymer showed similar thickening efficiency at 1 wt% as Sample Polymer 7 but increased clarity in all oils.

Example 7

[0178] Sample Polymer 10 - To a 500 ml reaction kettle outfitted with an overhead stirrer and a nitrogen port and 200 ml of toluene, 0.00586 moles of a hydrogenated polybutadiene having an Mn of about 3800 (Nisso GI-3000) and 0.0234 moles of a dimer diol (Pripol™ 2030) were added with stirring (350 rpm) and heated to 70°C. Then, 0.0322 moles of hexamethylene diisocyanate was added and stirred for 10 min. Three drops (~30 microliters) of a bismuth carboxylate catalyst (K-Kat™ 348 from King Industries) was added and an exotherm was immediately noticed. The reaction was allowed to run for 1 hour before 0.00585 moles of mono-hydroxyl-hydrogenated polybutadiene (Cray Valley HLBH-5000M; MW ~5000) was added, and the reaction was allowed to continue for an additional 1 hour until all of the isocyanate was reacted (by FTIR; peak at 2,270 cm-1). After solvent removal in vacuum, the polymer was collected. Mn=20K; PDI=3.1. Material when added at 1 wt% to sunflower oil showed a viscosity of 1.1 Pa.s (at 20 sec^{-1}) and no decrease in clarity.

Example 8

[0179] Sample Polymer 11 - To a 500 ml reaction kettle outfitted with an overhead stirrer and a nitrogen port was added 0.133 mole of dimer diol (Pripol 2030) and 0.1 mole of dimer acid (Pripol 1006) and mixed thoroughly at 300 rpm with a Teflon paddle stirring blade. 30 ppm of a bismuth carboxylate catalyst (K-Kat™ 348 from King Industries) was then added and the entire solution was heated to 125 °C. The reaction of the dimer acid with the dimer diol was followed by FTIR (carbonyl band shifts from ~1,700 cm-1 to 1,735 cm-1). The reaction was allowed to continue until all of the dimer acid was consumed to give a low viscosity water white liquid. The Mn of the resulting diol was 3150; PDI=2.4. To a 500 ml reaction kettle outfitted with an overhead stirrer and a nitrogen port and a Dean Stark trap, 200 ml of toluene, 0.0067 moles of the reaction product diol above and 0.0325 moles of a dimer diol (Pripol™ 2030) were added with stirring (350 rpm) and the solution was heated to reflux to remove any residual water through the toluene-water azeotrope. After water removal, the solution was cooled to 70 °C and 0.0422 moles of hexamethylene diisocyanate was added and stirred for 10 min. Three drops (~30 microliters) of a bismuth carboxylate catalyst (K-Kat™ 348 from King Industries) was added and an exotherm was immediately noticed. The reaction was allowed to run for 1 hour before 0.0079

moles of a 1-octadecylalcohol was added, and the reaction was allowed to continue for an additional 1 hour until all of the isocyanate was reacted (by FTIR; peak at 2,270 cm-1). After solvent removal in vacuum, the polymer was collected. Mn=11.3K; PDI=2.7. Addition of 1 wt% of this polymer to sunflower oil resulted in a hazy, but translucent gelled fluid with a viscosity of 1.2 Pa.s (at 20 sec^{-1})

Example 9

[0180] Sample polymer 12 - To a 500 ml reaction kettle outfitted with an overhead stirrer and a nitrogen port and 200 ml of toluene, 0.0115 moles of a hydrogenated polybutadiene having an Mn of about 3300 (Cray Valley HLBH-3000) and 0.0413 moles of a dimer diol (Pripol™ 2030) and 0.0011 moles of polydimethylsiloxane, hydroxyl terminated (Sigma Aldrich ~750 cSt; MW ~950) were added with stirring (350 rpm) and heated to 70°C. Then, 0.0593 moles of hexamethylene diisocyanate was added and stirred for 10 min. Three drops (~30 microliters) of a bismuth carboxylate catalyst (K-Kat™ 348 from King Industries) was added and an exotherm was immediately noticed. The reaction was allowed to run for 1 hour before 0.0108 moles of a 1-octadecylalcohol was added, and the reaction was allowed to continue for an additional 1 hour until all of the isocyanate was reacted (by FTIR; peak at 2,270 cm-1). After solvent removal in vacuum, the polymer was collected. Mn=25K; PDI=2.8. Material when added at 1 wt% to sunflower oil showed a viscosity of 1.2 Pa.s (at 20 sec^{-1}) and no decrease in clarity.

Example 10

[0181] Sample polymer 13 - To a 500 ml reaction kettle outfitted with an overhead stirrer and a nitrogen port and 200 ml of toluene, 0.0117 moles of a hydrogenated polybutadiene having an Mn of about 3300 (Cray Valley HLBH-3000) and 0.0413 moles of a dimer diol (Pripol™ 2030) were added with stirring (350 rpm) and heated to 70°C. Then, 0.05744 moles of hexamethylene diisocyanate was added and stirred for 10 min. Three drops (~30 microliters) of a bismuth carboxylate catalyst (K-Kat™ 348 from King Industries) was added and an exotherm was immediately noticed. The reaction was allowed to run for 1 hour before 0.0002 moles of polydimethylsiloxane, monohydroxy terminated (Sigma Aldrich; Mn ~4670) was added and an additional hour before 0.0108 moles of a 1-octadecylalcohol was added, and the reaction was allowed to continue for an additional 1 hour until all of the isocyanate was reacted

(by FTIR; peak at 2,270 cm-1). After solvent removal in vacuum, the polymer was collected. Mn=25K; PDI=2.8. Material when added at 1 wt% to sunflower oil showed a viscosity of 0.6 Pa.s and no decrease in clarity but a significant decrease in surface tension (from ~30 dyne/cm to ~20 dyne/cm).

[0182] Each of the documents referred to above is incorporated herein by reference, including any prior applications, whether or not specifically listed above, from which priority is claimed. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

[0183] As used herein, the transitional term “comprising,” which is synonymous with “including,” “containing,” or “characterized by,” is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of “comprising” herein, it is intended that the term also encompass, as alternative embodiments, the phrases “consisting essentially of” and “consisting of,” where “consisting of” excludes any element or step not specified and “consisting essentially of” permits the inclusion of additional un-recited elements or steps that do not materially affect the essential or basic and novel characteristics of the composition or method under consideration.

[0184] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. In this regard, the scope of the invention is to be limited only by the following claims.

What is claimed is:

1. An organic phase composition comprising
   A) from 0.01 to about 10 wt.% of a structurant polymer having a backbone comprised of:
      i) hard segments derived from:
         1. at least one linear non-branched aliphatic diisocyanate, or
         2. at least one linear non-branched aliphatic diisocyanate in combination with at least one chain extending compound, and
      ii) soft segments having an average molecular weight of between about 500 and 6000 derived from
         1. at least one hydrophobic oligomer, and
   B) a majority of an organic phase,
   wherein the average molecular weight between respective diisocyanates on the structurant polymer backbone is from between about 500 to about 2,000.
2. The composition of any previous claim, wherein the at least one hydrophobic oligomer is at least one polyol compound, polyamine compound, or mixtures thereof.

3. The composition of any previous claim, wherein the oligomer is chosen from at least one of a hydrogenated polybutadiene (HPBD), polytetrahydrofuran (pTHF), polypropylene glycol (PPG), polyester, polycaprolactone, polycarbonate, polycastor oil, fatty acid/alcohol adduct, or mixtures thereof.

4. The composition of any previous claim, wherein the oligomer can be in the form of an adduct with a lactone, diacid, or mixture thereof.

5. The composition of any previous claim wherein the oligomer is modified with an alcohol, amine, anhydride, or mixture thereof.

6. The composition of claim 8, wherein the oligomer is modified with no more than 2 mole% of a diamine.

7. The composition of any previous claim wherein the structurant polymer is a polyurethane.

8. The composition of any previous claim wherein the structurant polymer is a polyurea.

9. The composition of any previous claim wherein the structurant polymer is a mixed polyurethane/polyurea.

10. The composition of any previous claim, wherein the organic phase is derived from an animal oil, vegetable oil, mineral oil, synthetic oil, or mixture thereof.

11. The composition of any previous claim, wherein the organic phase is hydrogenated.

12. The composition of any previous claim wherein the ratio of the total hydrogen bonding donor sites to the total hydrogen bonding acceptor sites in the organic phase composition is about 1 or greater.

13. The composition of any previous claim wherein the ΔHSP between the oil and the oligomer is less than about 4.

14. The composition of claim 13, wherein the ΔHSP between the oil and the polymer is less than about 4.

15. A method of thickening an organic phase comprising adding to the organic phase up to about 10 wt.% of a structurant polymer comprising:

i) hard segments derived from:

1. at least one linear non-branched aliphatic diisocyanate, or
2. at least one linear non-branched aliphatic diisocyanate in combination with at least one chain extending compound, and

ii) soft segments having an average molecular weight of from about 500 to about 6,000 derived from

1. at least one hydrophobic oligomer

wherein the average molecular weight between the at least one linear non-branched aliphatic diisocyanate is from about 500 to about 2,000.

16. The method of claim 14 wherein the ratio of the total hydrogen bonding donor sites to the total hydrogen bonding acceptor sites in the oil composition is about 1 or greater.

17. The use of a thermoplastic polyurethane to thicken a cosmetically or pharmaceutically acceptable organic phase.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/063604

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61K8/87 C08L47/00 C08L75/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/135384 A2 (CRODA INT PLC [GB]; TOLLINGTON PETER JAMES [NL]; ROSCHZTTARDTZ FREDERI) 29 November 2007 (2007-11-29) examples SE1-SE7 table SE2 -----	1-17
X	US 5 554 586 A (PRATT SAMUEL [US]) 10 September 1996 (1996-09-10) examples II, V table I -----	1-17
X	R. GALLEGO ET AL.: "Isocyanate-Functionalized Chitin and Chitosan as GellingAgents of Castor Oil", MOLECULES, vol. 18, 3 June 2013 (2013-06-03), pages 6532-6549, XP002754099, ISSN: 1420-3049 paragraphs [0001], [0003] -----	1-17

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 February 2016	23/02/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Verrucci, Marinella

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2015/063604

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2007135384 A2	29-11-2007	AR 061025 A1	30-07-2008
		AU 2007253105 A1	29-11-2007
		BR PI0711768 A2	13-12-2011
		CA 2652373 A1	29-11-2007
		CN 101472474 A	01-07-2009
		EP 2020848 A2	11-02-2009
		MY 153177 A	29-01-2015
		TW 200812481 A	16-03-2008
		US 2010190648 A1	29-07-2010
		WO 2007135384 A2	29-11-2007
		ZA 200809738 A	25-11-2009
US 5554586 A	10-09-1996	NONE	

Form PCT/ISA/210 (patent family annex) (April 2005)

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 April 2008 (03.04.2008)

PCT

(10) International Publication Number
WO 2008/039466 A1

(51) International Patent Classification:
A61K 8/87 (2006.01) *A61Q 1/06* (2006.01)

(21) International Application Number:
PCT/US2007/020703

(22) International Filing Date:
25 September 2007 (25.09.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/846,991 25 September 2006 (25.09.2006) US

(71) Applicant *(for all designated States except US)*: **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **SUNKARA, Hari, Babu** [US/US]; 3 Fritze Court, Hockessin, DE 19707 (US).

(74) Agent: **LERMAN, Bart, E.**; E. I. Du Pont De Nemours And Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, DE 19805 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

WO 2008/039466 A1

(54) Title: COSMETIC COMPOSITIONS

(57) Abstract: This invention relates to cosmetic compositions containing aqueous nanodis- persions of polyurethane ionomers based on polytrimethylene ether glycol ("PO3G"), and an active cosmetic ingredient. In a particularly preferred embodiment, the PO3G is derived predominantly from monomers obtained from renewable resources, making the personal care products of this embodiment of the present invention more environmentally friendly in terms of their manufacture, use and disposal.

TITLE

COSMETIC COMPOSITIONS

FIELD OF THE INVENTION

This invention relates to cosmetic compositions containing aqueous dispersions of nano-sized polyurethane ionomers based on polytrimethylene ether glycol ("PO3G"). In a particularly preferred embodiment, the PO3G is derived predominantly from monomers obtained from renewable resources, making the cosmetic compositions of this embodiment of the present invention more environmentally friendly in terms of their manufacture, use and disposal.

BACKGROUND OF THE INVENTION

There are a large number of cosmetic products available, most of which are in the form of solutions, creams, ointments, lotions, gels, emulsions or solids. There are a variety of uses for these cosmetic products including, e.g., skin care, bath and body care, deodorants, hand and foot care, facial care, hair care, shaving products, dental care, toiletry and personal lubrication. The ingredients in the formulated products in general serve as emollients, humectants, moisturizers, emulsifiers, lubricants, antimicrobials, cosmetics, fragrances, rheology modifiers, etc. Some of the products are solvent-based and others are water-based.

Most often cosmetic products contain an active ingredient incorporated in a delivery vehicle. The desired effect of a cosmetic product is achieved either by the cosmetic active ingredients or by the vehicle itself at the site of application, in most cases on the skin, hair and/or nails.

The major types of cosmetic vehicles most frequently fall into the following categories: (a) solutions; (b) emulsions, both oil-in-water and water-in-oil, including (for example) lotions and creams; (c) suspensions; (d) gels; and (e) solids (including semi-solids) including (for example) stick products. An extensive discussion of personal care and cosmetic vehicles is found in Handbook of Cosmetic Science and Technology, Second Edition, edited by M Paye, A. O. Barel and H. I. Maibach, pages 99-123 (2005).

Cosmetic products based on aqueous polyurethane dispersions are in a general sense known in the art. See, for example, US5874072, US5968494, US5972354, US2002/0034558A1 and US2004/0141942A1.

The majority of ingredients used in these personal care products are synthetic and are derived from petrochemical sources. The recent trend of the industry is to provide products to consumers that are natural and reduced in petroleum-based product content.

Aqueous dispersions of polyurethane ionomers based in part on ingredients derived from renewable resources are disclosed in commonly owned U.S. Application Ser. No. 11/782098 (filed 24 July 2007, and entitled "Polytrimethylene Ether-Based Polyurethane Ionomers"). The use of these aqueous dispersions in personal care applications is mentioned but not exemplified.

There is a need for all manufactures to provide products reduced environmental impacts. There is also an environmental advantage for manufacturers to provide products of renewably based sources. There thus exists a need for cosmetic products comprised of ingredients not derived from petroleum but from renewable resources. In addition, there is a need for ingredients and products that are environmentally friendly in respect to their manufacturing processes, their uses and their disposal.

SUMMARY OF THE INVENTION

In a first aspect, the present invention relates to a cosmetic composition comprising an aqueous continuous phase having dispersed therein a nano-sized water-dispersible polyurethane and at least one cosmetic additive, wherein the water-dispersible polyurethane is a polyurethane ionomer comprising a polymeric backbone having ionic and/or ionizable functionality incorporated into, pendant from and/or terminating said polymeric backbone, wherein the polymeric backbone comprises one or more non-ionic segments derived from a reaction product of polytrimethylene ether glycol ("PO3G") and a polyisocyanate. Preferably, the polyurethane ionomer has sufficient ionic functionality in order to render the polyurethane dispersible in the aqueous continuous phase. Preferably, all of the ingredients (polyurethane, active cosmetic ingredient and optional additives) are substantially evenly and stably dispersed throughout the aqueous continuous phase, and/or can be readily substantially evenly redispersed, for example, by low energy mixing (such as hand shaking).

In a second aspect, the present invention relates to a cosmetic composition comprising a solid or semi-solid continuous phase having dispersed therein an aqueous vehicle, a nano-sized water-dispersible polyurethane and at least

one cosmetic additive, wherein the water-dispersible polyurethane is a polyurethane ionomer comprising a polymeric backbone having ionic and/or ionizable functionality incorporated into, pendant from and/or terminating said polymeric backbone, wherein the polymeric backbone comprises one or more non-ionic segments derived from a reaction product of PO3G and a polyisocyanate. Preferably, the polyurethane ionomer has sufficient ionic functionality in order to render the polyurethane dispersible in the aqueous vehicle. Preferably, all of the ingredients (aqueous vehicle, polyurethane, active cosmetic ingredient and optional additives) are substantially evenly and stably dispersed throughout the continuous phase.

All ingredients of the compositions in accordance with the present invention should be pharmacologically acceptable.

In a preferred embodiment, the polyurethane is a film-forming polyurethane.

In a particularly preferred embodiment of the present invention, the PO3G used in the polyurethane is produced predominantly from monomers (such as 1,3-propane diol) that are biologically-derived.

The cosmetic compositions in accordance with the first aspect of the present invention are typically prepared by mixing the active cosmetic ingredient (and other optional additives) into an aqueous dispersion of a nanoparticle-sized polyurethane ionomer. In a preferred embodiment, when the active cosmetic ingredient is neither soluble nor dispersble in the continuous phase, the polyurethane ionomer acts as a dispersing/emulsifying agent for the ingredient.

The cosmetic compositions in accordance with the second aspect of the present invention are typically prepared by mixing the active cosmetic ingredient (and other optional additives) into an aqueous dispersion of the nanoparticle-sized polyurethane ionomer, then adding a solidifying agent (such as a gelling agent) to result in a solid or semi-sold product.

Cosmetic compositions in accordance with the first aspect are flowable at ambient temperatures (such as 25°C) and include, for example, brushable lip gloss products, hair and skin lotions, shampoos, nail polishes, hair care styling products (such as intended for aerosol application) and the like.

Cosmetic compositions in accordance with the second aspect include, for example, lipsticks, gels, deodorant sticks and the like. While not intended to be flowable at ambient temperatures (such as 25°C), these compositions may become flowable/spreadable upon application to a warmer surface such as skin, lips and nails.

These and other features and advantages of the present invention will be more readily understood by those of ordinary skill in the art from a reading of the following detailed description.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

All publications, patent applications, patents and other references mentioned herein, if not otherwise indicated, are incorporated by reference herein for all purposes as if fully set forth.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including definitions, will control.

Except where expressly noted, trademarks are shown in upper case.

Unless stated otherwise, all percentages, parts, ratios, etc., are by weight.

When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

When the term "about" is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to.

As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-

exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Use of "a" or "an" are employed to describe elements and components of the invention. This is done merely for convenience and to give a general sense of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

The materials, methods, and examples herein are illustrative only and, except as specifically stated, are not intended to be limiting. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described herein.

The present invention is directed to cosmetics compositions that are derived from aqueous dispersions of polyurethane ionomers such as disclosed in previously incorporated U.S. Application Ser. No. 11/782098 (filed 24 July 2007, and entitled "Polytrimethylene Ether-Based Polyurethane Ionomers"). Particularly, the aqueous dispersions are of nanoparticle-sized polyurethane ionomers.

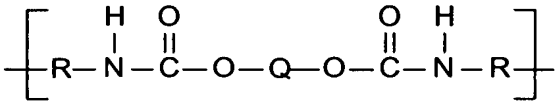
"Nanoparticle-sized" as used herein refers to particles of less than 1 micron. Preferably, the particle size is between about 0.005 to about 0.5 micron. The average particle size preferably should be less than about 0.5 micron, and preferably between about 0.005 to about 0.3 micron. The small particle size enhances the stability of the dispersed particles. As used herein, particle size refers to a number average particle size as measured by conventional particle size measuring techniques well known to those skilled in the art, such as sedimentation field flow fractionation, photon correlation spectroscopy (PCS), or disk centrifugation. When PCS is used as the method of particle sizing, the average particle diameter is the Z-average particle diameter known to those skilled in the art.

The cosmetic compositions in accordance with the present invention are either flowable (dispersions/emulsions/suspensions) or solid/semi-solid, containing at least one active cosmetic ingredient, a nanoparticle-sized polyurethane ionomer and an aqueous vehicle. The physical form of the cosmetic composition will determine how these various components are contained in the composition.

Polyurethane Ionomer

As indicated previously, the polyurethane ionomer comprises a polymeric backbone having ionic and/or ionizable functionality incorporated into, pendant from and/or terminating said polymeric backbone, wherein the polymeric backbone comprises one or more non-ionic segments derived from a reaction product of PO3G and a polyisocyanate, and wherein said polyurethane ionomer preferably has sufficient ionic functionality in order to render the polyurethane dispersible in the aqueous continuous phase (aqueous vehicle).

Preferably, at least about 20 wt%, more preferably at least about 25 wt%, and still more preferably at least about 40 wt%, of the polyurethane (based on the weight of the polyurethane) comprises one or more non-ionic segments of the general formula (I):



(I)

wherein:

each R individually is the residue of a diisocyanate compound after abstraction of the isocyanate groups; and

Q is the residue of an oligomeric or polymeric diol after abstraction of the hydroxyl groups, wherein the oligomeric or polymeric diol is PO3G.

Preferably, Q in and of itself constitutes at least about 20 wt%, more preferably at least about 25 wt%, and still more preferably at least about 40 wt%, of the polyurethane, based on the weight of the polyurethane.

The polyurethane is preferably prepared from (a) a polyol (2 or more OH groups) component comprising at least about 40 wt% PO3G, based on the weight of the polyol component; (b) a polyisocyanate component comprising a diisocyanate; and (c) a hydrophilic reactant comprising a compound selected

from the group consisting of (i) a mono or diisocyanate containing an ionic and/or ionizable group, and (ii) an isocyanate reactive ingredient containing an ionic and/or ionizable group. These components are reacted to form an isocyanate-functional prepolymer with ionic and/or ionizable functionality, which can then be chain extended and/or chain terminated as described in further detail below.

Polyol Component

As indicated above, the polyol component comprises at least about 40 wt% PO3G, more preferably at least about 50 wt% PO3G, still more preferably at least about 75 wt% PO3G, and even still more preferably at least about 90 wt% PO3G, based on the weight of the polyol component.

In one embodiment, the PO3G may be blended with other oligomeric and/or polymer polyfunctional isocyanate-reactive compounds such as, for example, polyols, polyamines, polythiols, polythioamines, polyhydroxythiols and polyhydroxylamines. When blended, it is preferred to use difunctional components and, more preferably, one or more diols including, for example, polyether diols, polyester diols, polycarbonate diols, polyacrylate diols, polyolefin diols and silicone diols.

In this embodiment, the PO3G is preferably blended with about 60 wt% or less, more preferably about 50 wt% or less, still more preferably about 25 wt% or less, and even still more preferably about 10 wt% or less, of the other isocyanate-reactive compounds.

Polytrimethylene Ether Glycol (PO3G)

Polytrimethylene ether glycols are oligomers and polymers in which at least 50% of the repeating units are trimethylene ether units. More preferably from about 75% to 100%, still more preferably from about 90% to 100%, and even more preferably from about 99% to 100%, of the repeating units are trimethylene ether units.

Polytrimethylene ether glycols are preferably prepared by polycondensation of monomers comprising 1,3-propanediol, thus resulting in polymers or copolymers containing $-(CH_2CH_2CH_2O)-$ linkage (e.g, trimethylene ether repeating units). As indicated above, at least 50% of the repeating units are trimethylene ether units.

In addition to the trimethylene ether units, lesser amounts of other units, such as other polyalkylene ether repeating units, may be present also. In the context of this disclosure, the term "polytrimethylene ether glycol" encompasses polytrimethylene ether glycol made from essentially pure 1,3-propanediol, as well as those oligomers and polymers (including those described below) containing up to about 50% by weight of comonomers.

The 1,3-propanediol employed for preparing the polytrimethylene ether glycols may be obtained by any of the various well known chemical routes or by biochemical transformation routes. Most preferably, the 1,3-propanediol is obtained biochemically from a renewable source ("biologically-derived" 1,3-propanediol).

The most preferred source of 1,3-propanediol is via a fermentation process using a renewable biological source. As an illustrative example of a starting material from a renewable source, biochemical routes to 1,3-propanediol (PDO) have been described that utilize feedstocks produced from biological and renewable resources such as corn feed stock. For example, bacterial strains able to convert glycerol into 1,3-propanediol are found in the species *Klebsiella, Citrobacter, Clostridium*, and *Lactobacillus*. The technique is disclosed in several patents, including US5633362, US5686276 and US5821092. For example, US5821092 discloses, *inter alia*, a process for the biological production of 1,3-propanediol from glycerol using recombinant organisms. The process incorporates *E. coli* bacteria, transformed with a heterologous pdu diol dehydratase gene, having specificity for 1,2-propanediol. The transformed *E. coli* is grown in the presence of glycerol as a carbon source and 1,3-propanediol is isolated from the growth media. Since both bacteria and yeasts can convert glucose (e.g., corn sugar) or other carbohydrates to glycerol, the processes disclosed in these publications provide a rapid, inexpensive and environmentally responsible source of 1,3-propanediol monomer.

The biologically-derived 1,3-propanediol, such as produced by the processes described and referenced above, contains carbon from the atmospheric carbon dioxide incorporated by plants, which compose the feedstock for the production of the 1,3-propanediol. In this way, the biologically-derived 1,3-propanediol preferred for use in the context of the present invention contains only renewable carbon, and not fossil fuel-based or petroleum-based carbon. The polytrimethylene ether glycol and personal care compositions of the present in-

vention utilizing the biologically-derived 1,3-propanediol, therefore, have less impact on the environment as the 1,3-propanediol used in the compositions does not deplete diminishing fossil fuels and, upon degradation, releases carbon back to the atmosphere for use by plants once again. Thus, the compositions present invention can be characterized as more natural and having less environmental impact than similar compositions comprising petroleum based glycols.

The biologically-derived 1,3-propanediol, and polytrimethylene ether glycols, may be distinguished from similar compounds produced from a petrochemical source or from fossil fuel carbon by dual carbon-isotopic finger printing. This method usefully distinguishes chemically-identical materials, and apportions carbon in the copolymer by source (and possibly year) of growth of the biospheric (plant) component. The isotopes, ^{14}C and ^{13}C, bring complementary information to this problem. The radiocarbon dating isotope (^{14}C), with its nuclear half life of 5730 years, clearly allows one to apportion specimen carbon between fossil ("dead") and biospheric ("alive") feedstocks (Currie, L. A. "Source Apportionment of Atmospheric Particles," Characterization of Environmental Particles, J. Buffle and H.P. van Leeuwen, Eds., 1 of Vol. I of the IUPAC Environmental Analytical Chemistry Series (Lewis Publishers, Inc) (1992) 3-74). The basic assumption in radiocarbon dating is that the constancy of ^{14}C concentration in the atmosphere leads to the constancy of ^{14}C in living organisms. When dealing with an isolated sample, the age of a sample can be deduced approximately by the relationship

$$t = (-5730/0.693)\ln(A/A_0)$$

where t = age, 5730 years is the half-life of radiocarbon, and A and A_0 are the specific ^{14}C activity of the sample and of the modern standard, respectively (Hsieh, Y., Soil Sci. Soc. Am J., 56, 460, (1992)). However, because of atmospheric nuclear testing since 1950 and the burning of fossil fuel since 1850, ^{14}C has acquired a second, geochemical time characteristic. Its concentration in atmospheric CO_2, and hence in the living biosphere, approximately doubled at the peak of nuclear testing, in the mid-1960s. It has since been gradually returning to the steady-state cosmogenic (atmospheric) baseline isotope rate ($^{14}C/^{12}C$) of *ca.* 1.2×10^{-12}, with an approximate relaxation "half-life" of 7-10 years. (This latter half-life must not be taken literally; rather, one must use the detailed atmospheric nuclear input/decay function to trace the variation of atmospheric and biospheric ^{14}C since the onset of the nuclear age.) It is this latter biospheric ^{14}C time characteristic that holds out the promise of annual dating of recent biospheric carbon.

^{14}C can be measured by accelerator mass spectrometry (AMS), with results given in units of "fraction of modern carbon" (f_M). f_M is defined by National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) 4990B and 4990C, known as oxalic acids standards HOxI and HOxII, respectively. The fundamental definition relates to 0.95 times the $^{14}C/^{12}C$ isotope ratio HOxI (referenced to AD 1950). This is roughly equivalent to decay-corrected pre-Industrial Revolution wood. For the current living biosphere (plant material), $f_M \approx 1.1$.

The stable carbon isotope ratio ($^{13}C/^{12}C$) provides a complementary route to source discrimination and apportionment. The $^{13}C/^{12}C$ ratio in a given bio-sourced material is a consequence of the $^{13}C/^{12}C$ ratio in atmospheric carbon dioxide at the time the carbon dioxide is fixed and also reflects the precise metabolic pathway. Regional variations also occur. Petroleum, C_3 plants (the broadleaf), C_4 plants (the grasses), and marine carbonates all show significant differences in $^{13}C/^{12}C$ and the corresponding $\delta^{13}C$ values. Furthermore, lipid matter of C_3 and C_4 plants analyze differently than materials derived from the carbohydrate components of the same plants as a consequence of the metabolic pathway. Within the precision of measurement, ^{13}C shows large variations due to isotopic fractionation effects, the most significant of which for the instant invention is the photosynthetic mechanism. The major cause of differences in the carbon isotope ratio in plants is closely associated with differences in the pathway of photosynthetic carbon metabolism in the plants, particularly the reaction occurring during the primary carboxylation, i.e., the initial fixation of atmospheric CO_2. Two large classes of vegetation are those that incorporate the "C_3" (or Calvin-Benson) photosynthetic cycle and those that incorporate the "C_4" (or Hatch-Slack) photosynthetic cycle. C_3 plants, such as hardwoods and conifers, are dominant in the temperate climate zones. In C_3 plants, the primary CO_2 fixation or carboxylation reaction involves the enzyme ribulose-1,5-diphosphate carboxylase and the first stable product is a 3-carbon compound. C_4 plants, on the other hand, include such plants as tropical grasses, corn and sugar cane. In C_4 plants, an additional carboxylation reaction involving another enzyme, phosphoenol-pyruvate carboxylase, is the primary carboxylation reaction. The first stable carbon compound is a 4-carbon acid, which is subsequently decarboxylated. The CO_2 thus released is refixed by the C_3 cycle.

Both C_4 and C_3 plants exhibit a range of $^{13}C/^{12}C$ isotopic ratios, but typical values are *ca.* -10 to -14 per mil (C_4) and -21 to -26 per mil (C_3) (Weber et al., J.

Agric. Food Chem., 45, 2942 (1997)). Coal and petroleum fall generally in this latter range. The ^{13}C measurement scale was originally defined by a zero set by pee dee belemnite (PDB) limestone, where values are given in parts per thousand deviations from this material. The "$\delta^{13}C$" values are in parts per thousand (per mil), abbreviated ‰, and are calculated as follows:

$$\delta^{13}C \equiv \frac{(^{13}C/^{12}C)\text{sample} - (^{13}C/^{12}C)\text{standard}}{(^{13}C/^{12}C)\text{standard}} \times 1000‰$$

Since the PDB reference material (RM) has been exhausted, a series of alternative RMs have been developed in cooperation with the IAEA, USGS, NIST, and other selected international isotope laboratories. Notations for the per mil deviations from PDB is $\delta^{13}C$. Measurements are made on CO_2 by high precision stable ratio mass spectrometry (IRMS) on molecular ions of masses 44, 45 and 46.

Biologically-derived 1,3-propanediol, and compositions comprising biologically-derived 1,3-propanediol, therefore, may be completely distinguished from their petrochemical derived counterparts on the basis of ^{14}C (f_M) and dual carbon-isotopic fingerprinting, indicating new compositions of matter. The ability to distinguish these products is beneficial in tracking these materials in commerce. For example, products comprising both "new" and "old" carbon isotope profiles may be distinguished from products made only of "old" materials. Hence, the instant materials may be followed in commerce on the basis of their unique profile and for the purposes of defining competition, for determining shelf life, and especially for assessing environmental impact.

Preferably the 1,3-propanediol used as the reactant or as a component of the reactant will have a purity of greater than about 99%, and more preferably greater than about 99.9%, by weight as determined by gas chromatographic analysis. Particularly preferred are the purified 1,3-propanediols as disclosed in US20040260125A1, US20040225161A1 and US20050069997A1, and polytrimethylene ether glycol made therefrom as disclosed in US20050020805A1.

The purified 1,3-propanediol preferably has the following characteristics:

(1) an ultraviolet absorption at 220 nm of less than about 0.200, and at 250 nm of less than about 0.075, and at 275 nm of less than about 0.075; and/or

(2) a composition having L*a*b* "b*" color value of less than about 0.15 (ASTM D6290), and an absorbance at 270 nm of less than about 0.075; and/or

(3) a peroxide composition of less than about 10 ppm; and/or

(4) a concentration of total organic impurities (organic compounds other than 1,3-propanediol) of less than about 400 ppm, more preferably less than about 300 ppm, and still more preferably less than about 150 ppm, as measured by gas chromatography.

The starting material for making polytrimethylene ether glycol will depend on the desired polytrimethylene ether glycol, availability of starting materials, catalysts, equipment, etc., and comprises "1,3-propanediol reactant." By "1,3-propanediol reactant" is meant 1,3-propanediol, and oligomers and prepolymers of 1,3-propanediol preferably having a degree of polymerization of 2 to 9, and mixtures thereof. In some instances, it may be desirable to use up to 10% or more of low molecular weight oligomers where they are available. Thus, preferably the starting material comprises 1,3-propanediol and the dimer and trimer thereof. A particularly preferred starting material is comprised of about 90% by weight or more 1,3-propanediol, and more preferably 99% by weight or more 1,3-propanediol, based on the weight of the 1,3-propanediol reactant.

Polytrimethylene ether glycol can be made via a number of processes known in the art, such as disclosed in US6977291 and US6720459. A preferred process is as set forth in previously incorporated US20050020805A1.

As indicated above, polytrimethylene ether glycol may contain lesser amounts of other polyalkylene ether repeating units in addition to the trimethylene ether units. The monomers for use in preparing polytrimethylene ether glycol can, therefore, contain up to 50% by weight (preferably about 20 wt% or less, more preferably about 10 wt% or less, and still more preferably about 2 wt% or less), of comonomer diols in addition to the 1,3-propanediol reactant. Comonomer diols that are suitable for use in the process include aliphatic diols, for example, ethylene glycol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,12-dodecanediol, 3,3,4,4,5,5-hexafluro-1,5-pentanediol, 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol, and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluoro-1,12-dodecanediol; cycloaliphatic diols, for example, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol and isosorbide; and polyhydroxy compounds, for example, glycerol, trimethylolpropane, and pentaerythritol. A preferred group of comonomer diols is selected from the group consisting of ethylene glycol,

2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, $C_6 - C_{10}$ diols (such as 1,6-hexanediol, 1,8-octanediol and 1,10-decanediol) and isosorbide, and mixtures thereof. A particularly preferred diol other than 1,3-propanediol is ethylene glycol, and $C_6 - C_{10}$ diols can be particularly useful as well.

One preferred polytrimethylene ether glycol containing comonomers is poly(trimethylene-ethylene ether) glycol such as described in US2004/0030095A1. Preferred poly(trimethylene-co-ethylene ether) glycols are prepared by acid catalyzed polycondensation of from 50 to about 99 mole% (preferably from about 60 to about 98 mole%, and more preferably from about 70 to about 98 mole%) 1,3-propanediol and up to 50 to about 1 mole% (preferably from about 40 to about 2 mole%, and more preferably from about 30 to about 2 mole%) ethylene glycol.

Polytrimethylene ether glycols useful in practicing this invention can contain small amounts of other repeat units, for example, from aliphatic or aromatic diacids or diesters, such as described in US6608168. This type of polytrimethylene ether glycol can also be called a "random polytrimethylene ether ester", and can be prepared by polycondensation of 1,3-propanediol reactant and about 10 to about 0.1 mole% of aliphatic or aromatic diacid or esters thereof, such as terephthalic acid, isophthalic acid, bibenzoic acid, naphthalic acid, bis(p-carboxyphenyl)methane, 1,5-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, 4,4'-sulfonyl dibenzoic acid, p-(hydroxyethoxy)benzoic acid, and combinations thereof, and dimethyl terephthalate, bibenzoate, isophthlate, naphthalate and phthalate; and combinations thereof. Of these, terephthalic acid, dimethyl terephthalate and dimethyl isophthalate are preferred.

The polytrimethylene ether glycols preferred for use herein generally have a number average molecular weight from about 200 to about 5000, and preferably from about 200 to about 2000. The polytrimethylene ether glycols preferred for use herein are typically polydisperse polymers having a polydispersity of preferably from about 1.0 to about 2.2, more preferably from about 1.2 to about 2.0, and still more preferably from about 1.2 to about 1.8.

The polytrimethylene ether glycols for use in the present invention preferably have a color value of less than about 100 APHA, and more preferably less than about 50 APHA.

Polytrimethylene ether glycol as described above should in general have low acute oral toxicity, and not be a skin or eye irritant, or a skin sensitizer.

Other Isocyanate-Reactive Components

As indicated above, the PO3G may be blended with other polyfunctional isocyanate-reactive components, preferably up to about 60 wt%, most notably oligomeric and/or polymeric polyols.

Suitable polyols contain at least two hydroxyl groups, and preferably have a molecular weight of from about 60 to about 6000. Of these, the polymeric polyols are best defined by the number average molecular weight, and can range from about 200 to about 6000, preferably from about 300 to about 3000, and more preferably from about 500 to about 2500. The molecular weights can be determined by hydroxyl group analysis (OH number).

Examples of polymeric polyols include polyesters, polyethers, polycarbonates, polyacetals, poly(meth)acrylates, polyester amides, polythioethers, and mixed polymers such as a polyester-polycarbonates where both ester and carbonate linkages are found in the same polymer. Also included are vegetable-based polyols. A combination of these polymers can also be used. For examples, a polyester polyol and a poly(meth)acrylate polyol may be used in the same polyurethane synthesis.

Suitable polyester polyols include reaction products of polyhydric, preferably dihydric alcohols to which trihydric alcohols may optionally be added, and polybasic (preferably dibasic) carboxylic acids. Instead of these polycarboxylic acids, the corresponding carboxylic acid anhydrides or polycarboxylic acid esters of lower alcohols or mixtures thereof may be used for preparing the polyesters.

The polycarboxylic acids may be aliphatic, cycloaliphatic, aromatic and/or heterocyclic or mixtures thereof and they may be substituted, for example, by halogen atoms, and/or unsaturated. The following are mentioned as examples: succinic acid; adipic acid; suberic acid; azelaic acid; sebacic acid; 1,12-dodecyldioic acid; phthalic acid; isophthalic acid; trimellitic acid; phthalic acid anhydride; tetrahydrophthalic acid anhydride; hexahydrophthalic acid anhydride;

tetrachlorophthalic acid anhydride; endomethylene tetrahydrophthalic acid anhydride; glutaric acid anhydride; maleic acid; maleic acid anhydride; fumaric acid; dimeric and trimeric fatty acids such as oleic acid, which may be mixed with monomeric fatty acids; dimethyl terephthalates and bis-glycol terephthalate.

Suitable polyhydric alcohols include, e.g., ethylene glycol; propylene glycol-(1,2) and -(1,3); butylene glycol-(1,4) and -(1,3); hexanediol-(1,6); octanediol-(1,8); neopentyl glycol; cyclohexanedimethanol (1,4-bis-hydroxymethyl-cyclohexane); 2-methyl-1,3-propanediol; 2,2,4-trimethyl-1, 3-pentanediol; diethylene glycol, triethylene glycol; tetraethylene glycol; polyethylene glycol; dipropylene glycol; polypropylene glycol; dibutylene glycol and polybutylene glycol; glycerine; trimethylolpropane; ether glycols thereof; and mixtures thereof. The polyester polyols may also contain a portion of carboxyl end groups. Polyesters of lactones, for example, epsilon-caprolactone, or hydroxycarboxylic acids, for example, omega-hydroxycaproic acid, may also be used.

Preferable polyester diols for blending with PO3G are hydroxyl-terminated poly(butylene adipate), poly(butylene succinate), poly(ethylene adipate), poly(1,2-proylene adipate), poly(trimethylene adipate), poly(trimethylene succinate), polylactic acid ester diol and polycaprolactone diol. Other hydroxyl terminated polyester diols are copolyethers comprising repeat units derived from a diol and a sulfonated dicarboxylic acid and prepared as described in US6316586. The preferred sulfonated dicarboxylic acid is 5-sulfo-isophthalic acid, and the preferred diol is 1,3-propanediol.

Suitable polyether polyols are obtained in a known manner by the reaction of starting compounds that contain reactive hydrogen atoms with alkylene oxides such as ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, styrene oxide, epichlorohydrin or mixtures of these. Suitable starting compounds containing reactive hydrogen atoms include the polyhydric alcohols set forth above and, in addition, water, methanol, ethanol, 1,2,6-hexane triol, 1,2,4-butane triol, trimethylol ethane, pentaerythritol, mannitol, sorbitol, methyl glycoside, sucrose, phenol, isononyl phenol, resorcinol, hydroquinone, 1,1,1- and 1,1,2-tris-(hydroxylphenyl)-ethane, dimethylolpropionic acid or dimethylolbutanoic acid.

Polyethers that have been obtained by the reaction of starting compounds containing amine compounds can also be used. Examples of these polyethers as well as suitable polyhydroxy polyacetals, polyhydroxy polyacrylates, polyhy-

droxy polyester amides, polyhydroxy polyamides and polyhydroxy polythioethers, are disclosed in US4701480.

Preferred polyether diols for blending with PO3G are polyethylene glycol, poly(1,2-propylene glycol), polytetramethylene glycol, copolyethers such as tetrahydrofuran/ethylene oxide and tetrahydrofuran/propylene oxide copolymers, and mixtures thereof.

Polycarbonates containing hydroxyl groups include those known, per se, such as the products obtained from the reaction of diols such as propanediol-(1,3), butanediol-(1,4) and/or hexanediol-(1,6), diethylene glycol, triethylene glycol or tetraethylene glycol, higher polyether diols with phosgene, diarylcarbonates such as diphenylcarbonate, dialkylcarbonates such as diethylcarbonate or with cyclic carbonates such as ethylene or propylene carbonate. Also suitable are polyester carbonates obtained from the above-mentioned polyesters or polylactones with phosgene, diaryl carbonates, dialkyl carbonates or cyclic carbonates.

Polycarbonate diols for blending are preferably selected from the group consisting of polyethylene carbonate diol, polytrimethylene carbonate diol, polybutylene carbonate diol and polyhexylene carbonate diol.

Poly(meth)acrylates containing hydroxyl groups include those common in the art of addition polymerization such as cationic, anionic and radical polymerization and the like. Examples are alpha-omega diols. An example of these type of diols are those which are prepared by a "living" or "control" or chain transfer polymerization processes which enables the placement of one hydroxyl group at or near the termini of the polymer. US6248839 and US5990245 have examples of protocol for making terminal diols. Other di-NCO reactive poly(meth)acrylate terminal polymers can be used. An example would be end groups other than hydroxyl such as amino or thiol, and may also include mixed end groups with hydroxyl.

Polyolefin diols are available from Shell as KRATON LIQUID L and Mitsubishi Chemical as POLYTAIL H.

Silicone glycols are well known, and representative examples are described in US4647643.

In some instances, vegetable oils may be the preferred blending component because of their biological origin and biodegradability. Examples of vegeta-

ble oils include but are not limited to sunflower oil, canola oil, rapeseed oil, corn oil, olive oil, soybean oil, castor oil and mixtures thereof. These oils are either partial or fully hydrogenated. Commercially available examples of such vegetable oils include Soyol R2-052-G (Urethane Soy Systems) and Pripol 2033 (Uniqema).

Other optional compounds for preparing the NCO-functional prepolymer include lower molecular weight, at least difunctional NCO-reactive compounds having an average molecular weight of up to about 400. Examples include the dihydric and higher functional alcohols, which have previously been described for the preparation of the polyester polyols and polyether polyols.

In addition to the above-mentioned components, which are preferably difunctional in the isocyanate polyaddition reaction, mono-functional and even small portions of trifunctional and higher functional components generally known in polyurethane chemistry, such as trimethylolpropane or 4-isocyanantomethyl-1,8-octamethylene diisocyanate, may be used in cases in which branching of the NCO prepolymer or polyurethane is desired.

It is, however, preferred that the NCO-functional prepolymers should be substantially linear, and this may be achieved by maintaining the average functionality of the prepolymer starting components at or below 2:1.

Similar NCO reactive materials can be used as described for hydroxy containing compounds and polymers, but which contain other NCO reactive groups. Examples would be dithiols, diamines, thioamines, and even hydroxythiols and hydroxylamines. These can either be compounds or polymers with the molecular weights or number average molecular weights as described for the polyols.

Other optional compounds include isocyanate-reactive compounds containing self-condensing moieties. The content of these compounds are dependent upon the desired level of self-condensation necessary to provide the desirable resin properties. 3-amino-1-triethoxysilyl-propane is an example of a compound that will react with isocyanates through the amino group and yet self-condense through the silyl group when inverted into water.

Other optional compounds include isocyanate-reactive compounds containing non-condensable silanes and/or fluorocarbons with isocyanate reactive groups, which can be used in place of or in conjunction with the isocyanate-

reactive compounds. US5760123 and US6046295 list examples of methods for use of these optional silane/fluoro-containing compounds.

Polyisocyanate Component

Suitable polyisocyanates are those that contain aromatic, cycloaliphatic and/or aliphatic groups bound to the isocyanate groups. Mixtures of these compounds may also be used. Preferred are compounds with isocyanates bound to a cycloaliphatic or aliphatic moieties. If aromatic isocyanates are used, cycloaliphatic or aliphatic isocyanates are preferably present as well.

Diisocyanates are preferred, and any diisocyanate useful in preparing polyurethanes and/or polyurethane-ureas from polyether glycols, diols and/or amines can be used in this invention.

Examples of suitable diisocyanates include, but are not limited to, 2,4-toluene diisocyanate (TDI); 2,6-toluene diisocyanate; trimethyl hexamethylene diisocyanate (TMDI); 4,4'-diphenylmethane diisocyanate (MDI); 4,4'-dicyclohexylmethane diisocyanate (H_{12}MDI); 3,3'-dimethyl-4,4'-biphenyl diisocyanate (TODI); Dodecane diisocyanate (C_{12}DI); m-tetramethylene xylylene diisocyanate (TMXDI); 1,4-benzene diisocyanate; trans-cyclohexane-1,4-diisocyanate; 1,5-naphthalene diisocyanate (NDI); 1,6-hexamethylene diisocyanate (HDI); 4,6-xylyene diisocyanate; isophorone diisocyanate (IPDI); and combinations thereof. IPDI and TMXDI are preferred.

Small amounts, preferably less than about 10 wt% based on the weight of the diisocyanate, of monoisocyanates or polyisocyanates can be used in mixture with the diisocyanate. Examples of useful monoisocyanates include alkyl isocyanates such as octadecyl isocyanate and aryl isocyanates such as phenyl isocyanate. An example of a polyisocyanate is triisocyanatotoluene HDI trimer (Desmodur 3300), and polymeric MDI (Mondur MR and MRS).

Ionic Reactants

The hydrophilic reactant contains ionic and/or ionizable groups (potentially ionic groups). Preferably, these reactants will contain one or two, more preferably two, isocyanate reactive groups, as well as at least one ionic or ionizable group.

Examples of ionic dispersing groups include carboxylate groups (-COOM), phosphate groups (-OPO_3 M_2), phosphonate groups (-PO_3 M_2), sulfonate groups (-SO_3 M), quaternary ammonium groups (-NR_3 Y, wherein Y is a monovalent anion such as chlorine or hydroxyl), or any other effective ionic group. M is a cation such as a monovalent metal ion (e.g., Na^+, K^+, Li^+, etc.), H^+, NR_4^+, and each R can be independently an alkyl, aralkyl, aryl, or hydrogen. These ionic dispersing groups are typically located pendant from the polyurethane backbone.

The ionizable groups in general correspond to the ionic groups, except they are in the acid (such as carboxyl –COOH) or base (such as primary, secondary or tertiary amine –NH_2, –NRH, or –NR_2) form. The ionizable groups are such that they are readily converted to their ionic form during the dispersion/polymer preparation process as discussed below.

The ionic or potentially ionic groups are chemically incorporated into the polyurethane in an amount to provide an ionic group content (with neutralization as needed) sufficient to render the polyurethane dispersible in the aqueous medium of the dispersion. Typical ionic group content will range from about 5 up to about 210 milliequivalents (meq), preferably from about 10 to about 140 meq, more preferably from about 20 to about 120 meq, and still more preferably from about 30 to about 90 meq, per 100 g of polyurethane.

Suitable compounds for incorporating these groups include (1) monoisocyanates or diisocyanates which contain ionic and/or ionizable groups, and (2) compounds which contain both isocyanate reactive groups and ionic and/or ionizable groups. In the context of this disclosure, the term "isocyanate reactive groups" is taken to include groups well known to those of ordinary skill in the relevant art to react with isocyanates, and preferably hydroxyl, primary amino and secondary amino groups.

Examples of isocyanates that contain ionic or potentially ionic groups are sulfonated toluene diisocyanate and sulfonated diphenylmethanediisocyanate.

With respect to compounds which contain isocyanate reactive groups and ionic or potentially ionic groups, the isocyanate reactive groups are typically amino and hydroxyl groups. The potentially ionic groups or their corresponding ionic groups may be cationic or anionic, although the anionic groups are preferred. Preferred examples of anionic groups include carboxylate and sulfonate

groups. Preferred examples of cationic groups include quaternary ammonium groups and sulfonium groups.

The neutralizing agents for converting the ionizable groups to ionic groups are described in the preceding incorporated publications, and are also discussed hereinafter. Within the context of this invention, the term "neutralizing agents" is meant to embrace all types of agents that are useful for converting ionizable groups to the more hydrophilic ionic (salt) groups.

Suitable compounds for incorporating the previously discussed carboxylate, sulfonate and quaternary nitrogen groups are described in US3479310, US4303774, US4108814 and US4408008.

Suitable compounds for incorporating tertiary sulfonium groups are described in US3419533.

Sulfonate groups for incorporation into the polyurethanes preferably are the diol sulfonates as disclosed in previously incorporated US4108814. Suitable diol sulfonate compounds also include hydroxyl terminated copolyethers comprising repeat units derived from a diol and a sulfonated dicarboxylic acid and prepared as described in previously incorporated US6316586. The preferred sulfonated dicarboxylic acid is 5-sulfo-isophthalic acid, and the preferred diol is 1,3-propanediol. Suitable sulfonates also include H_2N-CH_2-CH_2-NH-$(CH_2)_r$-SO_3Na, where r=2 or 3; and HO-CH_2-CH_2-C(SO_3Na)-CH_2-OH.

Examples of carboxylic group-containing compounds are the hydroxy-carboxylic acids corresponding to the formula $(HO)_xQ(COOH)_y$ wherein Q represents a straight or branched, hydrocarbon radical containing 1 to 12 carbon atoms, x is 1 or 2 (preferably 2), and y is 1 to 3 (preferably 1 or 2).

Examples of these hydroxy-carboxylic acids include citric acid, tartaric acid and hydroxypivalic acid.

The preferred acids are those of the above-mentioned formula wherein x=2 and y=1. These dihydroxy alkanoic acids are described in US3412054. The preferred group of dihydroxy alkanoic acids are the α,α-dimethylol alkanoic acids represented by the structural formula R^2-C-$(CH_2OH)_2$-COOH, wherein R^2 is hydrogen or an alkyl group containing 1 to 8 carbon atoms. Examples of these ionizable diols include but are not limited to dimethylolacetic acid, 2,2'-dimethylolbutanoic acid, 2,2'-dimethylolpropionic acid, and 2,2'-dimethylolbutyric

acid. The most preferred dihydroxy alkanoic acids is 2,2'-dimethylolpropionic acid ("DMPA").

When the ionic stabilizing groups are acids, the acid groups are incorporated in an amount sufficient to provide an acid group content, known by those skilled in the art as acid number (mg KOH per gram solid polymer), of at least about 5, preferably at least about 10 milligrams KOH per 1.0 gram of polyurethane. The upper limit for the acid number is about 90, and preferably about 60.

Suitable carboxylates also include H_2N-$(CH_2)_4$-$CH(CO_2H)$-NH_2, and H_2N-CH_2-CH_2-NH-CH_2-CH_2-CO_2Na.

In addition to the foregoing, cationic centers such as tertiary amines with one alkyl and two alkylol groups may also be used as the ionic or ionizable group.

Polyurethane and Dispersion Preparation

The process of preparing the dispersions used in the invention begins with preparation of the polyurethane, which can be prepared by mixture or stepwise methods.

In the mixture process, an isocyanate-terminated polyurethane prepolymer is prepared by mixing the polyol component, the ionic reactants and solvent, and then adding polyisocyanate component to the mixture. This reaction is conducted at from about 40°C to about 100°C, and more preferably from about 50°C to about 90°C. The preferred ratio of isocyanate to isocyanate reactive groups is from about 1.3:1 to about 1.05:1, and more preferably from about 1.25:1 to about 1.1:1. When the targeted percent isocyanate is reached (typically an isocyanate content of about 1 to about 20%, preferably about 1 to about 10% by weight, based on the weight of prepolymer solids), then the optional chain terminator can be added, as well as a base or acid to neutralize ionizable groups incorporated from the ionic reactant.

If some cases, addition of neutralization agent, preferably tertiary amines, may be beneficial during early stages of the polyurethane synthesis. Alternately, advantages may be achieved via the addition of the neutralization agent, preferably alkali base, simultaneously along with the water of inversion at high shear.

In the stepwise method, an isocyanate-terminated polyurethane prepolymer is prepared by dissolving the ionic reactant in solvent, and then adding the polyisocyanate component to the mixture. Once the initial percent isocyanate target is reached, the polyol component is added. This reaction is conducted at from about 40°C to about 100°C, and more preferably from about 50°C to about 90°C. The preferred ratio of isocyanate to isocyanate reactive groups is from about 1.3:1 to about 1.05:1, and more preferably from about 1.25:1 to about 1.1:1. Alternately, the polyol component may be reacted in the first step, and the ionic reactant may be added after the initial percent isocyanate target is reached. When the final targeted percent isocyanate is reached (typically an isocyanate content of about 1 to about 20%, preferably about 1 to about 10% by weight, based on the weight of prepolymer solids), then the optional chain terminator may be added, as well as a base or acid to neutralize ionizable groups incorporated from the ionic reactant.

The resulting polyurethane solution is then converted to an aqueous polyurethane dispersion via the addition of water under shear, as discussed in further detail below. The optional chain extender is added at this point, if the chain terminator is omitted or reduced to leave sufficient isocyanate functionality. Chain extension is typically performed at 30°C to 60°C under aqueous conditions. If present, the volatile solvent is distilled under reduced pressure.

Catalysts are often necessary to prepare the polyurethanes, and may provide advantages in their manufacture. The catalysts most widely used are tertiary amines such as tertiary ethylamine, organo-tin compounds such as stannous octoate, dibutyltin dioctoate, dibutyltin dilaurate, organo-titanates such as TYZOR® TPT or TYZOR® TBT (E.I. du Pont de Nemours and Company), organo-zirconates, and mixtures thereof.

Preparation of the polyurethane for subsequent conversion to a dispersion is facilitated by using solvent. Suitable solvents are those that are miscible with water and inert to isocyanates and other reactants utilized in forming the polyurethanes. If it is desired to prepare a solvent-free dispersion, then it is preferable to use a solvent with a high enough volatility to allow removal by distillation. Typical solvents useful in the practice of the invention are acetone, methyl ethyl ketone, toluene, and N-methyl pyrollidone. Preferably the amount of solvent used in the reaction will be from about 10% to about 50%, more preferably from about 20% to about 40% of the weight.

Polymerizable vinyl compounds may also be used as solvents, followed by free radical polymerization after inversion, thus forming a polyurethane/acrylic hybrid dispersion, as disclosed in previously incorporated US5173526, US4644030, US5488383 and US5569705.

Optional Chain Extenders/Terminators

The polyurethanes are typical prepared by chain extending the NCO-containing prepolymers. The function of a chain extender is to increase the molecular weight of the polyurethanes. Chain extension can take place prior to addition of water in the process, but typically takes place by combining the NCO-containing prepolymer, chain extender, water and other optional components under agitation.

The reactants used to prepare the polyurethanes may contain a chain extender, which is typically a polyol, polyamine or aminoalcohol. When polyol chain extenders are used, urethane linkages form as the hydroxyl groups of the polyol react with isocyanates. When polyamine chain extenders are used, urea linkages are formed as the amine groups react with the isocyanates. Both structural types are included within the meaning of "polyurethanes".

Preferably, the optional chain extender will be polyamine. Suitable polyamines for preparing the at least partially blocked polyamines have an average functionality, i.e., the number of amine nitrogens per molecule, of 2 to 6, preferably 2 to 4 and more preferably 2 to 3. The desired functionalities can be obtained by using mixtures of polyamines containing primary or secondary amino groups. The polyamines are generally aromatic, aliphatic or alicyclic amines and contain between 1 to 30, preferably 2 to 15 and more preferably 2 to 10 carbon atoms. These polyamines may contain additional substituents provided that they are not as reactive with isocyanate groups as the primary or secondary amines. These same polyamines can be partially or wholly blocked polyamines.

Diamine chain extenders useful in making the polyurethanes used in the invention include 1,2-ethylenediamine; 1,6-hexanediamine; 1,2-propanediamine; 4,4'-methylene-bis(3-chloroaniline) (also known as 3,3'-dichloro-4,4'-diaminodiphenylmethane) (MOCA or Mboca); isophorone diamine; dimethylthiotoluenediamine (DMTDA); 4,4'-diaminodiphenylmethane (DDM); 1,3-diaminobenzene; 1,4-diaminobenzene; 3,3'-dimethoxy-4,4'-diamino biphenyl; 3,3'-dimethyl-4,4'-diamino biphenyl; 4,4'-diamino biphenyl; 3,3'-dichloro-4,4'-

diamino biphenyl; hydrazine; and combinations thereof. Polyamines such as diethylene triamine (DETA), triethylene tetraamine (TETA), tetraethylene pentamine and pentaethylene hexamine are also useful.

Suitable polyamine chain extenders can optionally be partially or wholly blocked as disclosed in US4269748 and US4829122. These publications disclose the preparation of aqueous polyurethane dispersions by mixing NCO-containing prepolymers with at least partially blocked, diamine or hydrazine chain extenders in the absence of water and then adding the mixture to water. Upon contact with water the blocking agent is released and the resulting unblocked polyamine reacts with the NCO containing prepolymer to form the polyurethane.

Suitable blocked amines and hydrazines include the reaction products of polyamines with ketones and aldehydes to form ketimines and aldimines, and the reaction of hydrazine with ketones and aldehydes to form ketazines, aldazines, ketone hydrazones and aldehyde hydrazones. The at least partially blocked polyamines contain at most one primary or secondary amino group and at least one blocked primary or secondary amino group which releases a free primary or secondary amino group in the presence of water.

Water may also be employed as a chain extender. In this case, water will be present in a gross excess relative to the free isocyanate groups, and these ratios are not applicable since water functions as both dispersing medium and chain extender.

The reactants used to prepare the polyurethanes of the aqueous dispersions of the invention may also contain a chain terminator. The optional chain terminators control the molecular weight of the polyurethanes, and can be added before, during or after inversion of the pre-polymer.

Suitable chain terminators include amines or alcohols having an average functionality per molecule of 1, i.e., the number of primary or secondary amine nitrogens or alcohol oxygens would average 1 per molecule. The desired functionalities can be obtained by using primary or secondary amino groups. The amines or alcohols are generally aromatic, aliphatic or alicyclic and contain between 1 to 30, preferably 2 to 15 and more preferably 2 to 10 carbon atoms.

Preferred monoalcohols for use as chain terminators include C_1-C_{18} alkyl alcohols such as n-butanol, n-octanol, and n-decanol, n-dodecanol, stearyl alco-

hol and C_2-C_{12} fluorinated alcohols, and more preferably C_1-C_6 alkyl alcohols such as n-propanol, ethanol, and methanol.

Any primary or secondary monoamines reactive with isocyanates may be used as chain terminators. Aliphatic primary or secondary monoamines are preferred. Example of monoamines useful as chain terminators include but are not restricted to butylamine, hexylamine, 2-ethylhexyl amine, dodecyl amine, diisopropanol amine, stearyl amine, dibutyl amine, dinonyl amine, bis(2-ethylhexyl) amine, diethylamine, bis(methoxyethyl)amine, N- methylstearyl amine and N-methyl aniline. A more preferred isocyanate reactive chain terminator is bis(methoxyethyl)amine.

Urethane end groups are formed when alcohol chain terminators are used; urea end groups are formed when amine chain terminators are used. Both structural types are referred to herein as "polyurethanes".

Chain terminators and chain extenders can be used together, either as mixtures or as sequential additions to the NCO-prepolymer.

The amount of chain extender/terminator employed should be approximately equivalent to the free isocyanate groups in the prepolymer, the ratio of active hydrogens in the chain extender to isocyanate groups in the prepolymer preferably being in the range from about 0.6:1 to about 1.3:1, more preferably from about 0.6:1 to about 1.1:1, and still more preferably from about 0.7:1 to about 1.1:1, and even more preferably from about 0.9:1 to about 1.1:1, on an equivalent basis. Any isocyanate groups that are not chain extended/terminated with an amine or alcohol will react with water which, as indicated above, functions as a chain extender.

Neutralization

When the potential cationic or anionic groups of the polyurethane are neutralized, they provide hydrophilicity to the polymer and better enable it to be stably dispersed in water. The neutralization steps may be conducted (1) prior to polyurethane formation by treating the component containing the potentially ionic group(s), or (2) after polyurethane formation, but prior to dispersing the polyurethane, or (3) concurrently with the dispersion preparation. The reaction between the neutralizing agent and the potentially ionic groups may be conducted between about 20°C and about 150°C, but is normally conducted at temperatures

below about 100°C, preferably between about 30°C and about 80°C, and more preferably between about 50°C and about 70°C, with agitation of the reaction mixture.

In order to have a stable dispersion, a sufficient amount of the ionic groups (e.g., neutralized ionizable groups) must be present so that the resulting polyurethane will remain stably dispersed in the aqueous medium. Generally, at least about 70%, preferably at least about 80%, of the acid groups are neutralized to the corresponding carboxylate salt groups. Alternatively, cationic groups in the polyurethane can be quaternary ammonium groups (-NR_3Y, wherein Y is a monovalent anion such as chlorine or hydroxyl).

Suitable neutralizing agents for converting the acid groups to salt groups include tertiary amines, alkali metal cations and ammonia. Examples of these neutralizing agents are disclosed in previously incorporated US4701480, as well as US4501852. Preferred neutralizing agents are the trialkyl-substituted tertiary amines, such as triethyl amine, tripropyl amine, dimethylcyclohexyl amine, and dimethylethyl amine and alkali metal cations such as sodium or potassium. Substituted amines are also useful neutralizing groups such as diethyl ethanol amine or diethanol methyl amine.

Neutralization may take place at any point in the process. Typical procedures include at least some neutralization of the prepolymer, which is then chain extended/terminated in water in the presence of additional neutralizing agent.

The final product is a stable aqueous dispersion of polyurethane particles having a solids content of up to about 60% by weight, preferably from about 15 to about 60% by weight, and more preferably from about 30 to about 40% by weight. However, it is always possible to dilute the dispersions to any minimum solids content desired.

Dispersion Preparation

In accordance with the present invention the term "aqueous polyurethane dispersion" refers to aqueous dispersions of polymers containing urethane groups, as that term is understood by those of ordinary skill in the art. These polymers also preferably incorporate hydrophilic functionality to the extent required to maintain a stable dispersion of the polymer in water (the aqueous vehicle). The compositions of the invention that are based on aqueous dispersions

comprise a continuous phase comprising water, and a dispersed phase comprising polyurethane.

Following formation of the desired polyurethane, preferably in the presence of solvent as discussed above, the pH may be adjusted, if necessary, to insure conversion of ionizable groups to ionic groups (neutralization). For example, if the preferred dimethylolpropionic acid is the ionic or ionizable ingredient used in making the polyurethane, then sufficient aqueous base is added to convert the carboxyl groups to carboxylate anions.

Conversion to the aqueous dispersion is completed by addition of water. If desired, solvent can then be removed partially or substantially completely by distillation under reduced pressure. The total solids level of the aqueous dispersions are preferably in the range of from about 5 wt% to about 70 wt%, and more preferably from about 20 wt% to about 40 wt%, based on the total weight of the dispersion.

If desired, surfactant may be added to the dispersion to improve stability. The surfactant may be anionic, cationic or nonionic. If used, the preferred amount of surfactant is from about 0.1 wt% to about 2 wt%. Examples of preferred surfactants are dodecylbenzenesulfonate or TRITON X (Dow Chemical Co., Midland, MI).

The final product is a stable, aqueous polyurethane dispersion having a solids content of up to about 70% by weight, preferably from about 10% to about 60% by weight, and more preferably from about 20% to about 45% by weight. However, it is always possible to dilute the dispersions to any minimum solids content desired. The solids content of the resulting dispersion may be determined by drying the sample in an oven at 150°C for 2 hours and comparing the weights before and after drying. The particle size is generally below about 1.0 micron, and preferably between about 0.01 to about 0.5 micron. The average particle size should be less than about 0.5 micron, and preferably between about 0.01 to about 0.3 micron. The small particle size enhances the stability of the dispersed particles

Crosslinking

It is within the scope of the present invention to have some crosslinking in the polyurethane.

The means to achieve the crosslinking of the polyurethane generally relies on at least one component of the polyurethane (starting material and/or intermediate) having 3 or more functional reaction sites. Reaction of each of the 3 (or more) reaction sites will produce a crosslinked polyurethane (3-dimensional matrix). When only two reactive sites are available on each reactive components, only linear (albeit possibly high molecular weight) polyurethanes can be produced. Examples of crosslinking techniques include but are not limited to the following:

the isocyanate-reactive moiety has at least 3 reactive groups, for example polyfunctional amines or polyol;

the isocyanate has at least 3 isocyanate groups;

the prepolymer chain has at least 3 reactive sites that can react via reactions other than the isocyanate reaction, for example with amino trialkoxysilanes;

addition of a reactive component with at least 3 reactive sites to the polyurethane prior to its use, for example tri-functional epoxy crosslinkers;

addition of a water-dispersible crosslinker with oxazoline functionality;

synthesis of a polyurethane with carbonyl functionality, followed by addition of a dihydrazide compound;

and any combination of the these crosslinking methods and other crosslinking means known to those of ordinary skill in the relevant art.

Also, it is understood that these crosslinking components may only be a (small) fraction of the total reactive functionality added to the polyurethane. For example, when polyfunctional amines are added, mono- and difunctional amines may also be present for reaction with the isocyanates. The polyfunctional amine may be a minor portion of the amines.

The emulsion/dispersion stability of the crosslinked polyurethane can if needed be improved by added dispersants or emulsifiers.

When crosslinking is desired, the lower limit of crosslinking in the polyurethane is about 1% or greater, preferably about 4% or greater, and more preferably about 10% or greater, as measured by the THF insolubles test.

The amount of crosslinking can be measured by a standard tetrahydrofuran insolubles test. For the purposes of definition herein, the tetrahydrofuran (THF) insolubles of the polyurethane dispersoid is measured by mixing 1 gram of the polyurethane dispersoid with 30 grams of THF in a pre-weighed centrifuge tube. After the solution is centrifuged for 2 hours at 17000 rpm, the top liquid layer is poured out and the non-dissolved gel in the bottom is left. The centrifuge tube with the non-dissolved gel is re-weighed after the tube is put in the oven and dried for 2 hours at 110°C.

% THF insolubles of polyurethane = (weight of tube and non-dissolved gel - weight of tube)/(sample weight * polyurethane solid %)

An alternative way to achieve an effective amount of crosslinking in the polyurethane is to choose a polyurethane that has crosslinkable sites, then crosslink those sites via self-crosslinking and/or added crosslinking agents. Examples of self-crosslinking functionality includes, for example, silyl functionality (self-condensing) available from certain starting materials as indicated above, as well as combinations of reactive functionalities incorporated into the polyurethanes, such as epoxy/hydroxyl, epoxy/acid and isocyanate/hydroxyl. Examples of polyurethanes and complementary crosslinking agents include: (1) a polyurethane with isocyanate reactive sites (such as hydroxyl and/or amine groups) and an isocyanate crosslinking reactant, and 2) a polyurethane with unreacted isocyanate groups and an isocyanate-reactive crosslinking reactant (containing, for example, hydroxyl and/or amine groups). The complementary reactant can be added to the polyurethane, such that crosslinking can be done prior to its incorporation into a formulation.

Further details on crosslinked polyurethanes can be found, for example, in US20050215663A1.

Film-Forming Polyurethanes

For some applications in accordance with the present invention, such as lipsticks/lip gloss, nail polish and hair styling compositions, it is preferred that the polyurethane is film-forming. By "film-forming" is it meant that the polyurethane, after application to a surface, forms a coherent film (continuous phase) containing the active cosmetic ingredient (discontinuous phase) under application conditions.

The film-forming capabilities of a particularly polyurethane under specified applications conditions can be readily determined by a person of ordinary skill in the art without undue experimentation.

Active Cosmetic Ingredients

The cosmetic compositions of the invention comprise, in addition to the aqueous vehicle and polyurethane ionomer, one or more active cosmetics ingredients that provide some cosmetic benefit to the user's body, e.g., to the hair, nails and/or skin. Such materials are in general well-known to those persons of ordinary skill in the relevant cosmetic art and may include, for example, moisturizing agents, antiperspirants, anti-bacterials, sunscreen agents, insect repellents, cleaning agents, hair conditioning agents, hair styling agents, anti-dandruff agents, hair growth promoters, dyes and pigments, anesthetics, lubricants, soaps and perfumes. The cosmetic compositions in accordance with the presentinvention are intended for surface (external) application.

A wide variety of cosmetic agents are useful in the cosmetic compositions of the present invention to the extent that those agents do not interfere with the dispersibility of the polyurethane in the aqueous continuous phase.

The active cosmetic ingredients (and other ingredients of the personal care compositions as described below) can be categorized (including in multiple categories) by the benefit they provide or by their postulated mode of action. However, it is to be understood that the active cosmetic ingredients (and other ingredients) useful herein can in some instances provide more than one benefit or operate via more than one mode of action. Therefore, classifications herein are made for the sake of convenience and are not intended to limit the active to that particular application or applications listed.

Examples of substances that may suitably be included in the cosmetic compositions according to the present invention as active cosmetic ingredients include the following:

(1) perfumes and fragrances, which give rise to an olfactory response in the form of a fragrance, and deodorant perfumes which, in addition to providing a fragrance response, can also reduce body malodor;

(2) skin coolants, such as menthol, menthyl acetate, menthyl pyrrolidone carboxylate, N-ethyl-p-menthane-3-carboxamide and other derivatives of men-

thol, which give rise to a tactile response in the form of a cooling sensation on the skin;

(3) emollients, such as isopropylmyristate, silicone oils, mineral oils and vegetable oils, which give rise to a tactile response in the form of an increase in skin lubricity;

(4) deodorants other than perfumes, whose function is to reduce the level of or eliminate micro flora at the skin surface, especially those responsible for the development of body malodor, including precursors of deodorants;

(5) antiperspirant actives, whose function is to reduce or eliminate the appearance of perspiration at the skin surface;

(6) moisturizing agents, that keep the skin moist by either adding moisture or preventing from evaporating from the skin;

(7) sunscreen active ingredients that protect the skin and hair from UV and other harmful light rays from the sun;

(8) hair treatment agents that condition hair, clean hair, detangle hair, act as styling agents, anti-dandruff agents, hair growth promoters, hair dyes and pigments, hair perfumes, hair relaxers, hair bleaching agents, hair moisturizers, hair oil treatment agents and antifrizzing agents;

(9) beauty aids, such as powders, pigments and colorants; and

(10) medicinal agents.

Further examples of skin benefit agents include abrasives; absorbents; aesthetic components such as opacifying agents and pearlescent aids such as ethylene glycol distearate and TiO_2 coated mica; essential oils; skin sensates; cosmetic and drug astringents such as clove oil, menthol, camphor, eucalyptus oil, eugenol, menthyl lactate and witch hazel distillate; anti-acne agents such as resorcinol, sulfur, salicylic acid, benzoyl peroxide, erythromycin and zinc; anti-caking agents; antimicrobial agents such as iodopropyl butylcarbamate; antioxidants; cosmetic biocides; external analgesics; pH modifiers such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide and sodium carbonate; skin bleaching and lightening agents such as hydroquinone, kojic acid, ascorbic acid, magnesium ascorbyl phosphate and ascorbyl glucosamine; skin soothing and/or healing agents such as panthenol and derivatives like ethyl

panthenol, aloe vera, pantothenic acid and its derivatives, allantoin; bisabolol and dipotassium glycyrrhizinate; retinoids such as retinol palmitate); tocopheryl nicotinate; skin treating agents; vitamins and derivatives thereof; and other similar materials.

Humectants have been described as agents that control the moisture exchange between the product and air, both in the container and on the skin. Humectants have also been described as compounds that prevent drying of skin or that increase the water content of the top layers of skin (e.g., hygroscopic compounds). One potentially preferred humectant is PO3G (in and of itself) as described above.

Suitable moisturizing agents include hydrophobic agents, hydrophilic agents and combinations thereof. Examples of moisturizing agents are allantoin, glycerol, polyglycerylmethacrylate, panthenol, polyols, ceramide, borage oil (linoleic acid), tocopherol (Vitamin E), tocopherol linoleate, dimethicone, hyaluronic acid, sodium peroxylinecarbolic acid (sodium PCA), wheat protein (e.g., laurdimonium hydroxypropyl hydrolyzed wheat protein), hair keratin amino acids, panthenol; primrose oil; GLA 3 and other fish oils that may include, for example, the omega-3 and omega- 6 oils and/or linoleic acid; and flax seed oil, and mixtures thereof. Other moisturizing agents can also be used.

Numerous sunscreen agents are suitable for use in the personal care compositions of the present invention. Examples include, p-aminobenzoic acid, its salts and its derivatives, anthranilates, salicylates, cinnamic acid derivatives, dihydroxy cinnamic acid derivatives, trihydroxy cinnamic acid derivatives, dibenzalacetone, dibenzalacetophenone, naphtholsulfonates, dihydroxynaphtholic acid and its salts, coumarin derivatives, diazoles, quinine salts, quinoline derivatives, hydroxy- and methoxy-substituted benzophenones, uric and vilouric acids, tannic acid and its derivatives, hydroquinone and benzophenones. In accordance with this invention, an effective amount will normally be from about 0.01 to about 10% by weight, preferably from about 0.1 to about 5% by weight, based on the weight of the composition.

Typically, the active ingredient in deodorant-antiperspirant compositions is a basic aluminum compound. Examples of such materials are aluminum chlorhydroxide, basic aluminum bromide, iodide or nitrate, and basic aluminum hydroxy chloride-zirconyl hydroxy oxychloride.

Cleaning agents are typically anionic, cationic, non-ionic or amphoteric surfactants. Typical anionic surfactants are carboxylates, sulfonates, sulfates or phosphates, e.g. fatty acid soaps, salts of lauryl sulfate and salts of lauryl ether sulfate. Examples of cationic surfactants are aliphatic mono, di and polyamines derived from fatty and rosin acids, amine oxides, ethoxylated alkyl amines and imidazolines. Examples of non-ionic surfactants are polyoxyethylene surfactants, alkylphenol ethoxylates, carboxylic acid esters, e.g., mono and diglycerides, polyoxyethylene esters and fatty acid diethanolamine condensates. Amphoteric surfactants are those containing combinations of the anionic and cationic groups described above, particularly those containing both acid carboxyls and basic nitrogen groups. Typical amphoteric surfactants are imidazolines and betaines, e.g., lauric and myristic imidazolines and betaines, and amidopropylbetaines.

A variety of medicinal agents also may be present as active ingredients in the compositions of the invention. Non-limiting examples are anti-acne additives, anti-cellulite agents, antihistamines, anti-inflammatory agents, antimicrobials, spermicides, antiseptics, antifungal agents and antiviral agents, and local anesthetics.

Active Ingredient Incorporation

As indicated previously, the cosmetic compositions of the present invention are generally prepared by adding the active cosmetic ingredients into the aqueous polyurethane dispersion.

For active cosmetic ingredients that are soluble in the aqueous vehicle of the dispersion, these can be added under standard mixing conditions so as to result in a composition that, after mixing (or remixing), has a substantially uniform composition.

For active cosmetic ingredients that are not soluble in the aqueous vehicle of the dispersion, it is preferably that the polyurethane ionomer act as a dispersing/emulsifying agent, the mixing should occur under high shear conditions known to those of ordinary skill in the relevant art. Alternatively, separate dispersing/emulsifying agents can be utilized.

For example, pigmented dispersions can be prepared using any conventional milling process known in the art. Most milling processes use a two-step process involving a first mixing step followed by a second grinding step. The first

step comprises a mixing of all the ingredients, that is, pigment, aqueous dispersion and any optional additives to provide a blended "premix". Typically, any solid ingredients are added last. Mixing is generally done in a stirred mixing vessel, and high-speed dispersers (HSD) are particularly suitable for the mixing step. The second step comprises grinding of the premix to produce a pigmented dispersion. Preferably, grinding occurs by a media milling process, although other known milling techniques can also be used. Grinding can be accomplished by charging a media (such as zirconia) to the mill at a mill disc speed between 2000 rpm and 4000 rpm. The dispersion can be processed using a re-circulation grinding process, and flow rates though the mill are typically 200 to 500 grams/min. The milling may be done using a staged procedure. After completion of milling process, the dispersion is filled into a container, then typically further processed, for example, using conventional filtration procedures known in the art. The dispersions may be processed using ultrafiltration techniques that remove co-solvents and other contaminants, ions or impurities from the dispersion.

Typically, pigment levels (when pigments are used as the active cosmetic ingredient) are in the range of about 0.01 wt% to about 10 wt%, and more preferably from about 1 wt% to about 10 wt%, based on the weight of the cosmetic composition.

It is preferred that the resulting products are storage stable, which can be assessed after oven aging of samples for 1 week at 70°C. To the extent that the resulting products are not storage stable (separation of substantially uniform consistency of components), the consistency of the product should be readily restorable with simple mixing techniques (preferably low energy) such as container shaking.

Solidifying Agents

Solid/semi-sold compositions in accordance with the present invention are those considered non-flowable at ambient temperatures (25°C). Gels are generally included within the semi-solids classification. Examples of solid/semi-sold cosmetic compositions include lipsticks, antiperspirant sticks, stick mascara and eye liner, and the like.

The solids can be prepared by adding a solidifying to the aqueous dispersion of the polyurethane ionomer and cosmetic agent(s).

Solidifying agents include, for example, various waxes, gums and gelling agents.

Cellulosic gums can be used as solidifying agents. For instance, US2003/0198616A1 describes a moisturizing skin gel wherein a water-soluble hydroxyalkylcellulose polymer typically performs a dual function of gelling the composition and forming a moisture barrier to reduce transepidermal water loss. Preferred cellulosic gums include water-soluble hydroxyalkylcellulose polymers such as hydroxymethylcellulose, hydroxyethylcellulose and hydroxypropylcellulose. Other thickening agents which have been used in skin-contacting compounds, include acacia, agar, alginate, carrageenan, gum tragacanth, xanthan gum, collagen, carboxypolymethylene, glyceryl monostearate, polyvinylpyrrolidone and polyacrylamide.

Other Ingredients

Fillers, plasticizers, silica sols, other polymer dispersions and the known leveling agents, wetting agents, antifoaming agents, stabilizers, preservatives and other additives known for the desired end use, may also be incorporated into the dispersions.

Surfactants may be used in the cosmetic compositions of the invention. Typical surfactants are disclosed in US2003/0007939A1.

Although the polyurethane ionomer is preferably dispersible in a continuous aqueous medium with out adding any emulsifier or surfactant, additional emulsifiers may be used in many preferred embodiments of the invention. Most emulsifiers approved for cosmetic use can be used. Operable emulsifiers include nonionic, anionic, cationic, amphoteric or zwitterionic and blends thereof. Suitable emulsifiers are disclosed in US3755560 and US4421769. Examples are polyethylene glycol 20, sorbitan monolaurate (Polysorbate 20), polyethylene glycol 20 stearyl ether (Brij 78, Steareth 20), polyethylene glycol ether of lauryl alcohol (Laureth 23), polysorbate 80 (Tween 80), and lecithin.

Other commonly used ingredients in cosmetic compositions include preservatives, which may be selected from the many that are known in the art and commercially available. Examples include benzyl alcohol, methyl paraben, propyl paraben, DMDM hydantoin, methylchloroisothiaoline, methylisothiazolinone,

imidazolidinyl urea phenoxyethanol, sodium benzoate and benzoic acid. EDTA and salts thereof are often used to further enhance preservation.

Although additives such as those described above may be advantageously included in the compositions without limitation, the total amount of these additives generally ranges up to about 8.0 w%, and preferably up to about 3.0 wt%, based on the weight of the composition.

Well-known pharmacologically acceptable organic co-solvents may also be used in the cosmetic compositions of the present invention, although it is preferred that such compositions are substantially organic co-solvent free.

Product Forms

Cosmetic compositions based on the aqueous polyurethane dispersions are generally in the form of creams, emulsions, foams, gels, lotions, ointments, aerosols etc. The compositions thus may be in a wide variety of product types. These include but are not limited to solutions, lotions, emulsions, creams, gels, sticks, sprays, ointments, pastes, foams, mousses, shampoos, etc. Products employing these compositions include but are not restricted to skin care products, deodorants, anti-perspirants, insect repellants, anesthetics, shampoos, hair conditioners, sun care products, shower gels, soaps, hair styling gels, hair anti-dandruff compositions, hair growth promoter compositions, hair colorant compositions, hair bleaching agent compositions, hair anti-frizzing agent compositions, hair relaxer compositions, shaving product compositions, lubricating gel compositions, skin cleaning compositions, nail polish compositions and skin coloring compositions.

Most often cosmetic products contain an active ingredient incorporated in a delivery vehicle. The desired effect of a cosmetic product is achieved either by the cosmetically active ingredients or by the vehicle itself at the site of application, in most cases on the skin, nails or hair. With the aid of the vehicle, i.e. the vehicle acting as a carrier, the active ingredient is delivered to the application site where the desired effect is to be achieved.

The major types of personal care vehicles most frequently fall into the following categories: (a) solutions; (b) emulsions, both oil-in-water and water-in-oil; and including lotions and creams; (c) suspensions; (d) gels; and (e) solids and semi-solids including stick products. An extensive discussion of personal care

and cosmetic vehicles is found in the previously incorporated Handbook of Cosmetic Science and Technology, Second Edition, edited by M Paye, A. O. Barel and H. I. Maibach, pages 99-123 (2005).

Gels

A "gel" in accordance with the present invention is a colloid in which the disperse phase has combined with the continuous phase to produce a viscous, jelly-like product.

Gels in accordance with the present invention can be aqueous or non-aqueous. The gels will typically comprise, in addition to the aqueous disperson of the polyurethane and cosmetic additive, a gelling agent such as described above. The vehicle of the gels will also typically comprise some solvent (preferably water).

Gels, in particular aqueous gels, are becoming increasingly popular in personal care products. Examples include, but are not restricted to, skin care products, cosmetics, tooth pastes, deodorants, anti-perspirants, insect repellants, anesthetics, shampoos, hair conditioners, sun care products, shower gels, soaps, hair styling gels, hair anti-dandruff compositions, hair growth promoter compositions, hair colorant compositions, hair bleaching agent compositions, hair anti-frizzing agent compositions, hair relaxer compositions, shaving product compositions, lubricating gel compositions, spermicidal gel compositions and skin cleaning compositions.

Emulsions

Emulsions are widely used as cosmetic products. By "emulsion" is meant a stable mixture of two or more immiscible liquids held in suspension by small percentages of substances called emulsifiers, which may be nonionic, anionic, cationic or zwitterionic. In the case of oil-in-water emulsions, the oil phase is the internal or dispersed phase, and the water phase is the external (continuous) or carrier phase.

If emulsions are liquid (flowable at ambient temperature), they are generally referred to as lotions. Creams are emulsions that occur in substantially non-flowable form (at ambient temperature). Generally creams do not flow through orifices under gravity because of their heavier consistency when compared to lotions. The consistency, or viscosity, of emulsions depends on several factors,

including the ratio of internal to external phase, type of oil phase, and presence or absence of thickening agents in the continuous phase.

Two phase emulsion skin care preparations, such as lotions and creams, of the oil-in-water type are well-known in the cosmetic art and are useful in the subject invention. Triphase emulsion compositions, such as the water-in-oil-in-water type as disclosed in US4254105, are also useful in the subject invention. In general, such triphase emulsions contain water, emollients and emulsifiers as essential ingredients. Triple emulsion carrier systems comprising an oil-in-water-in-silicone fluid emulsion composition, as disclosed in US4960764, may also be useful in the subject invention.

Oils useful in emulsions, and also for co-solvents, include hydrocarbon oils and waxes (e.g., petrolatum, mineral oil, micro-crystalline waxes, polyalkenes, paraffins, cerasin, ozokerite, polyethylene, perhydrosqualene, poly alpha olefins, hydrogenated polyisobutenes and combinations thereof) and silicones (e.g., dimethicone copolyol, dimethylpolysiloxane, diethylpolysiloxane, mixed C1-C30 alkyl polysiloxanes, phenyl dimethicone, dimethiconol and combinations thereof). Preferred are non-volatile silicones selected from dimethicone, dimethiconol, mixed C1-C30 alkyl polysiloxane and combinations thereof; fatty acid derivatives, cholesterol, cholesterol derivatives, diglycerides and triglycerides (e.g., castor oil, soy bean oil, derivatized soybean oils such as maleated soy bean oil, safflower oil, cotton seed oil, corn oil, walnut oil, peanut oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil, sesame oil, vegetable oils and vegetable oil derivatives, sunflower seed oil, coconut oil and derivatized coconut oil, cottonseed oil and derivatized cottonseed oil, jojoba oil, cocoa butter and combinations thereof, as well as any of the aforementioned oils that have been partially or fully hydrogenated), acetoglyceride esters (e.g., acetylated monoglycerides), alkyl esters, alkenyl esters (e.g., oleyl myristate, oleyl stearate, oleyl oleate, and combinations thereof), lanolin and its derivatives (e.g., lanolin, lanolin oil, lanolin wax, lanolin alcohols, lanolin fatty acids, isopropyl lanolate, acetylated lanolin, acetylated lanolin alcohols, lanolin alcohol linoleate, lanolin alcohol ricinoleate, hydroxylated lanolin, hydrogenated lanolin and combinations thereof), wax esters (e.g., beeswax and beeswax derivatives, spermaceti, myristyl myristate, stearyl stearate and combinations thereof), sterols and phospholipids, and combinations thereof. Examples of alkyl esters include isopropyl esters of fatty acids and long chain esters of long chain fatty acids, e.g., SEFA (sucrose esters of fatty acids),

pentaerythritol esters, aromatic mono, di or triesters, cetyl ricinoleate, isopropyl palmitate, isopropyl myristate, cetyl ricinoleate and stearyl ricinoleate. Other examples include hexyl laurate, isohexyl laurate, isohexyl palmitate, decyl oleate, isodecyl oleate, hexadecyl stearate, decyl stearate, isopropyl isostearate, diisopropyl adipate, diisohexyl adipate, dihexyldecyl adipate, diisopropyl sebacate, acyl isononanoate lauryl lactate, myristyl lactate, cetyl lactate, and combinations thereof. Still other suitable oils include milk triglycerides (e.g., hydroxylated milk glyceride) and polyol fatty acid polyesters. Also useful are vegetable waxes such as carnauba and candelilla waxes; sterols such as cholesterol, cholesterol fatty acid esters; and phospholipids such as lecithin and derivatives, sphingo lipids, ceramides, glycosphingo lipids, and combinations thereof.

Oil-in-water emulsions are widely used in cosmetic products, preferably as skin care products, skin moisturizers, cosmetics, deodorants, anti-perspirants, insect repellants, anesthetics, medicinal agents, hair conditioners, sun care products, soaps, hair anti-dandruff compositions, hair growth promoter compositions, hair colorant compositions, hair bleaching agent compositions, hair anti-frizzing agent compositions, hair relaxer compositions and shaving product compositions.

Suspensions

Still another aspect of the invention is a personal care composition comprising a suspension. Suspensions consist of solid particles dispersed in a liquid or semi-solid medium. Sedimentation during storage is minimized by reducing particle size and/or by increasing the viscosity of the carrier phase. Typical uses of suspensions are essentially the same as those listed above for oil-in-water emulsions.

(Semi)Solids (Other than Gels)

Solid delivery vehicles are generally cast in an elongated form as sticks. By rubbing the sticks onto the skin a variety of personal care ingredients can be delivered. Examples are lipsticks and antiperspirant/deodorant sticks. There are several ways of achieving solid stick properties, such as mixtures of waxes, pigments and oils; solutions based on aqueous, propylene glycol and/or alcohol mixtures solidified usually by sodium stearate; and matrices consisting of a high-boiling silicone gelled by fatty alcohol (e.g. stearyl alcohol). Preferably, the solidifying agent is selected from the group consisting of a wax and sodium stearate.

Solid stick formulations are most frequently used in lipsticks, antiperspirants/deodorants, skin moisturizers, cosmetics, insect repellants, sun care products, soaps and other skin cleaning compositions, skin sanitizers, shaving product compositions, skin cleaning compositions and anesthetics.

Other Forms

It should be noted that most of the liquid vehicles described above can be in the form of foams, which are dispersions of gas in the liquid phase. The gas globules may be of any size, from colloidal to macroscopic, as in soap bubbles. Typical liquid foams are those used in shaving creams, etc.

Liquid or solid vehicle systems can also be applied as aerosols. By "aerosol" is meant a suspension of liquid or solid particles in a gas, the particles often being in the colloidal size range. Included are fine sprays (perfumes, insecticides, inhalants, anti-perspirants, etc.). Suspensions of various kinds are prepared by placing the components, together with a compressed gas, in a container (bomb). The pressure of the gas causes the mixture to be released as a fine spray (aerosol) when a valve is opened. Examples are perfumes, deodorants, shaving cream, and the like. The propellant gas may be, for example, a hydrocarbon (propane, isobutene), a chlorofluorocarbon, carbon dioxide or nitrous oxide.

Examples

Number-average molecular weights (Mn) were determined by end-group analysis using NMR spectroscopic methods.

Polydispersity (Mw/Mn) was measured by GPC.

Color was measured as APHA values (Platinum-Cobalt System) according to ASTM D-1209.

All percentages, parts, etc., are by weight unless otherwise indicated.

Example 1

This example illustrates preparation of a substantially organic solvent-free polyurethane dispersion from polytrimethylene ether glycol, isophorone diisocyanate and dimethylolpropionic acid ionic reactant, which was chain extended after inversion with a combination of diamine and polyamine.

A 2L reactor was loaded with 201.11 g PO3G (Mn of 2000) and heated to 100°C under vacuum until the contents had less than 500 ppm water. The reactor was cooled to 40°C, and acetone (99 g) and 0.13 g dibutyltin dilaurate catalyst were added. 53.01 g isophorone diisocyanate was added over 1 hr, and rinsed in with 2.6 g dry acetone. The reaction was allowed to continue at 50°C for 2.5 hr, and then the wt% NCO was determined to be below 3.5%. Dimethylol proprionic acid (12.98 g) and triethyl amine (8.82 g) were added, followed by a rinse with dry acetone (3.16 g). The reaction was held at 50°C for 2 hrs, and the wt% NCO was determined to be below 0.6%. The resulting polyurethane solution was inverted under high speed mixing while adding 575 g water immediately followed by ethylene diamine (7.52 g) and triethylene tetraamine (36.6 g). The acetone was distilled off under reduced pressure at 70°C.

The resulting PO3G-based polyurethane dispersion had a viscosity of 13.4 cPs, 30.2 wt% solids, a titrated acid number of 17.6 mg KOH/ g solids, and an average particle size of 37 nm with 95% below 63 nm.

Example 2 - Flowable Lipstick/Lip Gloss Formulation

Polyurethane dispersion	95 g
Pigment	1-2 g
Glycerol	1-3 g

Example 3 – Flowable Lipstick/Lip Gloss Formulation

Polyurethane dispersion	90 to 98 wt%
Bordeaux mica pigment	1 to 5 wt%
1,3-propane diol	1 to 5 wt% (preferably biologically derived)

Example 4 – Flowable Hair Care Formulation

Polyurethane dispersion	5 to 20 wt%
Diethyl ether	25 to 35 wt%
Ethanol	0 to 25 wt%
Deionized water	30 to 60 wt%

What is claimed is:

1. A cosmetic composition comprising:

(i) an aqueous continuous phase having dispersed therein a nano-sized water-dispersible polyurethane and at least one cosmetic additive, or

(ii) a solid or semi-solid continuous phase having dispersed therein an aqueous vehicle, a nano-sized water-dispersible polyurethane and at least one cosmetic additive,

wherein the water-dispersible polyurethane is a polyurethane ionomer comprising a polymeric backbone having ionic and/or ionizable functionality incorporated into, pendant from and/or terminating said polymeric backbone, wherein the polymeric backbone comprises one or more non-ionic segments derived from a reaction product of polytrimethylene ether glycol and a polyisocyanate.

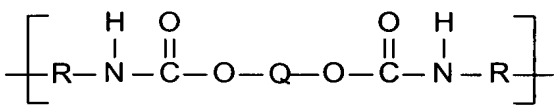
2. The cosmetic composition of claim 1, comprising an aqueous continuous phase having dispersed therein a nano-sized water-dispersible polyurethane and at least one cosmetic additive.

3. The cosmetic composition of claim 2, wherein the polyurethane ionomer has sufficient ionic functionality in order to render the polyurethane dispersible in the aqueous continuous phase.

4. The cosmetic composition of claim 2 or 3, which is an oil-in-water emulsion, a suspension or a gel.

5. The cosmetic composition of claim 1, comprising a solid or semi-solid continuous phase having dispersed therein an aqueous vehicle, a nano-sized water-dispersible polyurethane and at least one cosmetic additive.

6. The cosmetic composition of any of claims 1-5, wherein at least about 20 wt% of the polyurethane comprises one or more non-ionic segments of the general formula (I):



(I)

wherein:

each R individually is the residue of a diisocyanate compound after abstraction of the isocyanate groups; and

Q is the residue of an oligomeric or polymeric diol after abstraction of the hydroxyl groups, wherein the oligomeric or polymeric diol is polytrimethylene ether glycol.

7. The cosmetic composition of any of claims 1-6, wherein the polyurethane is obtained from (a) a polyol component comprising at least about 40 wt% polytrimethylene ether glycol, based on the weight of the polyol component; (b) a polyisocyanate component comprising a diisocyanate; and (c) a hydrophilic reactant comprising a compound selected from the group consisting of (i) mono or diisocyanate containing an ionic and/or ionizable group, and (ii) an isocyanate reactive ingredient containing an ionic and/or ionizable group.

8. The cosmetic composition of claim 7, wherein the polyol component of the polyurethane comprises at least about 90 wt% polytrimethylene ether glycol.

9. The cosmetic composition of any of claims 1-8, wherein the polytrimethylene ether glycol comprises trimethylene ether units from 1,3-propane diol having the following characteristics:

(1) an ultraviolet absorption at 220 nm of less than about 0.200, and at 250 nm of less than about 0.075, and at 275 nm of less than about 0.075; and/or

(2) a composition having L*a*b* "b*" color value of less than about 0.15 (ASTM D6290), and an absorbance at 270 nm of less than about 0.075; and/or

(3) a peroxide composition of less than about 10 ppm; and/or

(4) a concentration of total organic impurities (organic compounds other than 1,3-propanediol) of less than about 400 ppm, as measured by gas chromatography.

10. The cosmetic composition of any of claims 1-9, wherein the polytrimethylene ether glycol comprises trimethylene ether units from biologically-derived 1,3-propane diol.

11. A process for preparing a cosmetic composition comprising the steps of:

mixing an active cosmetic ingredient into an aqueous dispersion of a nanoparticle-sized polyurethane comprising an aqueous phase and a water-

dispersible polyurethane ionomer, wherein the water-dispersible polyurethane ionomer comprises a polymeric backbone having ionic and/or ionizable functionality incorporated into, pendant from and/or terminating said polymeric backbone, wherein the polymeric backbone comprises one or more non-ionic segments derived from a reaction product of polytrimethylene ether glycol and a polyisocyanate, and wherein said polyurethane ionomer has sufficient ionic functionality in order to render the polyurethane dispersible in the aqueous continuous phase,

wherein, if the cosmetic composition is a solid or semi-solid, the process comprises the further step of:

adding a solidifying agent to the aqueous dispersion to result in a solid or semi-sold product.

12. The process of claim 11, wherein the cosmetic composition is as set forth in any of claims 1-9.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/020703

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61K8/87 A61Q1/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61K A61Q

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 2008/013924 A (DU PONT DE NEMOURS AND COMPANY ET AL.) 31 January 2008 (2008-01-31) cited in the application page 28, lines 6-10; claims page 30, line 12 page 28, lines 11-14	1-12
Y	US 5 972 354 A (V. DE LA POTERIE ET AL) 26 October 1999 (1999-10-26) cited in the application claims	1,11
Y	US 2004/225107 A1 (H. SUNKARA ET AL) 11 November 2004 (2004-11-11) paragraph [0003]; claims	1,11

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 March 2008	11/03/2008

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Boeker, Ruth

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/020703

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004/141942 A1 (I. ROLLAT ET AL) 22 July 2004 (2004-07-22) cited in the application claims	1

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/020703

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2008013924 A	31-01-2008	US 2008039582 A1	14-02-2008
US 5972354 A	26-10-1999	AT 217184 T	15-05-2002
		BR 9604455 A	23-06-1998
		CA 2188691 A1	28-04-1997
		DE 69621104 D1	13-06-2002
		DE 69621104 T2	05-09-2002
		EP 0775483 A1	28-05-1997
		ES 2176415 T3	01-12-2002
		FR 2740330 A1	30-04-1997
		JP 3570829 B2	29-09-2004
		JP 9169615 A	30-06-1997
		JP 2000136117 A	16-05-2000
US 2004225107 A1	11-11-2004	BR PI0410508 A	20-06-2006
		CA 2522771 A1	25-11-2004
		EP 1620489 A2	01-02-2006
		JP 2007501324 T	25-01-2007
		KR 20060006959 A	20-01-2006
		MX PA05011829 A	26-01-2006
		US 2005020805 A1	27-01-2005
		WO 2004101469 A2	25-11-2004
US 2004141942 A1	22-07-2004	AU 8238701 A	13-02-2002
		EP 1307177 A2	07-05-2003
		WO 0209655 A2	07-02-2002
		JP 2004515466 T	27-05-2004
		US 6613314 B1	02-09-2003

Form PCT/ISA/210 (patent family annex) (April 2005)

PTO/SB/06 (09-11)
Approved for use through 1/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 18/066,105	Filing Date 12/14/2022	☐ To be Mailed

ENTITY: ☐ LARGE ☑ SMALL ☐ MICRO

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA		RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A		N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A		N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*		x $50 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $240 =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).				
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))					
* If the difference in column 1 is less than zero, enter "0" in column 2.				TOTAL	

APPLICATION AS AMENDED - PART II

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT	02/19/2025	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 53	Minus	** 53	= 0		x $80 =	0
	Independent (37 CFR 1.16(h))	* 2	Minus	*** 2	= 0		x $240 =	0
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	0

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.	SLIE
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/KATARA D SINGLETARY/
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".	
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.	

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC PAYMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
18/066,105	**02/19/2025 01:10:43 PM Z ET**	**GRAN-1012-U-D**

Title of Invention

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	1563	FILED BY	Carla Curado
PATENT CENTER #	69243882	AUTHORIZED BY	Lindsay Adams
CUSTOMER #	20311	FILING DATE	12/14/2022
CORRESPONDENCE ADDRESS	-	FIRST NAMED INVENTOR	Anna K. CROOM

Payment Information

PAYMENT METHOD	PAYMENT TRANSACTION ID	PAYMENT AUTHORIZED BY
CARD / 1054	**E20252ID11226666**	**Carla Curado**

FEE CODE	DESCRIPTION	ITEM PRICE($)	QUANTITY	ITEM TOTAL($)
2202	EACH CLAIM IN EXCESS OF 20	80.00	30	2400.00
			TOTAL AMOUNT:	**$2,400.00**

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage

submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
18/066,105	**02/19/2025 01:10:43 PM Z ET**	**GRAN-1012-U-D**

Title of Invention

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	1563	FILED BY	Carla Curado
PATENT CENTER #	69243882	FILING DATE	12/14/2022
CUSTOMER #	20311	FIRST NAMED INVENTOR	Anna K. CROOM
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Lindsay Adams

Documents

TOTAL DOCUMENTS: 1

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
GRAN1012UD_ResponseRR.pdf	11	Response to Election / Restriction Filed	99 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
GRAN1012UD_ResponseRR.pdf	C1E3FF87B16AE6DF7F496883A9216CD57EE88C9F1D11F270F920FA0D05D1BE342991A0BC5BD8DB44A9FC7586F92F6E9A093E85B5E0C973782CA4261A12E75D5C

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

Examiner: Brian M. GULLEDGE Art Unit: 1699

Re: Application of: Anna K. CROOM, et al.

Serial No.: 18/066,105

Filed: 12/14/2022

For: **BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE**

Confirmation No.: 1563

RESPONSE TO RESTRICTION REQUIREMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

February 19, 2025

Sir:

This is in response to the Restriction Requirement issued December 19, 2024. Please consider the following amendments and remarks for the above-identified patent application.

Amendments to the Claims begin on page **2** of this paper.

Remarks begin on page **8** of this paper.

CERTIFICATE OF ELECTRONIC TRANSMISSION
I hereby certify that this document is being electronically transmitted to the Commissioner for Patents via EFS-Web on February 19, 2025.

LUCAS & MERCANTI, LLP

BY: /Carla Curado /
Carla Curado

CLAIM AMENDMENTS:

This listing of claims will replace all prior versions and listings of claims in the application:

1. (Currently Amended) A process ~~method~~ of preparing a non-aqueous gel composition, comprising:

a) micronizing a cross-linked polyurethane elastomer rubber composition, comprising a cross-linked polyurethane elastomer rubber and a urethanation catalyst in the presence of a cosmetic emollient wherein the cosmetic emollient forms a solvent matrix substantially surrounding the cross-linked polyurethane elastomer rubber; and optionally,

b) combining the mixture resulting from step a) with a secondary solvent whereby a non-aqueous gel composition is formed.

2. (Original) The process of claim 1, wherein the secondary solvent is the secondary solvent is selected from the group consisting of triheptanoin; undecane; tridecane; or wherein the secondary solvents are naturally derived alkanes or naturally derived esters.

3. (Original) The process of claim 1, wherein the amount of the micronized cross-linked polyurethane elastomer rubber composition in the non-aqueous gel composition is from about 30 to about 5 weight %.

4. (Original) The process of claim 1, wherein the amount of the cosmetic emollient in the non-aqueous gel composition is from about 70 to about 95 weight %.

5. (Original) The process of claim 1, further comprising combining the non-aqueous gel composition with an active composition, optionally selected from the group consisting of selected from vitamins, sunscreens, plant extracts, fragrances and mixtures thereof.

6. (Original) The process of claim 1, further comprising combining the non-aqueous gel composition with a member of the group consisting of fragrances, colorants, preservatives, active compositions, and mixtures thereof.

7. (Original) The process of claim 1, wherein the micronized cross-linked polyurethane elastomer rubber composition has a cross-sectional diameter of from about 1 to about 61 microns.

8. (Original) The process of claim 1, wherein non-aqueous gel composition has a viscosity ranging from about 15,000 cP to about 1,000,000 cP.

9. (Original) The process of claim 1, wherein the cross-linked polyurethane elastomer rubber composition has a hardness force greater than 200 g, as measured by a texture analyzer prior to any milling or dilution and the cross-linked polyurethane elastomer rubber composition has a resilience greater than or equal to 70%.

10. (Original) The process of claim 1, wherein the cross-linked polyurethane rubber composition is formed with a prepolymer having at least two free hydroxyl groups.

11. (Original) The process of claim 1, wherein the solvent matrix comprises a second cosmetic emollient.

12. (Original) The process of claim 10, wherein the polyurethane elastomer rubber is formed with from about 5 to about 25 weight percent of a prepolymer having at least two free hydroxyl groups.

13. (Original) The process of claim 1, wherein the polyurethane elastomer rubber composition is formed with from about 1 to about 20 weight percent of an isocyanate functionalized molecule and a prepolymer having OH-groups.

14. (Currently Amended) The process of claim 10, wherein the prepolymer is a <u>dimer acid/diol</u> ~~polyester~~ reaction product of a diol and a dimer acid.

15. (Original) The process of claim 1, wherein the polyurethane elastomer rubber composition is formed with a polyisocyanate, optionally containing from about 15 to about 38 weight% NCO.

16. (Original) The process of claim 15, wherein the overall molar ratio between the NCO in the polyisocyanate and the OH groups in the prepolymer is from 2:1 to 1:2.

17. (Original) The process of claim 1, wherein the amount of urethanation catalyst in the cross-linked polyurethane elastomer rubber composition is from about 0.1 to about 2.5 weight%.

18. (Original) The process of claim 1, wherein the urethanation catalyst is a bismuth, zinc, or amine catalyst.

19. (Original) The process of claim 1, wherein the cross-linked polyurethane elastomer rubber composition includes an amount of a finisher containing an alcohol or an amine sufficient to quench unreacted isocyanate groups.

20. (Original) The process of claim 1, wherein the cross-linked polyurethane elastomer rubber composition is formed with a bio-based and biodegradable prepolymer.

21. (Original) The process of claim 15, wherein the prepolymer, the polyisocyanate, and the cosmetic emollient are bio-based and biodegradable.

22. (Original) The process of claim 1, wherein the cross-linked polyurethane elastomer rubber composition is comprised of greater than about 85% renewable, bio-based feedstocks.

23. (Original) The process of claim 21, wherein the bio-based and biodegradable polyisocyanate is 1,5-pentamethylene diisocyanate trimer.

24. (New) The process of claim 14, wherein the dimer acid/diol is a polyester reaction product of a diol and a dimer acid.

25. (New) The process of claim 14, wherein the prepolymer is a cross-linked prepolymer.

26. (New) The process of claim 24, wherein the polyester reaction product is a branched C_{36} dicarboxylic acid/diol copolymer.

27. (New) The process of claim 26, wherein the branched C_{36} dicarboxylic acid/diol copolymer is dilinoleic acid/propanediol copolymer or dilinoleic acid/butanediol.

28. (New) A cross-linked elastomer comprising a reaction product of a polyester and a multi-functional crosslinker.

29. (New) The cross-linked elastomer of claim 28, wherein the multi-functional crosslinker is polyisocyanate.

30. (New) The cross-linked elastomer of claim 28, wherein the polyester is castor oil.

31. (New) The cross-linked elastomer of claim 28, wherein the polyester is an esterified dilinoleic acid.

32. (New) The cross-linked elastomer of claim 28, wherein the polyester is a branched C_{36} dicarboxylic acid/diol copolymer.

33. (New) The cross-linked elastomer of claim 28, wherein the diol is propanediol or butanediol.

34. (New) The cross-linked elastomer of claim 28, where in the polyester is greater than 60% by weight of the total weight of the cross-linked elastomer.

35. (New) The cross-linked elastomer of claim 28, where in the polyester is greater than 75% by weight of the total weight of the cross-linked elastomer

36. (New) A cross-linked elastomer comprising the reaction product of a polyol and a multi-functional crosslinker.

37. (New) The cross-linked elastomer of claim 36, wherein the multi-functional crosslinker is polyisocyanate.

38. (New) The cross-linked elastomer of claim 36, wherein the polyol is castor oil.

39. (New) The cross-linked elastomer of claim 36, wherein the polyol is a dimer acid/diol.

40. (New) The cross-linked elastomer of claim 38, wherein the dimer acid/ diol is a branched C_{36} dicarboxylic acid/diol copolymer.

41. (New) The cross-linked elastomer of claim 36, wherein the diol is propanediol or butanediol.

42. (New) The cross-linked elastomer of claim 40, wherein the branched C_{36} dicarboxylic acid/diol copolymer is dilinoleic acid/propanediol copolymer, or dilinoleic acid/butanediol copolymer.

43. (New) The cross-linked elastomer of claim 36, wherein the polyol is a diol or a polyol-functionalized polyester having an effective molecular weight of 280 to 3000 g/mol.

44. (New) The cross-linked elastomer of claim 36, wherein the polyol includes glycerol or polyglycerol.

45. (New) The process of claim 1, wherein the non-aqueous gel composition is silicone-free.

46. (New) The cross-linked elastomer of claim 28, wherein the cross-linked elastomer is silicone-free.

47. (New) The cross-linked elastomer of claims 36, wherein the cross-linked elastomer is silicone-free.

48. (New) A cosmetic and personal care composition comprising the non-aqueous gel composition of claim 1.

49. (New) The cosmetic and personal care composition of claim 48, further comprising a water phase and an oil phase.

50. (New) A cosmetic and personal care composition comprising the cross-linked elastomer of claim 28 and a carrier fluid.

51. (New) The cosmetic and personal care composition of claim 45, further comprising a water phase and an oil phase.

52. (New) A cosmetic and personal care composition comprising the cross-linked elastomer of claim 36 and a carrier fluid.

53. (New) The cosmetic and personal care composition of claim 52, further comprising a water phase and an oil phase.

REMARKS

CLAIMS STATUS AND AMENDMENTS

Claims 1-23 were previously pending. Claim 1 and 14 are amended herewith while claims 24-53 are newly presented herein.

Claim 1 has been amended to correct an obvious error. Applicant has replaced "method" with "process".

Claim 14 has been amended to recite that the prepolymer of claim 10 is a "dimer acid/diol" to more generically describe the polyester reaction product. Support for a "dimer acid/diol" is found in the specification, as filed, in the listing at page 10, line 10. Applicant points out that the prepolymer elected below, dilinoleic acid/propanediol copolymer ("DAPD"), is a representative example of a "dimer acid/diol".

New claims 24-27 further limit the subject matter of claim 14. Claim 24 recites that the dimer acid/diol of claim 14 is a polyester reaction product of a diol and a dimer acid. Support is found in original claim 14.

Claim 25 recites that the prepolymer is a cross-linked prepolymer. Support is found at page 3, line 25.

Claim 26 recites a sub-genus for the polyester reaction product of claim 24. Examples of the polyester reaction products are dilinoleic acid/propane diol copolymer, as elected below, and dilinoleic acid/dilinoleic diol copolymer. One skilled in the art will immediately recognize that both copolymers are "branched C_{36} dicarboxylic acid/diol copolymers" as recited in claim 26. This is because the copolymers are copolymers of dilinoleic acid (i.e., a branched C_{36} dicarboxylic acid, or a dimer of a C_{18} fatty acid) and a diol being either propanediol or dilinoleic diol. Thus, new claim 26 has support in the specification, as filed.

Claim 27 that the branched C_{36} dicarboxylic acid/diol copolymer is dilinoleic acid/propanediol copolymer ("DAPD"), as elected below, or dilinoleic acid/butanediol copolymer ("DABD"). One skilled in the art will immediately recognize that both copolymers are a branched C_{36} dicarboxylic acid.

Claims 28-34 presents claims encompassing another embodiment of the cross-linked elastomer used in the process of the present invention. Claim 28 recites that the cross-linked

elastomer is a reaction product of a polyester and a multi-functional crosslinker. Support is found in the specification, as filed, at page 4, lines 4-6.

Support for the polyisocyanate of claim 29 is found, inter alia, at page 6, line 4, page 8, line 16, among others.

Support for castor oil in claim 30 is found, inter alia, at the paragraph at page 11, between lines 1 and 10, as well as in example 11.

Support for the esterified dilinoleic acid in claim 31 is found in examples 1-5, which shows the use of dilinoleic acid/propanediol copolymer ("DAPD"). One skilled in the art will immediately recognize that DAPD is an esterified dilinoleic acid.

Support for a branched C_{36} dicarboxylic acid/diol copolymer in claim 32 is supported by dilinoleic acid/propanediol copolymer ("DAPD"), as elected below, or dilinoleic acid/butanediol copolymer ("DABD") as originally described claim 27. One skilled in the art will immediately recognize that both copolymers, which are polyesters, are a branched C_{36} dicarboxylic acid.

Support for the propanediol or butanediol in claim 33 is found in the disclosure of dilinoleic acid/propanediol copolymer ("DAPD"), as elected below, or dilinoleic acid/butanediol copolymer ("DABD") as originally described claim 27.

Support is for the polyester being greater than 60% by weight of the total weight of the cross-linked elastomer in claim 34, and greater than 75% in claim 35, is found in tables 1 and 2.

Claims 36 differs from 28-in that the polyester of claim 28 being replaced with a polyol as found in in 36. Support for an elastomer made from a polyol is found, inter alia, at page 5, lines 24-25, page 11, lines. 8-10, page 13, lines 3-5, and examples 1-5.

Support for dependent claims 37-42 is the same as dependent claims 29-33 as noted above.

Support for claims 43 and 44 is found at pages 10 and 11 of the specification, as filed.

Support for claims 45-47 is found at page 4, lines 10-17.

Support for a cosmetic and personal care composition of claim 48 is found, inter alia, in examples 14 and 20.

Support for the cosmetic and personal care composition of claim 49 including a water phase and an oil phase is found, inter alia, in example 16.

Support for the cosmetic and personal care composition of claim 50 including a carrier fluid is found, inter alia, at page 8, lines 9-13.

Support for claim 51 is the same as claim 49.

Support for claim 52 is the same as claim 50.

Support for claim 52 is the same as claim 49.

No new matter is being added. Entry of the amendments is respectfully requested.

SPECIES ELECTION

Applicants elect, without traverse, the following species: 1,5-pentamethylene diisocyanate trimer as the polyisocyanate; and dilinoleic acid/propanediol copolymer ("DAPD") as the prepolymer.

The elected specie read on claims 1, 3, 7, 9, 10, 12, 13, 14, 15, 16, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 31, 32, 33, 34, 35, 36, 37, 39, 40, 41, 42, and 43.

Applicant further submits that a search of the new claims noted above will not provide an undue burden on the Examiner. This is because prior art uncovered for claim 1 due to the election of species is also relevant to the new claims noted above.

Consideration and search of the above noted claim is respectfully requested.

REJOINDER

Applicant reserves the right to request rejoinder of all appropriate claims removed by the Examiner.

FEES

This response is filed within a shortened period of reply. Accordingly, no further fees are believed to be due. If, on the other hand, it is determined that any fees are due or any overpayment has been made, the Commissioner is hereby authorized to debit or credit such sum to Deposit Account No. 02-2275.

Pursuant to 37 C.F.R. § 1.136(a)(3), please treat this and any concurrent or future reply in this application that requires a petition for an extension of time for its timely submission as incorporating a petition for extension of time for the appropriate length of time. The fee associated therewith is to be charged to Deposit Account No. 02-2275.

CONCLUSION

In view of the actions taken and arguments presented, it is respectfully submitted that each of the matters raised by the Examiner has been addressed.

An early and favorable action on the merits is earnestly solicited.

Respectfully submitted,

LUCAS & MERCANTI, LLP

By: /Lindsay S. Adams/
Lindsay S. Adams
Registration No. 36,425

LUCAS & MERCANTI, LLP
30 Broad Street
New York, NY 10004
Phone: 212-661-8000

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
18/066,105	12/14/2022	Anna K. CROOM	GRAN-1012-U-D	1563

20311 7590 02/28/2025

LUCAS & MERCANTI, LLP
30 BROAD STREET
21st FLOOR
NEW YORK, NY 10004

EXAMINER	
GULLEDGE, BRIAN M	

ART UNIT	PAPER NUMBER
1699	

NOTIFICATION DATE	DELIVERY MODE
02/28/2025	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

info@lmiplaw.com

Office Action Summary	Application No. 18/066,105	Applicant(s) CROOM et al.	
	Examiner Brian Gulledge	Art Unit 1699	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 2 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☑ Responsive to communication(s) filed on 19 February 2025.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL.** 2b) ☑ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5) ☑ Claim(s) 1-53 is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6) ☐ Claim(s) _____ is/are allowed.

7) ☐ Claim(s) _____ is/are rejected.

8) ☐ Claim(s) _____ is/are objected to.

9) ☑ Claim(s) 1-53 are subject to restriction and/or election requirement

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to **PPHfeedback@uspto.gov.**

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☐ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date _____.

4) ☐ Other: _____.

DETAILED ACTION

Response to Election of Species

Applicant's election without traverse of the species for the cross-linked polyurethane elastomer rubber in the reply filed on 19 February 2025 is acknowledged. The Applicant has added additional claims, and in response to these newly added claims, the additional restriction requirement is being presented.

Election/Restriction

Restriction to one of the following inventions is required under 35 U.S.C. 121:

I. Claims 1-27 and 45, drawn to processes for preparing a non-aqueous gel composition, classified in A61Q 2800/54.

II. Claims 28-44 and 46-47, drawn to cross-linked polyurethane elastomer rubber, classified in A61Q 17/04.

III. Claims 48-53, drawn to cosmetic and personal care compositions, classified in A61K 8/042.

The inventions are independent or distinct, each from the other because:

Inventions (I and II) and (I and III) are unrelated. Inventions are unrelated if it can be shown that they are not disclosed as capable of use together and they have different designs, modes of operation, and effects (MPEP § 802.01 and § 806.06). In the instant case, the different inventions the method neither uses nor prepares the inventions of the other two Groups.

Inventions II and III are directed to related products. The related inventions are distinct if: (1) the inventions as claimed are either not capable of use together or can have a materially

different design, mode of operation, function, or effect; (2) the inventions do not overlap in scope, i.e., are mutually exclusive; and (3) the inventions as claimed are not obvious variants. See MPEP § 806.05(j). In the instant case, the inventions as claimed have materially different designs. Furthermore, the inventions as claimed do not encompass overlapping subject matter and there is nothing of record to show them to be obvious variants.

Restriction for examination purposes as indicated is proper because all the inventions listed in this action are independent or distinct for the reasons given above and there would be a serious search and/or examination burden if restriction were not required because one or more of the following reasons apply:

(a) the inventions have acquired a separate status in the art in view of their different classification;

(b) the inventions have acquired a separate status in the art due to their recognized divergent subject matter;

(c) the inventions require a different field of search (for example, searching different classes/subclasses or electronic resources, or employing different search queries).

Applicant is advised that the reply to this requirement to be complete must include (i) an election of an invention to be examined even though the requirement may be traversed (37 CFR 1.143) **and (ii) identification of the claims encompassing the elected invention**.

The election of an invention may be made with or without traverse. To reserve a right to petition, the election must be made with traverse. If the reply does not distinctly and specifically point out supposed errors in the restriction requirement, the election shall be treated as an election without traverse. Traversal must be presented at the time of election in order to be considered timely. Failure to timely traverse the requirement will result in the loss of right to petition under

37 CFR 1.144. If claims are added after the election, applicant must indicate which of these claims are readable upon the elected invention.

Should applicant traverse on the ground that the inventions are not patentably distinct, applicant should submit evidence or identify such evidence now of record showing the inventions to be obvious variants or clearly admit on the record that this is the case. In either instance, if the examiner finds one of the inventions unpatentable over the prior art, the evidence or admission may be used in a rejection under 35 U.S.C. 103 or pre-AIA 35 U.S.C. 103(a) of the other invention.

Inventorship

Applicant is reminded that upon the cancellation of claims to a non-elected invention, the inventorship must be corrected in compliance with 37 CFR 1.48(a) if one or more of the currently named inventors is no longer an inventor of at least one claim remaining in the application. A request to correct inventorship under 37 CFR 1.48(a) must be accompanied by an application data sheet in accordance with 37 CFR 1.76 that identifies each inventor by his or her legal name and by the processing fee required under 37 CFR 1.17(i).

Rejoinder

The examiner has required restriction between product or apparatus claims and process claims. Where applicant elects claims directed to the product/apparatus, and all product/apparatus claims are subsequently found allowable, withdrawn process claims that include all the limitations of the allowable product/apparatus claims should be considered for rejoinder. All claims directed to a nonelected process invention must include all the limitations of an allowable product/apparatus claim for that process invention to be rejoined.

In the event of rejoinder, the requirement for restriction between the product/apparatus claims and the rejoined process claims will be withdrawn, and the rejoined process claims will be fully examined for patentability in accordance with 37 CFR 1.104. Thus, to be allowable, the rejoined claims must meet all criteria for patentability including the requirements of 35 U.S.C. 101, 102, 103 and 112. Until all claims to the elected product/apparatus are found allowable, an otherwise proper restriction requirement between product/apparatus claims and process claims may be maintained. Withdrawn process claims that are not commensurate in scope with an allowable product/apparatus claim will not be rejoined. See MPEP § 821.04. Additionally, in order for rejoinder to occur, applicant is advised that the process claims should be amended during prosecution to require the limitations of the product/apparatus claims. **Failure to do so may result in no rejoinder.** Further, note that the prohibition against double patenting rejections of 35 U.S.C. 121 does not apply where the restriction requirement is withdrawn by the examiner before the patent issues. See MPEP § 804.01.

Conclusion

A telephone call was not made to request an oral election to the above restriction requirement because the Examiner considers the requirement complex.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Brian Gulledge whose telephone number is (571) 270-5756. The examiner can normally be reached Monday - Friday 7am - 4pm.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is

encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Fereydoun Sajjadi can be reached on (571) 272-3311. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of published or unpublished applications may be obtained from Patent Center. Unpublished application information in Patent Center is available to registered users. To file and manage patent submissions in Patent Center, visit: https://patentcenter.uspto.gov. Visit https://www.uspto.gov/patents/apply/patent-center for more information about Patent Center and https://www.uspto.gov/patents/docx for information about filing in DOCX format. For additional questions, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Brian Gulledge/
Primary Examiner, Art Unit 1699

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
18/066,105	**03/14/2025 01:33:04 PM Z ET**	**GRAN-1012-U-D**

Title of Invention

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	1563	FILED BY	Carla Curado
PATENT CENTER #	69584125	FILING DATE	12/14/2022
CUSTOMER #	20311	FIRST NAMED INVENTOR	Anna K. CROOM
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Michael Mercanti

Documents

TOTAL DOCUMENTS: 1

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
ResponseRR_GRAN1012UD .pdf	2	Response to Election / Restriction Filed	89 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
ResponseRR_GRAN1012UD.pdf	5F82447F0E302F8084C49D54D23AA9106E12ECA3F1115277D E8926C2769275DC0899583CCD9B1E9BD9C9B0DC049DE61FA 145727853169D8A02390B93EC45694D

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

Examiner: Brian M. GULLEDGE Art Unit: 1699

Re: Application of: Anna K. CROOM, et al.

Serial No.: 18/066,105

Filed: 12/14/2022

For: **BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE**

Confirmation No.: 1563

RESPONSE TO RESTRICTION REQUIREMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

March 14, 2025

Sir:

This is in response to the Restriction Requirement dated February 28, 2025.

A. RESTRICTION REQUIREMENT

In response to the Restriction Requirement, Applicants select, without traverse, Group II, claims 28-44 and 46-47, drawn to cross-linked polyurethane elastomer rubber.

B. REJOINDER

Applicants reserve the right to request rejoinder of all appropriate claims removed by the Examiner.

C. FEES

This response is filed within a shortened period of reply. No further fee is believed to be due. If, on the other hand, it is determined that any fees are due or any overpayment has been made, the Assistant Commissioner is hereby authorized to debit or credit such sum to Deposit Account No. 02-2275.

Pursuant to 37 C.F.R. § 1.136(a)(3), please treat this and any concurrent or future reply in this application that requires a petition for an extension of time for its timely submission as incorporating a petition for extension of time for the appropriate length of time. The fee associated therewith is to be charged to Deposit Account No. 02-2275.

An early and favorable action on the merits is earnestly solicited.

Respectfully submitted,

LUCAS & MERCANTI, LLP

By: /Michael N. Mercanti/
Michael N. Mercanti
Registration No. 33,966

LUCAS & MERCANTI, LLP
30 Broad Street
21st Floor
New York, NY 10004
Phone: 212-661-8000 ext. 120

CERTIFICATE OF ELECTRONIC FILING
I hereby certify that this document is being electronically transmitted to the Commissioner for Patents via EFS-Web on March 14, 2025.

LUCAS & MERCANTI, LLP

BY: /Carla Curado/
Carla Curado

PTO/SB/06 (09-11)
Approved for use through 1/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 18/066,105	Filing Date 12/14/2022	☐ To be Mailed

ENTITY: ☐ LARGE ☑ SMALL ☐ MICRO

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA		RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A		N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A		N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*		x $50 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $240 =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).				
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))					
* If the difference in column 1 is less than zero, enter "0" in column 2.				TOTAL	

APPLICATION AS AMENDED - PART II

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT	03/14/2025	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 53	Minus	** 53	= 0		x $80 =	0
	Independent (37 CFR 1.16(h))	* 3	Minus	*** 3	= 0		x $240 =	0
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	0

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.	CRU Paralegal
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/RENEE M PRESTON/
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".	
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.	

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC PAYMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
18/066,105	**04/07/2025 12:00:04 PM Z ET**	**GRAN-1012-U-D**

Title of Invention

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	1563	FILED BY	Carla Curado
PATENT CENTER #	69891624	AUTHORIZED BY	Michael Mercanti
CUSTOMER #	20311	FILING DATE	12/14/2022
CORRESPONDENCE ADDRESS	-	FIRST NAMED INVENTOR	Anna K. CROOM

Payment Information

PAYMENT METHOD	PAYMENT TRANSACTION ID	PAYMENT AUTHORIZED BY
CARD / 1054	**E202547C00596067**	**Carla Curado**

FEE CODE	DESCRIPTION	ITEM PRICE($)	QUANTITY	ITEM TOTAL($)
2832	FILING AN INFORMATION DISCLOSURE STATEMENT THAT CAUSES THE CUMULATIVE NUMBER OF APPLICANT-PROVIDED ITEMS OF INFORMATION TO EXCEED 50 BUT NOT EXCEED 100	200.00	1	200.00
			TOTAL AMOUNT:	**$200.00**

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement

Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/08 (01-25)
Approved for use through 11/30/2027. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM, et al.
Art Unit	1699
Examiner Name	Brian M. GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

U.S. PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Inventor of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
	1	3627719	A	1971-12-14	SELLET	

If you wish to add additional U.S. Patent citation information, please click the Add button. Add

U.S. PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Inventor or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
	1					

If you wish to add additional U.S. Published Application citation information, please click the Add button Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							☐

If you wish to add additional Foreign Patent Document citation information, please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT		
	Application Number	18066105
	Filing Date	2022-12-14
	First Named Inventor	Anna K. CROOM, et al.
	Art Unit	1699
	Examiner Name	Brian M. GULLEDGE
	Attorney Docket Number	GRAN-1012-U-D

	1	Hamid YEGANEH, et al., "Preparation and properties of novel biodegradable polyurethane networks based on castor oil and poly(ethylene glycol)" Polymer Degradation and Stability, vol. 92, pp. 480-489, 2007.	☐

If you wish to add additional non-patent literature document citation information, please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered and whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM, et al.
Art Unit	1699
Examiner Name	Brian M. GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

TIMING STATEMENT

Please see 37 CFR 1.97(e) to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached timing statement under 37 CFR 1.97(e).

☒ A timing statement under 37 CFR 1.97(e) is not submitted herewith.

TIMING FEE

☐ The fee set forth in 37 CFR 1.17(p) has been submitted herewith.

COPIES

☐ An identification of an earlier application pursuant to 37 CFR 1.98(d)(1) is attached.

SIZE FEE ASSERTION

Please see 37 CFR 1.17(v) and the IDS Auto-Load Instructions for completing this form to make the appropriate selection of an assertion under 37 CFR 1.98. For the information disclosure statement (IDS) submitted herewith, the applicant or patent owner certifies the following with respect to the cumulative number of applicant-provided or patent-owner provided items of information submitted to date including those in the accompanying IDS (select only one):

☐ No IDS size fee is required under 37 CFR 1.17(v) at this time.

☒ The IDS is accompanied by the IDS size fee under 37 CFR 1.17(v)(1).

☐ The IDS is accompanied by the IDS size fee under 37 CFR 1.17(v)(2).

☐ The IDS is accompanied by the IDS size fee under 37 CFR 1.17(v)(3).

SIGNATURE

A signature of the applicant or representative is required in accordance with 37 CFR 1.33 and 11.18. Please see 37 CFR 1.4(d) for the form of the signature.

Signature	/Michael N. Mercanti/	Date (YYYY-MM-DD)	2025-04-07
Name/Print	Michael N. Mercanti	Registration Number	33966

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM, et al.
Art Unit	1699
Examiner Name	Brian M. GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
18/066,105	**04/07/2025 12:00:04 PM Z ET**	**GRAN-1012-U-D**

Title of Invention

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	1563	FILED BY	Carla Curado
PATENT CENTER #	69891624	FILING DATE	12/14/2022
CUSTOMER #	20311	FIRST NAMED INVENTOR	Anna K. CROOM
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Michael Mercanti

Documents

TOTAL DOCUMENTS: 2

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
Suppl_IDSSB08_GRAN1012UD.pdf	5	Information Disclosure Statement (IDS) Form (SB08)	1314 KB
Hamid_Yeganeh.pdf	10	Non Patent Literature	1229 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
Suppl_IDSSB08_GRAN1012UD.pdf	5A5B6A3826EB7B2E2D99D13650AE27C9A84038BA711A76310C976D0FBEB77AF1F403B7E5951A43E4043EBEA82D499B5DB881AC4C897595939FB386D4624102E4
Hamid_Yeganeh.pdf	FB54932CAEED445C64AECF33172B8DE750AD33901EC9BD540A81E4DFD10355D6EFE1D6D12CF65ACD811C0597EEE0B57

DDCE7D1BF776D78F5F2ED3E5A15B74C56

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Notice of References Cited	Application/Control No. 18/066,105	Applicant(s)/Patent Under Reexamination CROOM et al.	
	Examiner Brian Gulledge	Art Unit 1699	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date YYYY-MM-DD	Name	CPC Classification	US Classification
*	A	US-3192185-A	1965-06-29	MARVIN ACHTERHOF	B29C48/022	264/328.17
	B					
	C					
	D					
	E					
	F					
	G					
	H					
	I					
	J					
	K					
	L					
	M					

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date YYYY-MM-DD	Country	Name	CPC Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title, Date, Publisher, Edition or Volume, Pertinent Pages
	U	
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in YYYY-MM-DD format are publication dates. Classifications may be US or foreign.

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	18/066,105	CROOM et al.
	Examiner	Art Unit
	Brian Gulledge	1699

CPC - Searched*		
Symbol	Date	Examiner

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	Date	Examiner
Inventor search performed in PDP	03/18/2025	BMG
SciFinder search performed: see attached transcripts	03/18/2025	BMG

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (01-22)
Approved for use through 05/31/2024. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM
Art Unit	1699
Examiner Name	Brian M GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	5908631	A	1999-06-01	ARNAUD, et al.	
	2	7799874	B2	2010-09-21	CARR, et al.	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20120270992	A1	2012-10-25	LAROCK, et al.	
	2	20130149260	A1	2013-06-13	DELVALLE, et al.	

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	2018090662	JP	A	2018-06-14	MITSUI CHEMICALS INC	English Abstract	☒

PC 6.1.24

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(**Not for submission under 37 CFR 1.99)**

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM
Art Unit	1699
Examiner Name	Brian M GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	AGUILAR-CASTRO et al., "Biobased polyester obtained from bifunctional monomers through metathesis of fatty acids as precursor to synthesis of polyurethanes." J. Appl. Polym. Sci., 136: 47095 (2018).	☐
	2	Jones, Charla, 'What Is Coco-Caprylate Doing In My Natural Skin Care Products?" Eu2Be (08 May 2015): pages 1-2 <https://eu2be.com/blogs/discover/19389252-what-is-coco-caprylate-doing-in-my-natural-skin-care-producls>; page 2	☐

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature	/Brian Gulledge/	Date Considered	03/18/2025

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM
Art Unit	1699
Examiner Name	Brian M GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

CERTIFICATION STATEMENT

Please see 37 CFR 1.97(e) to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☒ A certification statement is not submitted herewith.

FEE

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

COPIES

☐ An identification of an earlier application pursuant to 37 CFR 1.98 (d) (1) is attached.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Michael N. Mercanti/	Date (YYYY-MM-DD)	2024-07-09
Name/Print	Michael N. Mercanti	Registration Number	33966

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

CAS SciFinder

Task History

Initiating Search

March 18, 2025, 12:27 PM

Substances: Dilinoleic acid

Search Tasks

Task	Search Type	View
Returned Substance Results (19)	Substances	View Results
Exported: Retrieved Related Reference Results + Filters (47)	References	View Results
Filtered By:		
Search Within Results: elastomer		

Copyright © 2025 American Chemical Society (ACS). All Rights Reserved.
Internal use only. Redistribution is subject to the terms of your CAS SciFinder License Agreement and CAS Information Use Policies.

CAS SciFinder

References (47)

View in CAS SciFinder

1

Solid matte composition comprising a particular non-polar hydrocarbon oil, a lipophilic clay and process using same

34 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
France, FR3145685 A1 2024-08-16 | Language: French, Database: CAplus

The present invention relates to a solid matte cosmetic composition, preferably in the form of a cosmetic stick, intended to be applied to the skin and/or the lips, comprising: * at least 5% by weight, relative to the total weight of the compos ition, of at least one first saturated or unsaturated, preferably saturated, linear or branched, preferably branched, non- polar C_{14}-C_{19} hydrocarbon oil, * at least one mineral or organic filler comprising at least one filler of lipophilic clay type comprising at least one quaternary ammonium group, said filler of lipophilic clay type being present in an amount of between 1 and 3% by weight, relative to the total weight of the composition, *at least one second oil chosen from polar or non- polar, non-volatile hydrocarbon oils different from the first oil, or non-volatile silicone oils, * at least one silicone elastomer in a form carried in at least one oil identical to or different from the first or second oil. The invention also relates to a process for making up and/or caring for the skin and/or the lips, which consists in applying said composition

Keywords: solid matte nonpolar hydrocarbon oil lipophilic clay cosmetic

PatentPak available

Substances (34) | Reactions (0) | Citing (0)

2

Solid matte composition comprising a particular non-polar hydrocarbon oil, a lipophilic clay and process using same

34 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
World Intellectual Property Organization, WO2024165589 A1 2024-08-15 | Language: English, Database: CAplus

The present invention relates to a solid matte cosmetic composition, preferably in the form of a cosmetic stick, intended to be applied to the skin and/or the lips, comprising: * at least 5% by weight, relative to the total weight of the compos ition, of at least one first saturated or unsaturated, preferably saturated, linear or branched, preferably branched, non- polar C_{14}-C_{19} hydrocarbon oil, * at least one mineral or organic filler comprising at least one filler of lipophilic clay type comprising at least one quaternary ammonium group, said filler of lipophilic clay type being present in an amount of between 1 and 3% by weight, relative to the total weight of the composition, *at least one second oil chosen from polar or non- polar, non-volatile hydrocarbon oils different from the first oil, or non-volatile silicone oils, * at least one silicone elastomer in a form carried in at least one oil identical to or different from the first or second oil. The invention also relates to a process for making up and/or caring for the skin and/or the lips, which consists in applying said composition

Keywords: solid matte nonpolar hydrocarbon oil lipophilic clay cosmetic

PatentPak available

Substances (34) | Reactions (0) | Citing (0)

3

Eco-Designing Cosmetic Products while Preserving the Sensorial-Application Properties: An Instrumental Approach toward Sustainable Formulations

29 Substances • 0 Reactions • 2 Citations

By: Tafuro, Giovanni; Costantini, Alessia; Platto, Mario; Lucchetti, Silvia; Francescato, Stefano ; Busata, Laura; Baratto, Giovanni; Semenzato, Alessandra
Cosmetics (2024), 11(2), 60 | Language: English, Database: CAplus

Driven by growing environmental concerns and regulations, cosmetic companies are seeking reliable methods to promptly assess the possibility of replacing high-impact ingredients with sustainable alternatives. In this work, we exploited rheol. and texture analyses to evaluate the possibility of using natural and biodegradable raw materials for reformulating three com. oil-in-water skin care emulsions from an eco-design perspective. Synthetic texturizers, like nylon-12 and PMMA, were replaced with starch, maltodextrin, and silica, while acrylic rheol. modifiers were substituted with polysaccharide associations of sclerotium gum, xanthan gum, diutan gum, and carrageenan. Plant-based emollients and a biodegradable elastomer were used as alternatives to silicone oils. The flow and viscoelastic properties of the samples were characterized using rheol. tests under continuous and oscillatory flow conditions. The immersion/de-immersion texture anal. allowed us to measure the mech. properties of firmness, adhesiveness, and stringiness. A double-blind sensory test assessed the products' application and sensory characteristics. The results revealed that rheol. and texture anal. are complementary and correlated techniques, useful for predicting cosmetics' sensory characteristics. While perfect replication of the original formulas might not be achievable, this protocol can aid formulators in selecting new eco-friendly ingredients ensuring the products' desired application and sensory properties without compromising consumer experience.

Keywords: polymethyl methacrylate maltodextrin skin care emulsion cosmetic product formulation

Substances (29) | Reactions (0) | Citing (2)

4

Preparation method of environment-friendly material with effect of improving fatigue resistance and flexure resistance of rubber product

22 Substances • 0 Reactions • 0 Citations

Assignee: Anhui Ruibang Rubber Additives Group Ltd.
China, CN117070058 A 2023-11-17 | Language: Chinese, Database: CAplus

The present invention provides a preparation method of environment-friendly material with effect of improving fatigue resistance and flexure resistance of rubber product, which falls within the tech. field of rubber filler preparation The environment-friendly material in the present invention is made of powd. rCB 90-95 parts, alcoholized vegetable oil soapstock 0. 1-2. 0 parts, emulsifier 0. 1-3. 0 parts, binder 0. 1-2. 0 parts and modifier 0. 1-3. 0 parts; wherein the powder rCB has at least one of the three features of a mesh count being controlled at 325-1500 mesh, a toluene light transmittance of 0. 1-10%, and an external sp. surface area of 40-70 m2/g. In the present invention, the black solid product and vegetable oil soapstock after thermal cracking of waste tires are used as raw materials, with sufficient supply and stable quality, so as to achieve the purpose of recycling waste resources with high added value. When the powd. rCB and the alcoholized vegetable oil soapstock of the present invention are applied to a rubber composite material, the fatigue and flex resistance of the rubber composite material is significantly improved, and the production cost thereof is greatly reduced.

Keywords: environment friendly material fatigue flexure resistance rubber

PatentPak available

Substances (22) | Reactions (0) | Citing (0)

5

Colored solid cosmetic composition with a non-silicone elastomer and a phospholipid

25 Substances • 0 Reactions • 0 Citations

Assignee: L V M H Recherche
France, FR3124728 A1 2023-01-06 | Language: French, Database: CAplus

The present invention relates to a solid, preferably anhydrous, composition comprising, in a physiol. acceptable medium: (i) a crossl inked polyurethane elastomer gel comprising at least one solvent and a single crossl inked polyurethane elastomer or a mixture of at least two crosslinked polyurethane elastomers, said elastomer or said elastomer mixture being obtained from a prepolymer having at least two hydroxyl groups and from a (poly)isocyanate, (ii) a phospho lipid, preferably a lecithin, and (iii) one or more pigments.

Keywords: colored solid cosmetic polyurethane elastomer phospholipid

PatentPak available

Substances (25) | Reactions (0) | Citing (0)

6

Colored solid cosmetic composition with a non-silicone elastomer and a phospholipid

25 Substances • 0 Reactions • 0 Citations

Assignee: L V M H Recherche
World Intellectual Property Organization, WO2023275497 A1 2023-01-05 | Language: French, Database: CAplus

The present invention relates to a solid, preferably anhydrous, composition comprising, in a physiol. acceptable medium: (i) a crossl inked polyurethane elastomer gel comprising at least one solvent and a single crossl inked polyurethane elastomer or a mixture of at least two crosslinked polyurethane elastomers, said elastomer or said elastomer mixture being obtained from a prepolymer having at least two hydroxyl groups and from a (poly)isocyanate, (ii) a phospho lipid, preferably a lecithin, and (iii) one or more pigments.

Keywords: colored solid cosmetic polyurethane elastomer phospholipid

PatentPak available

Substances (25) | Reactions (0) | Citing (0)

7

Composition with nonsilicone elastomer and pasty fatty substance

9 Substances • 0 Reactions • 0 Citations

Assignee: LVMH Recherche
France, FR3117353 A1 2022-06-17 | Language: French, Database: CAplus

The present invention relates to a cosmetic composition, which is preferably solid, comprising, in a physiol. acceptable medium: - a crosslinked polyurethane elastomer gel comprising a single crossl inked polyurethane elastomer (copolymer) or a mixture of at least two crosslinked polyurethane elastomers (copolymers), wherein said copolymer or said mixture of copolymers is obtained from a prepolymer having at least two hydroxyl groups and from a (poly)isocyanate and at least one solvent, in particular from a carboxylic acid dimer or trimer, from at least one polyol and from a diisocyanate, and - one or more pasty fatty substances chosen from the group consisting of (i) esters of polyol(s) and of a fatty acid dimer diacid, or of an ester thereof, (ii) hydrog enated castor oil esters, (iii) glycerol oligomer esters, in particular diglycerol esters, (*iv*) and mixtures thereof.

Keywords: nonsilicone elastomer pasty fatty substance cosmetic

PatentPak available

Substances (9) | Reactions (0) | Citing (0)

8

Composition with nonsilicone elastomer and pasty fatty substance

14 Substances • 0 Reactions • 0 Citations

Assignee: LVMH Recherche
World Intellectual Property Organization, WO2022123184 A1 2022-06-16 | Language: French, Database: CAplus

The present invention relates to a cosmetic composition, which is preferably solid, comprising, in a physiol. acceptable medium: - a crosslinked polyurethane elastomer gel comprising a single crossl inked polyurethane elastomer (copolymer) or a mixture of at least two crosslinked polyurethane elastomers (copolymers), wherein said copolymer or said mixture of copolymers is obtained from a prepolymer having at least two hydroxyl groups and from a (poly)isocyanate and at least one solvent, in particular from a carboxylic acid dimer or trimer, from at least one polyol and from a diisocyanate, and - one or more pasty fatty substances chosen from the group consisting of (i) esters of polyol(s) and of a fatty acid dimer diacid, or of an ester thereof, (ii) hydrog enated castor oil esters, (iii) glycerol oligomer esters, in particular diglycerol esters, (*iv*) and mixtures thereof.

Keywords: nonsilicone elastomer pasty fatty substance cosmetic

PatentPak available

Substances (14) | Reactions (0) | Citing (0)

9

In Vivo Biocompatibility of an Innovative Elastomer for Heart Assist Devices

4 Substances • 0 Reactions • 1 Citation

By: Zawidlak-Wegrzynska, Barbara; Fray, Mirosława El ; Janiczak, Karolina; Kustosz, Roman; Gonsior, Małgorzata; Grabarek, Beniamin Oskar

Polymers (Basel, Switzerland) (2022), 14(5), 1002 | Language: English, Database: CAplus and MEDLINE

Cardiac surgical approaches require the development of new materials regardless of the polyurethanes used for pulsatile blood pumps; therefore, an innovative biomaterial, a copolymer of poly(ethylene terephthalate) and dimer fatty acid (dilinoleic acid) modified with D-glucitol, hereafter referred to as PET/DLA, has been developed, showing non-hemolytic and atrombogenic properties and resistance to biodegradation The aim of this work was to evaluate in vivo inflam matory responses to i.m. implan tation of PET/DLA biomaterials of different compositions (hard to soft segments). Two copolymers containing 70 and 65 weight% of hard segments, as in poly(ethylene terephthalate) and dilinoleic acid in soft segments modified with D- glucitol, were used for implantation tests to monitor tissue response. Medical grade polyurethanes Bionate II 90A and Bionate II 55 were used as reference materials. After euthanasia of animals (New Zealand White rabbits, n = 49), internal organs and tissues that contacted the material were collected for histopathol. examination The following parameters were determined: peripheral blood count, blood smear with May Grunwald-Giemsa staining, and serum C-reactive protein (CRPP). The healing process observed at the implan tation site of the new materials after 12 wk indicated normal progressive collagenization of the scar, with an indication of the inflammatory-resorptive process. The anal. of the chem. structure of explants 12 wk after implan tation showed good stability of the tested copolymers in contact with living tissues. Overall, the obtained results indicate great potential for PET/DLA in medical applications; however, final verification of its applicability as a structural material in prostheses is needed.

Keywords: glucitol modified polyethylene terephthalate dilinoleic acid heart assist device; New Zealand white rabbits; P ET; biocompability; biomaterials; fatty acid; inflammatory process; wound healing

Substances (4) | Reactions (0) | Citing (1)

10

Non-isocyanate polyurethane elastomer, gel composition, gel paste and topical formulation

16 Substances • 0 Reactions • 0 Citations

Assignee: PhD Biosciences

World Intellectual Property Organization, WO2021231527 A1 2021-11-18 | Language: English, Database: CAplus

Title non-isocyanate polyurethane (NIPU) elastomer is represented by A-[B-R^1-B-O-CO-N (R^2)-R^3-N(R^4)-CO]$_n$-D; wherein, n is 2 to 100,000; A is an end group selected from a cycloca rbonate and an amine; B is selected from - CH[$(CH_2)_x$-CH(OH)R^5]- and -$(CH_2)_x$-C(OH)R^5-; x is 0-4; R^1 and R^3 are C_{1-30} (un)substituted (un)branched aliphatic group, cycloaliphatic group, aryl group, hetero cycloaliphatic group, or heteroaryl group, optionally comprising a heteroatom; R^2, R^4 and R^5 are independently H or any group given for R^1; and D is an end group selected from a cycloca rbonate and an amine. The gel composition comprises the title elastomer prepared from the reaction of: (a) a polycarbonate, or a mixture of polycar bonates containing two or more carbonate functional groups; (b) a polyamine or mixture of polyamines containing two or more primary or secondary amine functional groups; (c) an optional NIPU reaction catalyst; and (d) an optional topically acceptable carrier fluid 50- 99.9 wt% of the gel composition; wherein the topically acceptable carrier fluid is a reaction solvent or the topically acceptable carrier fluid is added after elastomer formation. The gel composition further comprises a pharmaceutically active ingredient, and the ingredient is incorporated into the gel composition via a pre-load method or a post-load method. The topical formulation comprises the gel composition, wherein, the pharmaceutically active ingredient is a personal care active ingredient or a healthcare active ingred ient. The invention discloses the manufacture method of gel paste.

Keywords: nonisocyanate polyurethane elastomer gel topical formulation

PatentPak available

Substances (16) | Reactions (0) | Citing (0)

11

Method for preparation of flame-retardant high temperature-resistant cable material

14 Substances • 0 Reactions • 1 Citation

Assignee: Unknown
China, CN106432843 A 2017-02-22 | Language: Chinese, Database: CAplus

The title method comprises (1) preparing a flame retardant from hexa-amino cyclotriphosphazene, ethylenediamine, and dimeric linoleic acid, (2) preparing mixed component I from neoprene rubber, silicone rubber, maleated ethylene-vinyl acetate copolymer, semi-reinforcing carbon black, melamine, filler, zinc stearate, and antiox idant 1010, (3) preparing mixed component II from elastic acrylic emulsion, maleated PE, styrene-series elastomer, EVA, dipentaerythritol, antiaging agent OD, dioctyl phthalate, paraffin wax, zinc borate, and solvent oil number 200, (4) mixing component I, component II, and part of the flame retardant, and milling, (5) extruding, and (6) spraying the rest of the flame retardant and drying.

Keywords: fireproofing rubber polymer composite cable insulator high temperature resistance

PatentPak available

Substances (14) | Reactions (0) | Citing (1)

12

Asphalt concrete binding material and asphalt concrete comprising waste incineration fly ash

26 Substances • 0 Reactions • 0 Citations

Assignee: Unknown
China, CN106167689 A 2016-11-30 | Language: Chinese, Database: CAplus

The title asphalt concrete binding material is composed of an A component and a B component at a weight ratio of 1-1.5:1. The A component is composed of (by parts, the same below) petroleum asphalt 30-60, epoxy resin (bisphenol A epoxy resin, bisphenol F epoxy resin, etc.) 10-30, diluent (polypropylene glycol diglycidyl ether, 1,4-butanediol diglycidyl ether, etc.) 10-20, compatibilizer (modified asphalt, tar, etc.) 5-10, and waste incineration fly ash 1-10. The B component is composed of epoxy curing agent (modified amine-based curing agent or polyamide-based curing agent) 5-20, curing accelerator (N,N-dimethylbenzylamine, N,N-dimethylpr opylamine, etc.) 1-10, petroleum asphalt 40-70, toughener (modified hydroxyl-terminated liquid polybutadiene rubber, polypro pylene glycol diglycidyl ether, etc.) 3-10, heavy metal chelating agent (polymethylacrylic acid, hydrolytic polymaleic anhydride, etc.) 1-10, and coupling agent (γ-aminopropyltriethoxysilane, γ-aminopropyltrimethoxysilane, etc.) 5-20. Title asphalt concrete is prepared by mixing the A component and base asphalt at 160-170°C, adding coarse aggregate, fine aggregate and ore powder, uniformly mixing, adding the B component, and uniformly mixing to obtain final product. The inventive binding material can form strong interaction together with asphalt, coarse aggregate, fine aggregate and fly ash, and form a three-dimensional network structure under the conditions of construction and maintenance of the asphalt concrete, so that the heavy metal leaching amount of a solidified substance is lower than the heavy metal emission standard of hazardous wastes, and the harmlessness and recycling of the waste incineration fly ash are realized.

Keywords: waste incineration fly ash asphalt concrete binding material

PatentPak available

Substances (26) | Reactions (0) | Citing (0)

13

Solid powder cosmetic containing silicone elastomer powder and ascorbyl phosphate

20 Substances • 0 Reactions • 0 Citations

Assignee: Nippon Menard Cosmetic Co., Ltd.
Japan, JP2015137245 A 2015-07-30 | Language: Japanese, Database: CAplus

The invention provides a solid powder cosmetic composition containing elastic powders, that provides better feeling of use and has excellent impact resistance. The solid powder cosmetic compos ition contains (A) silicone elastomer powder and (B) ascorbic acid-2-phosphate salt. More specifi cally, the elastomer powder (A) has an average particle diameter of 2- 35 μm, and a A-durometer hardness of 25-80. The compos ition may further contain a paste-type oily component.

Keywords: silicone elastomer powder ascorbyl phosphate solid cosmetic

PatentPak available

Substances (20) | Reactions (0) | Citing (0)

14

Solid powder cosmetic containing elastomer powders and ascoarbyl phosphate salt

23 Substances • 0 Reactions • 0 Citations

Assignee: Nippon Menard Cosmetic Co., Ltd.
Japan, JP2015137246 A 2015-07-30 | Language: Japanese, Database: CAplus

The invention provides a solid powder cosmetic composition containing elastic powder, that has improved impact resistance while providing good feeling of use, extended time of application and smoothness, and increased marketability. The solid powder cosmetic contains (A) one or two or more kinds of elastic powder selected from a group consisting of polyurethane powder, and alkyl polyacrylate powder, and (B) ascorbic acid-2-phosphate salt.

Keywords: solid powder cosmetic elastomer powder ascorbyl phosphate

PatentPak available

Substances (23) | Reactions (0) | Citing (0)

15

Curable compositions, epoxy adhesive compositions and cured product

9 Substances • 1 Reaction • 1 Citation

Assignee: Dow Global Technologies LLC
World Intellectual Property Organization, WO2015013084 A1 2015-01-29 | Language: English, Database: CAplus

A curable composition comprises (a) ≥1 epoxy resin, (b) ≥1 curing agent, (c) ≥1 core shell rubber toughening agent, and (d) ≥1 nonreactive diluent such as a poly(alkylene) glycol adapted for reducing the difference in temper ature between T_g1 and T_g2. A process for preparing a cured thermoset comprises the steps of (1) admixing (a) ≥1 epoxy resin, (b) ≥1 curing agent, (c) ≥1 core shell rubber toughening agent, and (d) ≥1 non-reactive diluent adapted for reducing the difference in temper ature between T_g1 and T_g2, and (2) heating the admixture of step (1).

Keywords: epoxy resin hardener adhesive toughener diluent

PatentPak available

Substances (9) | Reaction (1) | Citing (1)

16

Impact-resistant PVC water supply pipe and its preparation method

27 Substances • 0 Reactions • 0 Citations

Assignee: Anhui Zhenyun Plastic and Rubber Co., Ltd.
China, CN104098850 A 2014-10-15 | Language: Chinese, Database: CAplus

The water supply pipe is prepared from SG-4 type PVC resin 62-84, polypropylene 36-48, polyethylene-octene elastomer 14-26, molybdenum disilicide micropowder 18-27, carbon nanofiber 10-15, tri-Bu octadecanoyl citrate 12-18, diethylene glycol monobutyl ether adipate 10-15, tall oleic acid diethanolamide 2-4, PTFE powder 4-6, oxidized polyethylene wax 3-5, calcium myristate 2-3, zinc naphthenate 1-2, nano β-mol. sieve 2-4, stearoyl benzoyl methane 1.5-2.5, 2-hydroxy-4-methoxy benzophenone 1-2, distearyl pentaerythritol diphosphite 4-8, dimeric diisooctyl phosphate magnesium stearate 2-3, and filler masterbatch 20-25 weight parts. The filler masterbatch is prepared from sillimanite 30-40, obsidian 20-30, coal gangue 15-20, illite 10-15, iso-Pr tris(dioctyl pyrophosphoric acid acyloxy) titanate 2-3, ethoxyaminopropyl polydimethylsiloxane 1.5-2.5, stearic acid 3-5, trioctyl trimellitate 8-12, dioctyl phthalate 5-10, dimeric linoleic acid copolymer 2-3, octyl dodecanol beeswax acid ester 2-3, OP wax 4-6, ethylene-propylene-styrene-acrylonitrile copolymer 25-35, ethylene-vinyl acetate copolymer 20-30, and high-d. polyethylene 40-50 weight parts. The filler master batch is prepared by (1) mixing uniformly sillimanite and illite, grinding into 150-200 mesh, calcining at 850-880° for 1-2 h, cooling to room temperature, adding iso-Pr tris(dioctyl pyrophosphoric acid acyloxy) titanate, trioctyl trimellitate and octyl dodecanol beeswax acid ester, mixing at high speed for 4-6 min, adding ethylene-propylene-styrene-acrylonitrile copolymer, feeding in a twin-screw extruder, melting, extruding, granulating to obtain masterbatch A, (2) mixing uniformly obsidian and coal gangue, grinding into 150-200 mesh, calcining at 900-950° for 1-2 h, cooling to room temperature, adding ethoxyaminopropyl polydimethylsiloxane, dioctyl phthalate and dimeric linoleic acid copolymer, mixing at high speed for 3-5 min, adding ethylene-vinyl acetate copolymer, feeding in a twin-screw extruder, melting, extruding, granulating to obtain masterbatch B, and (3) mixing uniformly master batch A, master batch B, high-d. polyethylene, OP wax and stearic acid, feeding in a twin-screw extruder, melting, extruding, granulating. The water supply pipe is prepared by (1) placing SG-4 type PVC resin, polyethylene-octene elastomer, filler masterbatch, molybdenum disilicide micropowder, tri-Bu octadecanoyl citrate, oxidized polyethylene wax, tall oleic acid diethanolamide, nano β-mol. sieve and dimeric diisooctyl phosphate magnesium stearate in a kneading machine, kneading to 90-100° by friction, discharging in a cooling mixer, cooling to <45°C, discharging to obtain mixture A, (2) feeding the rest of raw materials in kneading machine, kneading to 80-90° by friction, discharging in a cooling mixer, cooling to <40°, discharging to obtain mixture B, and (3) mixing uniformly mixture A and mixture B, feeding in a twin-screw extruder, extruding, molding.

Keywords: impact resistant PVC water supply pipe

PatentPak available

Substances (27) | Reactions (0) | Citing (0)

17

Solvent- and wear-resistant full-resin thermal transfer printing ribbons

9 Substances • 0 Reactions • 0 Citations

Assignee: Unknown
China, CN104057733 A 2014-09-24 | Language: Chinese, Database: CAplus

The printing ribbons comprise a base ribbon, a back coating layer disposed on one side of the base ribbon, a release layer, a protective layer, an ink layer, and a transfer printing resin layer sequentially disposed on the other side of the base ribbon, wherein the protective layer comprises 90-95% organosilicon resins and 5-10% epoxy resin curing agents (polyamide resin or amino resin); the ink layer contains 20-50% polyesters, 50-80% coloring agents, and fillers; the transfer printing resin layer comprises 80-95% polyesters and 5-20% epoxy resins; and the back coating layer contains polyurethane elastomer or organosilicon resins. The printing ribbons can be used for printing various substrates, such as paper, PET, PVC, polypropylene, etc.

Keywords: solvent wear resistance thermal transfer printing ribbon

PatentPak available

Substances (9) | Reactions (0) | Citing (0)

18

The effect of catalyst and segmental composition on the crystallization of multiblock polyesters for biomedical applications (rapid communication)

6 Substances • 1 Reaction • 3 Citations

By: Staniszewski, Zygmunt; Piegat, Agnieszka; Piatek-Hnat, Marta; El Fray, Miroslawa
Polimery (Warsaw, Poland) (2014), 59(7/8), 592-597 | Language: English, Database: CAplus

In the present work, segmented thermoplastic elastomers (TPE) containing hard segments of poly(ethylene terephthalate) (PET) and soft segments comprising amorphous fatty acid ester sequences based on dilinoleic acid (DLA) were synthesized. The aim was to obtain transparent materials with high strength and flexib ility. Thermal properties of the obtained PET/DLA copolymers were examined using differential scanning calorimetry (DSC). It was found that segmental compos ition and new type of catalyst used for the synthesis of PET/DLA copolymers has influence on materials transpa rency.

Keywords: catalyst segmental composition crystallization multiblock polyester biomedical applic ation

Substances (6) | Reaction (1) | Citing (3)

19

Vehicle compositions comprising hydrophobic solvent and viscosity modifiers, essentially free of pharmaceutically active agents for the improved treatment of acne and related disorders

143 Substances • 0 Reactions • 0 Citations

Assignee: Foamix Ltd.
United States, US20140186269 A1 2014-07-03 | Language: English, Database: CAplus

The present invention relates to the use of a topical vehicle composition which is essentially free of pharmaceutically active agents for the treatment of human skin, especially in the treatment of acne, acne-related symptoms, a tetracycline antibiotic responsive acne related disorder, skin disorder caused by a bacteria, and a tetracycline antibiotic responsive sebaceous gland disease, Propionibacterium acne-associated disorders, and other superficial infections, including skin infections. The vehicle composition, such as a hydrophobic gel or foam comprises (a) about 60% to 99% by weight of at least one hydrop hobic solvent, and (b) at least one viscosity modifying agent comprising a wax and a fatty alc., a fatty acid, or both. Thus, the foam vehicle comprising light mineral oil, cyclomethicone, coconut oil, soybean oil, hydrogenated castor oil, beeswax, myristyl alc., cetostearyl alc., stearyl alc., behenyl alc., fumed silica, stearic acid, and Propellant AP-70, as the carrier of 1% and 4% minocycline HCl compositions, greatly contributed to the decrease in the number of inflammatory lesions. The patients with acne vulgaris who received vehicle had about a 50% or more decrease in the number of non-inflammatory lesions starting from week 6, reaching almost a 60% decrease at week 12 which continued also 4 wk after the end of treatment; the results were better that those obtained by oral treatments with minocycline (no improvement at week 12).

Keywords: hydrophobic solvent viscosity modifier topical vehicle acne skin disease; fatty acid alc hydrop hobic solvent wax topical vehicle acne

PatentPak available

Substances (143) | Reactions (0) | Citing (0)

20

Lubricating fluid composition and its preparation method

48 Substances • 0 Reactions • 0 Citations

Assignee: China Petroleum & Chemical Corp.
China, CN103571578 A 2014-02-12 | Language: Chinese, Database: CAplus

The present invention relates to a lubricating fluid composition and its preparation method, mainly to solve problems of the prior art, including compatibility with rubber and corrosion to Al alloy. The composition comprises (by weight parts) base oil 10- 30, corrosion inhibitor 15-35, an emulsifier 8-20, oily agent 1-6, and H_2O 5-40. The corrosion inhibitor is selected from boric acid, borate, carboxylic acid, amide, alc. amine, and sulfonate. The emulsifier is selected from fatty alc. polyoxyethylene ether, alkyl phenol polyoxyethylene ether, polyoxyethylene ester, polyalc. ester, Na sulfonate, fatty acid soaps, and alkyl alc. amide. The oily agent is selected from palmitic acid, stearic acid, oleic acid, linoleic acid, dilinoleic acid, ricinoleic acid, abietic acid, and linolenic acid. The invention can be used in industrial production of lubricating fluid for tire assembly.

Keywords: lubricating fluid tire

PatentPak available

Substances (48) | Reactions (0) | Citing (0)

21

High-cleanliness environmentally-friendly alcohol ether fuel for automotive

58 Substances • 0 Reactions • 1 Citation

Assignee: Unknown
China, CN103275769 A 2013-09-04 | Language: Chinese, Database: CAplus

The present invention provides a high-cleanliness environmentally-friendly alc. ether fuel for automo tive, the composition of raw materials comprises: methanol and/or ethanol 600-800, ether stabilizer for alc. fuel 100- 350, antioxidant and antigum inhibitor 1-6, metal deactivators 2-5, corrosion inhibitor 1-3, catalytic combustion improver 1-40, antistatic agent 2-4, antiknock stabilizer 10-100, clean dispersant 1-6, wear-resistant repair agent 1-6, metal corrosion inhibitor 1-6, swelling corrosion inhibitor of rubber parts 2-6, alc.-modified cosolvent 10-50, bactericide 0.2-0.8, and identifying agents 0.04-0.1 parts. The fuel of the invention has stable perfor mance, strong power, full combustion, good seismic performance, good acceleration, easy starting, no air resistance, no layering, low fuel consumption, clean emissions, and does not need to change the existing structure of ignition engines, can be used alone, or used interchangeably and used with regular gasoline.

Keywords: alc ether fuel automotive cleanliness

PatentPak available

Substances (58) | Reactions (0) | Citing (1)

22

Copolyester thermoplastic elastomer containing nanofiller and process for the preparation of copolyester thermoplastic elastomers containing nanofiller

17 Substances • 7 Reactions • 0 Citations

Assignees: Zachodniopomorskiego Uniwersytetu Technologicznego w Szczecinie; Fundacja Rozwoju Kardiochirurgii im. prof. Zbigniewa Religi

Poland, PL213745 B1 2013-04-30 | Language: Polish, Database: CAplus

A thermoplastic polyester elastomer composition comprises a polyester rubber comprising a hard and a soft fragments and a filler comprising pyrolytic carbon having sp. surface 10 - 250 m^2/g or carbon nanotubes. Thus, mixing in a steel reactor 334 weight parts dilinoleic acid, 73 weight parts ethylene glycol and 0.03 weight part titania supported on silica, heating at stirring to 190° with removing formed water; after receiving the stoichiometric amount of water adding to the reactor 150 weight parts di- Me terepht halate, 47 weight parts ethylene glycol and 0.03 weight part titania supported on silica, heating at stirring at 190 - 200° with removing formed methanol, heating to 265° while reducing pressure to 0.1 hPA, extruding the formed polymer under N_2 and granulating and drying to a constant weight gave a polyester having hard segment content 30%, m.p. 143°, glass transition temper ature -20° and elongation at break 275%.

Keywords: polyester thermoplastic elastomer nanofiller

PatentPak available

Substances (17) | Reactions (7) | Citing (0)

23

Composite additive for methanol gasoline

17 Substances • 0 Reactions • 0 Citations

Assignees: Shanxi Huadun Industrial Co., Ltd.

China, CN102965167 A 2013-03-13 | Language: Chinese, Database: CAplus

The composite additive is composed of metal corrosion inhibitor 35-50, rubber swelling inhibitor 5-15, tri-Ph phosphate antiwear agent 1-5, and C_{1-5} alc. 30-60 wt%, and is manufactured by adding raw materials to a reactor in turn, and then stirring at 40- 60°C for 1-2 h. The metal corrosion inhibitor is composed of benzotriazole and its derivatives and/or triethanolamine 30-50, polyoleic acid 40-60, organic amine 5-10 wt%; rubber swelling inhibitor is di-Me phthalate and/or propynol; the antiwear agent is tri- Ph phosphate or isopropylated tri-Ph phosphate. Polyoleic acid is oleic acid dimer or linoleic acid dimer; the organic amine is ≥1 of methyl amine, ethylamine, divinylamine. The inventive additive is suitable for >M70 or M5- M30 methanol gasoline, and can effect ively inhibit corrosion of high/low methanol gasoline on engine and metal parts, prevent swelling of oil-supply system rubber and plastic material, antiwear and antifriction effects.

Keywords: methanol gasoline composite additive antiwear antifriction corrosion inhibitor

PatentPak available

Substances (17) | Reactions (0) | Citing (0)

24

Methanol diesel fuel additive

10 Substances • 0 Reactions • 0 Citations

Assignee: Unknown
China, CN102690695 A 2012-09-26 | Language: Chinese, Database: CAplus

The formula for the MeOH diesel fuel additive is composed of MeOH 58-64, return vegetable oil 15-25, oleic acid 5-10, naphthalene 3-8, cetane 3-10, ferrocene 0.05-0.2, corrosion inhibitor 0.05-0.2 and dispersant 0.02-0.1%. The dispersant is monosuccinimide. The corrosion inhibitor can be mixture of maleic anhydride, primary amine and N-containing heterocyclic compound The corrosion inhibitor can be mixture of triazole series, dilinoleic acid and phenol series antioxidant. The corrosion inhibitor can be mixture of succinic anhydride, fatty acid, unsaturated carboxylic acid and polyamine polyol efin. The corrosion inhibitor can be mixture of amine series, organic phosphate series, organic carboxylic acid series, N-containing heterocyclic compound and hindered phenol. The return vegetable oil can improve the integral viscosity and make the combustion more sufficient; the oleic acid has a certain corrosion resistance and can prevent the plugging of oil spray hole; the naphthalene mainly solves the swelling problem, and can inhibit the reaction with rubber product and avoid the swelling deformation of sealing element; the cetane can improve the cetane value of MeOH diesel fuel to the corresponding standard; the ferrocene can improve the power performance of MeOH diesel fuel and has the effects of supporting combustion and reducing C deposit at the nozzle; the dispersant can eliminate the high temper ature air lock; and the corrosion inhibitor is used for decreasing corrosion of the Me OH diesel fuel and prolonging the service life of equipment.

Keywords: methanol diesel fuel additive

PatentPak available

Substances (10) | Reactions (0) | Citing (0)

25

Influence of PEG molecular masses on electrospinning of new multiblock terpoly(ester-ether-ester)s

7 Substances • 0 Reactions • 8 Citations

By: El Fray, M.; Wagner, H. D.
Designed Monomers and Polymers (2012), 15(6), 547-559 | Language: English, Database: CAplus

With the growing progress in tissue engineering, the search for new scaffolding materials has recently intensified considerably. Focusing on this, we synthesized hydrophilic-hydrophobic terpolymers containing poly(ethylene glycol) (PEG) and two different polyester units: butylene terephthalate and butylene linoleate. The spinna bility of the materials was verified by the electros pinning process. The influence of different mol. masses of PEG on thermal and mech. properties as well as on electros pinning of new terpoly(ester-ether-ester) elastomeric materials was investigated. The thermal properties data revealed the crystall ization of soft segments in materials containing PEG of high mol. mass (4600 g/mol). Increased crystallinity contributed to increased mech. properties of terpolymers. We also investigated the effect of the temperature transitions and the degree of crystallinity on the electrospinning process for nanofiber prepar ation It was found that polymers containing crystallizable soft segments of PEG_{4600} are more suitable for electrospinning compared to terpolymers (TEEE) containing PEG_{1000}.

Keywords: polyoxyethylene mol mass electrospinning multiblock polyester polyether elastomer nanofiber

Substances (7) | Reactions (0) | Citing (8)

26

Fire-resistant flame-retardant cable

14 Substances • 0 Reactions • 0 Citations

Assignee: Unknown
China, CN102117675 A 2011-07-06 | Language: Chinese, Database: CAplus

The invention relates to a fire-resistant flame-retardant cable. It is composed of an insulation rubber outer sheath, an insulation rubber inner sheath and conductive wires enwrapped in the insulation rubber inner sheath. Each conductive wire is composed of a sheath and a copper wire; multiple conductive wires are twisted together; the conductive wire sheaths are applied with fire-resistant coating; and fillers are filled between the insulation rubber outer sheath and the insulation rubber inner sheath. Test results indicate that the mech. performance, aging performance, low temperature resistance, insulation resistance, smoke opacity, smoke damage index, toxicity index, and smoke acid number of the inventive fire-resistant flame-retardant cable all reach or excel the international electrotech. commission (IEC) standards

Keywords: fire resistant flame retardant cable

Substances (14) Reactions (0) Citing (0)

27

Elastomer nanocomposite and method of production of elastomer nanocomposite

15 Substances • 3 Reactions • 0 Citations

Assignee: Zachodniopomorski Uniwersytet Technologiczny w Szczecinie
Poland, PL 208936 B1 2011-06-30 | Language: Polish, Database: CAplus

A method for manufacturing elastomeric nanocomposites comprising polyesters with rigid and flexible fragments comprises transesterification alkylene terephthalates with dilinoleic acid in the presence of catalysts and nanopar ticles. Thus, mixing 336 weight parts di-Me terephthalate and 430 weight parts 1,4-butanediol, heating to 120°, adding 2 weight parts a 10% solution tetrabutoxytitanium in butanol, heating at stirring to 190°, heating until obtaining 95% of theor. value of methanol formed, adding 533 weight parts dilinoleic acid and 0.2 volume% of silica nanoparticles having BET surface area 20 m^3/g and 1 weight parts a 10% solution tetrabutoxytitanium in butanol, heating slowly to 250° and pressure 1 Torr, heating 120 min in vacuum at 260° and granul ating gave a copolyester exhibiting m.p. 155°, glass transition temperature -35° elongation at break 890%.

Keywords: elastomeric nanocomposite rigid flexible fragment manufacturing polyester rubber

PatentPak available

Substances (15) Reactions (3) Citing (0)

28

Flame retardant cable for power station and power plant

10 Substances • 0 Reactions • 0 Citations

Assignee: Unknown
China, CN102074289 A 2011-05-25 | Language: Chinese, Database: CAplus

The title cable is characterized in that the insulating rubber of the cable wraps three wires, which are coated with insulating layers, twisted with each other, and coated with fireproof coating. The cable has excellent phys. and mech. properties, temperature tolerance and flame retardance, long thermostable time at 200 °C, and high breaking extension, tensile strength, impact brittle temperature, volume resistivity, dielec. strength and insulation resistance.

Keywords: flame retardance elec cable

PatentPak available

Substances (10) | Reactions (0) | Citing (0)

29

Fireproof and flame retardant cable for power station and power plant

18 Substances • 0 Reactions • 0 Citations

Assignee: Unknown
China, CN102074288 A 2011-05-25 | Language: Chinese, Database: CAplus

The title cable is characterized in that the insulating rubber of the cable wraps three wires, which are coated with insulating layers, twisted with each other, and coated with fireproof coating, and space between the wires in the insulating rubber is filled with filling material. The filling material is made from (by weight parts) talc powder 18-38, limestone powder 12-30, calcium-magnesium powder 10-20, hydroxypropyl methylcellulose 2-5, adhesive 0.2-3.5, calcium stearate 1-8, tourmaline powder 0.2-5, and diatomite 0.2-2. The cable has excellent phys. and mech. properties, temperature tolerance and flame retardance, long thermostable time at 200°, and high breaking extension, tensile strength, impact brittle temperature, volume resistivity, dielec. strength and insulation resistance.

Keywords: fireproof elec cable power station

PatentPak available

Substances (18) | Reactions (0) | Citing (0)

30

Clean methanol gasoline for vehicle and its preparation

11 Substances • 0 Reactions • 0 Citations

Assignee: Henan Coal Chemical Industry Group Co., Ltd.
China, CN101885999 A 2010-11-17 | Language: Chinese, Database: CAplus

The title clean methanol gasoline is prepared from methanol, gasoline, C4 fraction, Me tert-Bu ether (MTBE), fatty alc. polyoxye thylene ether AEO-4, methanol solution and gasoline solution; wherein the methanol solution is prepared from acetyla niline 3%, benzotriazole 5%, dilinoleic acid 10%, 2, 6-di-tert-butyl-p-cresol 3% and methanol 79%; and the gasoline solution is prepared from polyisobutene amine 4%, polyetheramine 1%, and gasoline 95%. The four specific preparation methods for the methanol gasoline are also disclosed. The invention has the following advantages of (1) solving technique issues of methanol gasoline such as stability, corrosion resistance, swelling performance to rubber, and cold start of engine; (2) reducing raw material cost by changing catalyst; simplifying process (without separation of product from excess methanol) ; and (3) reducing olefin content in gasoline, and enhancing quality of product gasoline.

Keywords: vehicle engine fuel additive catalyst methanol gasoline

PatentPak available

Substances (11) | Reactions (0) | Citing (0)

31

Nanocomposite elastomeric biomaterials for myocardial tissue engineering using embryonic stem cell-derived cardiomyocytes

3 Substances • 0 Reactions • 7 Citations

By: Jawad, Hedeer; El Fray, Miroslawa; Boccaccini, Aldo R.; Harding, Sian E.; Wright, Jamie S.; Chen, Qizhi; Piegat, Agnieszka; Ali, Nadire N.
Advanced Biomaterials (Weinheim, Germany) (2010), (9), B664-B674 | Language: English, Database: CAplus

Regeneration or repair of the damaged myocardium requires different strategies including engineered constructs for more efficient cell delivery. This study was undertaken to examine the potential of a new nanostructured elastomer to deliver embryonic stem cell-derived cardiomyocytes (ESC-CM) to an infarcted area of the myocardium. Engineered materials were biocompatible, mech. stable, and elastomeric nanocomposites serving as substrates for delivery of ESC-CM and as a left ventricular support device in myocardial regeneration strategies. Materials investigated were soft and strong poly(aliphatic/aromatic-ester) multiblock thermoplastic elastomers with poly(ethylene terephthalate) (PET) hard segments and dimerized fatty acid, i.e., dilinoleic acid (D LA) soft segments, resp., with and without addition of 0.2 wt% TiO_2 nanoparticles to form nanocomposites. The PET/DLA-TiO_2 nanocomposite exhibited over 8 MPa tensile strength and 900% elongation at break. Addition of TiO_2 nanoparticles significantly altered surface roughness and enhanced adhesion and spreading of ESC-CM derived from mouse and human embryonic stem cells. The newly developed materials did not affect the functional activity of spontaneously beating hESC-CM, as demonstrated by unaltered rate of their beating, and the cells continued to demonstrate contractile activity on the materials for more than two months in culture (the longest time tested). Quant. proliferation and survival assays using fibroblasts confirmed the ability of the new materials to support cells as well as or better than the present com.-type thermoplastic elastomer analog. The results indicate that PET/DLA and PET/DLA-TiO_2 are promising candidates for the manufacture of engineered patches to deliver ESC-CMs.

Keywords: nanocomposite elastomer PET DLA titanium dioxide myocardium heart patch; tissue engineering regeneration

Substances (3) | Reactions (0) | Citing (7)

32

Solid powder cosmetics containing hydrophobic fumed silica, silicone elastomer powder, and semisolid oils

6 Substances • 0 Reactions • 3 Citations

Assignee: Shiseido Co., Ltd.
Japan, JP2009209139 A 2009-09-17 | Language: Japanese, Database: CAplus

Title cosmetics, which are long-lasting, show good spreada bility and impact resistance, and have smooth texture, contain (A) hydrop hobic fumed silica of average primary particle size 1- 20 nm 0.1-3, (B) spherical silicone elastomer powders 0.1-20, and (C) semisolid oils of hardness 0.1-10 N at 25° 0.1-50%. Thus, a pressed foundation was formulated containing silicone-treated Fe oxide, KSP 100 (vinyldimethicone-methiconesilsesquioxane crosspolymer, average primary particle size 5 nm) , KSP 300 (diphenylmethicone-vinyldiphenylmethicone-silsesquioxane crosspolymer, average primary particle size 5 nm) , Aerosil R 972 (dimethyls ilylated SiO_2, average primary particle size 516 μm), and dimeric linoleic acid phytos teryl behenyl ester (hardness 5.4 N) . The foundation was resistant to cracking due to falling.

Keywords: solid powder cosmetics hydrophobic fumed silica spherical silicone elastomer; phytosteryl behenyl dilinoleate fumed silica spherical silicone elastomer foundation

PatentPak available

Substances (6) | Reactions (0) | Citing (3)

33

Synthetic base stocks for low-viscosity motor oils

10 Substances • 0 Reactions • 5 Citations

By: Willschke, A.; Humbert, D.; Rossi, A.
Journal of Synthetic Lubrication (1988), 5(1), 31-53 | Language: English, Database: CAplus

Poly(α-olefins), dialkylbenzenes, and several esters were evaluated for the viscosity characte ristics, pour points, volatilities, elastomer compatibility, oxidative stability, and Cu/Pb bearing corrosi veness, and antiwear properties. A blend of poly(α-olefins) with polyol esters is suitable for the production of semisynthetic 10W-30 oils.

Keywords: lubricating oil motor synthetic ester; polyalkene lubric ating oil synthetic

Substances (10) | Reactions (0) | Citing (5)

34

Sag-resistant two-component epoxy structural adhesive

12 Substances • 0 Reactions • 3 Citations

Assignee: Ashland Oil, Inc.
United States, US4661539 A 1987-04-28 | Language: English, Database: CAplus

A 2-component structural adhesive comprises a 1st epoxy component composed of an epoxy resin with >1 epoxy group and containing 0.5-8 weight% fumed silica and a 2nd hardener component containing 20- 50 weight% kaolin and ≥1 substance selected from the reaction products of bis(aminopropyl)piperazine (**I**) with dimerized linoleic acid (**II**), amino Et piperazine (**III**), poly(propylene ether) diamine (**IV**), and bisphenol A (**V**); of ethylenediamine (**VI**) with **I**, **II**, **III**, **IV**, and **V**; of **IV** with **V**; of **I** with **II**, **III**, **IV**, and **V**; and of **VI** with linoleic acid, **V**, **III**, **IV**, and **I**. The epoxy component may contain a rubber or urethane elastomer. An epoxy component was prepared from liquid bisphenol A diglycidyl ether 375.3, a carboxylic acid-terminated acrylonitrile-butadiene copolymer 29, tri-Ph phosphine 0.7, dry talc filler 115, and fumed silica 22 g; sep. a hardener was prepared by reacting **I** 84.1 with **II** 117.7, then **III**, **IV**, and **V**. A 1:1 mixture of the 2 components showed non-sag behavior in adhesive tests on cardboard.

Keywords: sag resistant two component adhesive; epoxy resin hardener adhesive mix

PatentPak available

Substances (12) | Reactions (0) | Citing (3)

35

Adhesives and segmented, thermoplastic copolyesters

18 Substances • 0 Reactions • 0 Citations

Assignee: Minnesota Mining and Manufacturing Co.
Federal Republic of Germany, DE2629102 A1 1977-01-13 | Language: German, Database: CAplus

Elastic segmented thermoplastics containing polyester and polyether [or polycap rolactonediol, poly(ethylene carbonate) diol, or hydroxy-terminated polybutadiene [9003-17-2]] segments are prepared which are useful as adhesives or as binders for magnetic recording topes. Thus, adipic acid 30.7, 1,4-cyclohexanedimethanol 27.2, poly(oxytetramethylene) glycol (mol. weight 2000) 42.1, and Sb glycoxide 0.021 part were kept 3 h at 170°, 1 h at 145°/0.25-5 mm, and 4 h at 200- 20°/0.15 mm to give a copoly ester (I) [62073-14-7] adhesive with open time 4 min, compared to <1 min for an adipic acid- cyclohexanedimethanol copolymer adhesive (which in contrast to I was unsuitable for plastics).

Keywords: polyester polyether elastomer adhesive; magnetic tape binder polyester

PatentPak available

Substances (18) | Reactions (0) | Citing (0)

36

Scorching inhibitors for halogenated butyl rubber

11 Substances • 0 Reactions • 1 Citation

Assignee: Polysar Ltd.
Federal Republic of Germany, DE2358435 A1 1974-06-27 | Language: German, Database: CAplus

Vulcanizable compositions containing halogenated butyl rubber, e.g. bromobutyl rubber (I), contained linoleic acid oligomers or salts, e.g., linoleic acid dimer calcium salt (II) [53202-31-6], as scorch inhibitors. Thus, a mixture containing I (2.1% Br) 550, natural rubber 185, stearic acid 7.3, carbon black 440, paraffin oil 110, and resin 29 g was compounded 5 min at 130°, and Zn O 33.1, benzothiazolyl disulfide 3.3, and alkylphenyl disulfide 6.6 g were added at 29° to 1200 g of this mixture A compos ition containing this mixture 200, MgO 1.1, and II 1.1 g had scorch time 15.33 min at 125° vs. 6.62 min for a I I-free composition and gave vulcanizate samples (30 min at 165°) of tensile strength 101 kg/cm2, 300% modulus 43 kg/cm2, and elongation 570%.

Keywords: scorch halogenated butyl rubber; bromobutyl rubber vulcanization prevention; linoleic acid scorch inhibitor

Substances (11) | Reactions (0) | Citing (1)

37

Chloroprene latex with high solid content

7 Substances • 0 Reactions • 0 Citations

Assignee: Petro-Tex Chemical Corp.
Federal Republic of Germany, DE2355419 A1 1974-05-16 | Language: German, Database: CAplus

The title latexes were manufacture by polymerization of a portion of the total monomer to be polymerized until a peak viscosity was observed in water containing Empol 1022 [6144-28-1] 0.15-1.0, Daxad 11 KLS [53127-09-6] 0.30-4.0, and Resin 731-SA [53126-09-3] 1.4-4.0 parts per 100 parts monomer present up to the point of initial peak viscosity and then polymer ization of the remaining monomer until a .geq.50% solid emulsion was obtained.

Keywords: chloroprene rubber latex; solid content rubber latex; wood rosin disproportionated surfactant; formaldehyde alkylnap hthalenesulfonic acid surfactant; linoleic acid surfactant; neoprene rubber latex

Substances (7) | Reactions (0) | Citing (0)

38

Polyurethane plastics

1 Substance • 0 Reactions • 2 Citations

Assignee: Mobay Chemical Co.
United States, US3505250 A 1970-04-07 | Language: English, Database: CAplus

Polyurethanes were prepared with improved fillers and extenders. The rigid and flexible foam were useful in insula tion, gaskets, and moldi ngs. Thus, ~50 parts of a mixture of polymerized fatty acids from the dimerizatio n of linoleic acid and 35 parts butanediol was added to 500 parts of a pre polymer from poly(ethylene adipate) and 4,4'-diphenylmethane diisocyanate. The system was cast and cured at room temperature and the elastomeric product (I) demolded after ~30 min. A 2nd sample (I I) was prepared using tall oil instead of the mixed fatty acids. Tests on I and II, resp., showed (lb/in. tensile strength, % elonga tion, Shore A hardness, and lb/in. tear strength given): 2580, 600, 83, 265; 27078 459, 70, 107. Similarly used were N, N,N',N' - tetrakis (2 - hydroxy propyl)ethylenediamine, CCl3F, polyhydric poly (alkylene ethers), tolylene diisocyanate, stannous octanoate, N,N,N',N'-tetramethyl - 1, 3-butanediamine, and N,N,H',N'-tetrakis(2-hydroxyethyl)ethylenediamine.

Keywords: polyurethane rigid foam; foam flexible polyru ethane

Substance (1) | Reactions (0) | Citing (2)

39

Acidic curing agents for organic polyepoxides

10 Substances • 0 Reactions • 1 Citation

Assignee: Unknown
United States, US3487027 A 1969-12-30 | Language: English, Database: CAplus

Emery Dimer Acid 1024 (I, a 3:1 linoleic acid dimer-trimer mixture), heated with an inorganic Cr, Li, or Fe compound, produced a homogeneous liquid curing agent. Thus, 2.35 g I and 0.45 g (iso- PrO)4Ti (II) were mixed and heated for 3 min at 150° to form a curing agent. After cooling to room temperature, 3.5 g epoxidized soybean oil (I II) was added, and the mixture, left standing for 1 hr, gave a very soft rubber, or for 5 days, gave a moderately tough, strong rubber. The process was repeated, replacing I II with glycerol tris(epoxyoleate) (trivernolin):the cure took about twice as long, and yielded a softer, more flexible product. Alterna tively, II refluxed with a stoichiometric amount of com. oleyl alc. yielded crude undisted. tetraoleyl titanate, which was used in place of I I to give a product similar to the 1st, but cured somewhat slower than the former. Similarly strong rubbers were cured with compos itions in which II was replaced by ferric distea rate, ferric acetylacetonate, chromic acetylacetonate, or chromic triste arate.

Keywords: polyepoxides curing agent; curing agent polyepo xides; titanates curing rubber; linoleic acid dimer trimer; ferric compound curing rubber; epoxidized soybean oil; chromic compound curing rubber; rubber curing agent; acetylac etonates curing rubber

Substances (10) | Reactions (0) | Citing (1)

40

Vulcanizable rubber compositions containing polymeric fatty amines as accelerators

1 Substance • 0 Reactions • 0 Citations

Assignee: General Mills, Inc.
United States, US3268493 1966-08-23 | Language: Undetermined, Database: CAplus

Polymeric secondary amines having recurring structural units of the formula -$NHCH_2RCH_2$-, in which R is a dimeric fatty acid radical accelerate the vulcanization of diene rubbers, especially when used with mercapto benzothiazole. The amount of amine used is 1-10% by weight of the rubber. Compositions containing these amines have improved tackiness and the cured rubbers are removed more easily from the mold. Thus, 417 g. distilled dimer nitrile prepared for dimerized linoleic acid, and 20 g. Cu chromite catalyst were sealed under H at 150 psi. in a stirred autoclave and rapidly heated to 200°. The autoclave was flushed with H at 240 psi. and vented so that autoclave pressure was 230 psi. The autoclave was heated to 270° for 2 hrs., then cooled to <200°, and the catalyst filtered. The product had a Brookfield viscosity of 20000 poises at 25° mol. weight 9900, inherent viscosity 0.334 as a 0.5% solution in m-cresol. It contained 7.0% primary, 81.4% secondary, and 7.6% tertiary amine groups, and no nitrile groups. This product (10 parts) was mixed into GR-S 1507 100, stearic acid 3, dioctyl phthalate 1.5, phenyl- β-naphthylamine 1.5, ZnO 3, carbon black 47.5, S 3, and mercaptobenzothiazole 1.0 part and the mixture was cured for 60 min. at 40 psi. The tensile strength of the product was 2560 psi., the elongation 325%, and the 300% modulus 2468 psi. Without the amine additive, the resp. figures were: 3035 psi., 400%, and 1315 psi.

Substance (1) | Reactions (0) | Citing (0)

41

Polyurethan-polyamide soldering composition for automobile bodies

3 Substances • 0 Reactions • 0 Citations

Assignee: General Motors Corp.
United States, US3249563 1966-05-03 | Language: Undetermined, Database: CAplus

A thermoplastic solder for automobile bodies consists of 70- 80% Al powder or SiO_2 and a binder containing: (a) 5-40% thermoplastic polyamide resin (I) from an alkylene diamine and dilinoleic acid (II) with a mol. weight of 6000- 9000, m.p. 105-190°, and an amino number >10; and (b) polyurethan (III) of m.p. 105-190°, e.g. derived from a polyalkylene glycol of OH number 50-200 and an organic diisocyanate. Thus, 75 parts fine SiO_2 flour was compounded on a hot 2- roll rubber mill with 5 parts I from ethylene diamine and II, and 10 parts III from 1 equivalent of the reaction product from 1 mole adipic acid with 1.3 moles ethylene glycol, and 1.2 equivalent 4,4'-diphenylmethane diisocyanate. The compound was applied at 180° to a panel preheated to 230°, leveled with a cold-metal roller, and finished as usual.

Substances (3) | Reactions (0) | Citing (0)

42

Chlorine-containing polyethylene elastomers and articles therefrom

2 Substances • 0 Reactions • 0 Citations

Assignee: Allied Chemical Corp.
Netherlands, NL6510573 1966-02-14 | Language: Undetermined, Database: CAplus

A heat-curable composition is prepared by mixing a chlori nated polyethylene (28-42% Cl) and an intrinsic viscosity (in o- $C_6H_4Cl_2$ at 100°) 1.0-6.0, prepared by chlorinating a linear polyethylene with high d. and an average mol. weight of 10^5 to 5×10^6 with a vulcani zation agent consisting of a polyamide of a dimerized fatty acid of a drying oil with an aliphatic diamine, containing free amino groups and having an amino number of 50-250, e.g. the polyamide of the dimer of linoleic acid and ethylene diamine. The linear polyethylene can be prepared by polymerizing C_2H_4 in the gas phase, below the softening point of the polyethylene formed, to a polymer in the dispersed state, containing ≤0.001 weight % polymerization catalyst consisting of Cr and SiO_2 or SiO_2-Al_2O_3. The composition is cured by heating at 100- 200° and 3.5-71 kg./cm.^{2} pressure. The polyamide plasticizer is permanently fixed by the elastomer. The product has excellent phys. properties and improved aging resist ance. Thus, polyethylene with an intrinsic viscosity in Decalin at 135° of ~1.95 dl./g., a d. of 0.94, a melt index of 0.2 g./10 min., and an average mol. weight of 1.3×10^5 was chlorinated at 100° at a rate of 0.2 part Cl/part polyethylene/hr. When 10 weight % Cl had been absorbed, the temper ature was raised to 115° and chlorination was continued until the Cl content was 34%. Then the temper ature was raised to 140° and the Cl content was increased to 36%. Chlorination was continued until the Cl content was 40 weight %. The product had an intrinsic viscosity of 1.4 (at 100° in o-$C_6H_4Cl_2$), a glass-transition temperature of -16°, and was not at all crysta lline To 100 parts of this product, 20 parts liquid Versamid 140 (condensation product of the dimer of linoleic acid with ethylene diamine), having an amine number of 350-400, a viscosity of 2-6 poises at 75°, and a d. of 0.97 was obtained. The mixture was mixed in a rubber mill. The composition was worked up to films 1.9 mm. thick (10 × 10 cm.). The films were cured at 160° and 35 kg./cm.^{2} for 30 min. The properties were: initial hardness 75, hardness after 15 sec. 64, tensile strength 98.1 kg./cm.^{2}, elongation 354%, tensile modulus at 100% 263, at 200% 498, at 300% 952; gel 86%; permanent deformation at break 19%; and weight loss after 15 hrs. heating at 150° 3.6%.

Substances (2) | Reactions (0) | Citing (0)

43

Polyamides of polymeric fatty acids

3 Substances • 0 Reactions • 1 Citation

Assignee: Drayton Research Ltd.
United Kingdom, GB902688 1962-08-09 | Language: Undetermined, Database: CAplus

The title compounds are prepared by condensation of hexamethylenediamine (I) with a mixture of a polymeric fatty acid and isopht halic acid (II). Thus, 135 g. of a mixture of dimeric linoleic acids (Empol- 1022) and 13 g. II were mixed with 375 g.I. The mixture was heated 3 hrs. at 160-5°. The product was a tough rubber thermoplastic material. It was dissolved in a mixture of equal parts Bu OH and toluene and mixed with Epon-822. The resultant varnish was applied to a metal sheet surface and stoved 4 hrs. at 160- 70° to give a film of good heat resistance and surface adherence.

Substances (3) | Reactions (0) | Citing (1)

44

Improving drainage rate of cellulosic papermaking slurries

4 Substances • 0 Reactions • 0 Citations

Assignee: Armstrong Cork Co.
United States, US3008868 1961-11-14 | Language: Undetermined, Database: CAplus

A dramatic decrease in drainage time of a cellulosic papermaking stock without the necessity of coating the individual fibers with a rubber and a smoother sheet possessing greater flexib ility and H_2O resistance than previous sheets are obtained by treating the cellulosic fibers with a trivalent ion of Al, Cr, or Fe and then with a H_2O-soluble salt of an organic, aliphatic, polycar boxylic acid containing at least 36 C atoms, such as dimerized or trimerized fatty acids. Thus, 40 parts sulfite pulp in 4000 parts H_2O was beaten for 15 min. to give a stock having a Canadian 3-g. freeness of 370 cc. and a drainage time in a 12 × 12- in. laboratory sheet mold of 29 sec. The stock was treated with 1 part $Al_2(SO_4)_3$ in 50 parts H_2O and then with a solution prepared by placing 1.5 parts hydrog enated dilinoleic acid into 50 parts H_2O and adding enough K OH to dissolve the acid. The freeness of the treated stock was 570 cc., and the drainage time was 13 sec. The resulting sheet was smoother, more flexible, and possessed greater H_2O resistance than an identical sheet made from untreated stock. Modifications are discussed.

Substances (4) | Reactions (0) | Citing (0)

45

Priming coat for pressure-sensitive adhesives

2 Substances • 0 Reactions • 1 Citation

Assignee: Colora G. m. b. H.
Germany, DE1105542 1961-04-27 | Language: Undetermined, Database: CAplus

The priming coat, suitable for hydrophilic and hydrophobic supports, contains a polyamine resin, condensed from di- or trimerized unsaturated fatty acids, preferably linoleic acid, and polyam ines, besides small amounts of an elastomer, e.g. crude rubber. One part elastomer is used with 5- 20 parts polyamide resin, if necessary, both being dissolved in organic solvents, e.g. iso- PrOH, toluene, or gasoline.

Substances (2) | Reactions (0) | Citing (1)

46

Preparation of high-molecular-weight polyurethans with triethylenediamine as a catalyst

6 Substances • 0 Reactions • 5 Citations

Assignee: Houdry Process Corp.
United States, US2939851 1960-06-07 | Language: Undetermined, Database: CAplus

The reaction between an isocyanate and an organic OH compound is accelerated by use of triethyle nediamine (diazabicyclo[2.2,.2] octane) (I) as a catalyst. For example, I 2 was dissolved in H_2O 5 and lecithin 15 was added as an emulsifying agent, followed by a hydroxy polyester (average mol. weight 2000) 300 parts by weight, prepared by esterification of dimerized linoleic acid with diethylene glycol. The mixture was homogenized and 85 parts tolylene 2, 4-diisocyanate was added rapidly with stirring. The reaction mixture was poured into a mold. In a few sec., the polyurethan foam filled the mold and set to a soft, spongy product which was easily removed from the mold. It was light-cream colored, of fine texture and satisf actory resilience. It was free of unpleasant odor. For nonfoamed polymers useful for thermoplastic elastomers, insulation, coating compositions, etc., curing or cross-linking is effected in the absence of H_2O, e.g. with alcs. or amines.

Substances (6) | Reactions (0) | Citing (5)

47

Chlorosulfonated polyethylene elastomeric coating compositions

3 Substances • 0 Reactions • 1 Citation

Assignee: E. I. du Pont de Nemours & Co.
United States, US2914496 1959-11-24 | Language: Undetermined, Database: CAplus

The title compositions are elastomers which are cured to transparent forms at low temperatures They contain 0.04-3.0% S and 25-50% Cl and include a polyamide condensation product of a dimerized drying-oil acid and an aliphatic diamine. The polyamides having an amine value of 50-250 are present in the composition in an amount of 0.1-1.0 meq./g. of chlorosulfonated polyethylene (I). Thus, a com. chlorosulfonated I containing 29% Cl and 1.25% S (as S O_2Cl groups) was dissolved in toluene to give a 20% solution To this was added enough of a 50% solution of a condensation product of 2 moles of the dimer of linoleic acid with approx. 3 moles of ethylenediamine (terminal NH_2 groups about 0.00157 equivalent/g.) to give 0.047 amine equivalents in the composition A mixture was obtained containing 30 parts of the condensation product per 100 parts of the chlorosulfonated I. Films prepared from this mixture were cured at room temperature for 28 days. They had a tensile strength of 850 lb./sq. in., an elongation at break of 860%, a permanent set at break of 35%, and H_2O pick-up of 33%. Salts and other coloring materials may be added to such compositions before curing. The products are useful as coating compositions

Substances (3) | Reactions (0) | Citing (1)

Copyright © 2025 American Chemical Society (ACS). All Rights Reserved.
Copyright © 2025 U.S. National Library of Medicine.
Internal use only. Redistribution is subject to the terms of your CAS SciFinder License Agreement and CAS information Use Policies.

CAS SciFinder

Task History

Initiating Search

March 18, 2025, 12:25 PM

Substances: Dilinoleic acid/butanediol copolymer

Search Tasks

Task	Search Type	View
Returned Substance Results (2)	Substances	View Results
Exported: Retrieved Related Reference Results (42)	References	View Results

Copyright © 2025 American Chemical Society (ACS). All Rights Reserved.
Internal use only. Redistribution is subject to the terms of your CAS SciFinder License Agreement and CAS information Use Policies.

CAS SciFinder

References (42)

View in CAS SciFinder

1

Process for treating keratin fibres using a composition comprising at least two different particular fatty acids and at least one oligo/poly-ester

99 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
France, FR3150426 A1 2025-01-03 | Language: French, Database: CAplus

The present invention relates to a process for treating keratin fibers using a composition comprising at least two different particular fatty acids and at least one oligo/poly-ester.

Keywords: hair cosmetic fatty acid oligoester polyester

PatentPak available

Substances (99) | Reactions (0) | Citing (0)

2

Process for treating keratin fibres using a composition comprising at least two different particular fatty acids and at least one oligo/poly-ester

106 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
France, FR3150426 A1 2025-01-03 | Language: French, Database: CAplus

The present invention relates to a process for treating keratin fibers using a composition comprising at least two different particular fatty acids and at least one oligo/poly-ester.

Keywords: hair cosmetic fatty acid oligoester polyester

PatentPak available

Substances (106) | Reactions (0) | Citing (0)

3

Process for treating keratin fibres using a composition comprising at least one particular fatty acid, at least one oxygenated terpene compound and at least one oligo/poly-ester

116 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
France, FR3150427 A1 2025-01-03 | Language: French, Database: CAplus

The present invention relates to a process for treating keratin fibers using a composition comprising at least one particular fatty acid, at least one oxygenated terpene compound and at least one oligo/poly-ester.

Keywords: hair cosmetic fatty acid oligoester polyester oxygenated terpene

PatentPak available

Substances (116) | Reactions (0) | Citing (0)

4

Process for treating keratin fibres using a composition comprising at least one particular fatty acid, at least one oxygenated terpene compound and at least one oligo/poly-ester and at least a pigment

123 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
France, FR3150420 A1 2025-01-03 | Language: French, Database: CAplus

The present invention relates to a process for treating keratin fibers using a composition comprising at least one particular fatty acid, at least one oxygenated terpene compound and at least one oligo/poly-ester.

Keywords: hair cosmetic fatty acid oligoester polyester oxygenated terpene

PatentPak available

Substances (123) | Reactions (0) | Citing (0)

5

Process for treating keratin fibres using a composition comprising at least one particular fatty acid, at least one oxygenated terpene compound and at least one oligo/poly-ester

116 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
World Intellectual Property Organization, WO2025003165 A1 2025-01-02 | Language: English, Database: CAplus

The present invention relates to a process for treating keratin fibers using a composition comprising at least one particular fatty acid, at least one oxygenated terpene compound and at least one oligo/poly-ester.

Keywords: hair cosmetic fatty acid oligoester polyester oxygenated terpene

PatentPak available

Substances (116) | Reactions (0) | Citing (0)

6

Process for treating keratin fibres using a composition comprising at least two different particular fatty acids and at least one oligo/poly-ester

99 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
World Intellectual Property Organization, WO2025003163 A1 2025-01-02 | Language: English, Database: CAplus

The present invention relates to a process for treating keratin fibers using a composition comprising at least two different particular fatty acids and at least one oligo/poly-ester.

Keywords: hair cosmetic fatty acid oligoester polyester

PatentPak available

Substances (99) | Reactions (0) | Citing (0)

7

Liquid composition including natural dyes and charcoal powder and process implementing it

27 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
France, FR3148370 A1 2024-11-08 | Language: French, Database: CAplus

The present invention has as an aim a liquid composition of make-up for keratinous matters like the skin and/or the lips, compri sing: (A) a natural dye; (B) charcoal powder; (and C) hydroc arbon or silicone nonvolatile oil; (D) possibly of water with a content not exceeding 10% of weight, compared to the total weight of the composition It also has a process of make- up consisting in applying such a composition

Keywords: lip makeup natural dye charcoal powder

PatentPak available

Substances (27) | Reactions (0) | Citing (0)

8

Composition including a natural dye or of natural origin, reflective spangles, at least an oil and/or a solid fat and process implementing it

27 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
France, FR3148369 A1 2024-11-08 | Language: French, Database: CAplus

Various formulations of cosmetics, e.g., eye makeups, are disclosed, with instru ctions for manufacture

Keywords: eye makeup formulations manufacturing

PatentPak available

Substances (27) | Reactions (0) | Citing (0)

9

Universal mineral based sunscreen and related methods of manufacture

49 Substances • 0 Reactions • 0 Citations

Assignee: Unknown
United States, US20240252421 A1 2024-08-01 | Language: English, Database: CAplus

Methods for manufacturing universal mineral based sunscreens that is good for all skin colors and prevents any ashy visual appearance on all colors of skin, is provided in this invention.

Keywords: cosmetic universal skin color independent sunscreen

PatentPak available

Substances (49) | Reactions (0) | Citing (0)

10

Preparation of universal mineral based sunscreen

57 Substances • 0 Reactions • 0 Citations

Assignee: Unknown
United States, US11896691 B1 2024-02-13 | Language: English, Database: CAplus

A universal mineral based sunscreen that is good for all skin colors and prevents any ashy visual appearance on all colors of skin.

Keywords: Camellia Amaranthus cosmetic sunscreen skin toner

PatentPak available

Substances (57) | Reactions (0) | Citing (0)

11

Eye makeup composition based on a volatile mixture of alkanes

23 Substances • 0 Reactions • 0 Citations

Assignee: BioSynthis
France, FR3133129 A1 2023-09-08 | Language: French, Database: CAplus

The invention relates to an eye makeup composition characterized in that it comprises a volatile mixture of alkanes, said volatile mixture of alkanes comprising: a) from 20 to 100% of a fraction A which comprises at least one C≤10 branched alkane; b) from 0 to 80% of a fraction B which comprises at least one C>10 linear or branched alkane; and characterized in that said volatile mixture of alkanes has a flash point of less than 55°C measured in accordance with standard ASTM D93 and represents a weight percentage greater than or equal to 10% relative to the total weight of the composition The invention also relates to the process for preparing said composition

Keywords: eye makeup volatile alkanes

PatentPak available

Substances (23) | Reactions (0) | Citing (0)

12

Eye makeup composition based on a volatile mixture of alkanes

23 Substances • 0 Reactions • 0 Citations

Assignee: BioSynthis

World Intellectual Property Organization, WO2023166198 A1 2023-09-07 | Language: French, Database: CAplus

The invention relates to an eye makeup composition characterized in that it comprises a volatile mixture of alkanes, said volatile mixture of alkanes comprising: a) from 20 to 100% of a fraction A which comprises at least one C≤10 branched alkane; b) from 0 to 80% of a fraction B which comprises at least one C>10 linear or branched alkane; and characterized in that said volatile mixture of alkanes has a flash point of less than 55°C measured in accordance with standard ASTM D93 and represents a weight percentage greater than or equal to 10% relative to the total weight of the composition The invention also relates to the process for preparing said composition

Keywords: eye makeup volatile alkanes

PatentPak available

Substances (23) | Reactions (0) | Citing (0)

13

Cosmetic composition comprising a polyhydroxyalkanoate copolymer bearing a(n) (un)saturated hydrocarbon-based chain and a mixture of volatile oil and non-volatile oil

138 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal

France, FR3131210 A1 2023-06-30 | Language: French, Database: CAplus

The present invention relates to a cosmetic composition comprising a) one or more polyhydroxyalkanoate (PHA) copolymers which contain, and preferably consist of, several repeating units chosen from the units (A) below, and also the optical or geometrical isomers thereof, the organic or mineral acid or base salts thereof, and the solvates thereof such as hydrates: -[-O-CH(R^1)-CH_2-C(O)-]- unit (A) in which polymer units (A): - R^1 is as defined in the description; b) one or more volatile oils; c) one or more non- volatile oils; and it being understood that the mass ratio U between the sum of the masses of volatile oils b) and the sum of the masses of non-volatile oils c) is non-zero and less than 900.

Keywords: cosmetics polyhydroxyalkanoate copolymers makeups

PatentPak available

Substances (138) | Reactions (0) | Citing (0)

14

Cosmetic composition comprising a polyhydroxyalkanoate copolymer bearing a(n) (un)saturated hydrocarbon-based chain and a mixture of volatile oil and non-volatile oil

140 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
World Intellectual Property Organization, WO2023118481 A1 2023-06-29 | Language: English, Database: CAplus

The present invention relates to a cosmetic composition comprising a) one or more polyhydroxyalkanoate (PHA) copolymers which contain, and preferably consist of, several repeating units chosen from the units (A) below, and also the optical or geometrical isomers thereof, the organic or mineral acid or base salts thereof, and the solvates thereof such as hydrates: -[-O-CH(R^1)-CH_2-C(O)-]- unit (A) in which polymer units (A): - R^1 is as defined in the description; b) one or more volatile oils; c) one or more non- volatile oils; and it being understood that the mass ratio U between the sum of the masses of volatile oils b) and the sum of the masses of non-volatile oils c) is non-zero and less than 900.

Keywords: cosmetic polyhydroxyalkanoate copolymers makeups

PatentPak available

Substances (140) | Reactions (0) | Citing (0)

15

Liquid composition comprising natural dyes

26 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
World Intellectual Property Organization, WO2023083858 A1 2023-05-19 | Language: English, Database: CAplus

The invention relates to a liquid composition for making up and/or caring for keratin materials such as the skin and/or the lips, having a viscosity of between 6 and 18 Pa.s, comprising: (A) at least one natural dye chosen from anthocy anins, anthocyanidins, proanthocyanins, proanthocyanidins, (B) at least one liquid polyester obtained from a mono- or poly- unsaturated fatty acid dimer; the fatty acid comprising from 16 to 22 carbon atoms; (C) at least a first non-volatile oil chosen from apolar hydroc arbon-based oils, silicone oils, ester, ether or carbonate hydrocarbon-based oils, these oils being different from the liquid polyesters (B) and devoid of free hydroxyl groups, plant oils with the exception of castor oil and lesquerella oil. Another object relates to a liquid compos ition comprising: (A) at least one natural dye chosen from anthocy anins, anthocyanidins, proanthocyanins, proanthocyanidins; (B) at least 40% by weight of one liquid polyester obtained from a mono- or poly- unsaturated fatty acid dimer; the fatty acid comprising from 16 to 22 carbon atoms; (C) at least a first non-volatile oil as previously described; (D) 3% to 10% by weight of glyceryl trihydrox ystearate The invention also relates to a process for making up and/or caring for keratin materials which consists in applying said composition

Keywords: hair dyes liquid natural products

PatentPak available

Substances (26) | Reactions (0) | Citing (0)

16

Liquid composition including natural dyes

19 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
France, FR3128878 A1 2023-05-12 | Language: French, Database: CAplus

Liquid makeup formulations for coloring keratinous structures such as the lips and skin are disclosed that contain natural pigments such as anthocyanins, anthocyanidins, proanthocyanins, and proanthocyanidins. They also contain liquid polyesters derived from unsaturated fatty acids, apolar hydrocarbon oils, ether, or carbonates, and various vegetable oils excluding castor oil and lesquerella oil.

Keywords: makeup natural dyes liquid formulations

PatentPak available

Substances (19) | Reactions (0) | Citing (0)

17

Inverse emulsion comprising at least one fatty alcohol, a non-ionic sugar ester, ethylcellulose and method employing it

51 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
World Intellectual Property Organization, WO2022136106 A1 2022-06-30 | Language: English, Database: CAplus

A subject-matter of the present invention is a composition in the form of a water-in-oil emulsion, comprising ethylcellulose; at least one first non-volatile oil which is liquid at 25°C chosen from saturated or unsaturated, linear or branched, C_{10}-C_{26} fatty alcs.; at least one second non-volatile hydrocarbon-based oil which is liquid at 25°C chosen from ethers of formula R-O-R' or carbonates of formula RO(CO)OR', in which formulas, identical or not, the R and R' groups represent a saturated or unsaturated, branched or unbranched, hydrocarbon-based group comprising at most 16 carbon atoms, preferably a C_3-C_{16} group; and also their mixtures; at least one first non-ionic hydrocarbon-based surfactant. It relates to a transparent or translucent composition in the form of an inverse emulsion comprising from 11% to 14% by weight, with respect to the total weight of the composition, of ethylcellulose; from 30% to 50% by weight, with respect to the total weight of the composition, of octyldodecanol; at least dicaprylyl ether as second oil, optionally in combination with dicapryiyl carbonate or pentaerythrityl tetrastearate; the first oil(s)/s oil(s) ratio by weight varying from 50/50 to 70/30; from 2% to 7% by weight, with respect to the total weight of the composition, of a mixture of sucrose laurate and of sucrose palmitate; from 10% to 20% by weight, with respect to the total weight of the composition, of water and of glycerol; optionally at least one water-soluble solvent chosen from saturated C_1-C_5 monoalcs.; the content of water, polyol(s), if appropriate water-soluble solvent(s) and surfactants being of between 15% and 25% by weight, with respect to the total weight of the composition; at least one fat-soluble or water-soluble dye. It finally relates to a method for making up and/or caring for human keratin materials which employs them.

Keywords: emulsion fatty alc number ionic sugar ester ethylcellulose

PatentPak available

Substances (51) | Reactions (0) | Citing (0)

18

Cosmetic composition in emulsion form containing a copolymer obtained from a carboxylic acid dimer or trimer, from at least one polyol and from a diisocyanate

16 Substances • 0 Reactions • 3 Citations

Assignee: LVMH Recherche
World Intellectual Property Organization, WO2022129790 A1 2022-06-23 | Language: French, Database: CAplus

The invention relates to a cosmetic composition in the form of a water- in-oil emulsion comprising from 0.1% to 20% of water, from 5% to 40% of at least one volatile oil, a monoalc., a copolymer or a blend of copolymers obtained from a dilinoleic acid dimer or trimer, from a polyol and from a diisocyanate, a polymer solubilized or dispersed in the volatile oil, and a non- ionic surfactant, the percentages being expressed by mass relative to the mass of the compos ition

Keywords: cosmetic emulsion copolymer carboxylate dimer trimer polyol diisocyanate

PatentPak available

Substances (16) | Reactions (0) | Citing (3)

19

Inverse emulsion comprising at least one fatty alcohol, a non-ionic sugar ester, ethylcellulose and method employing it

51 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
France, FR3117822 A1 2022-06-24 | Language: French, Database: CAplus

A subject-matter of the present invention is a compos ition in the form of a water- in-oil emulsion, comprising ethylcellulose; at least one first non-volatile oil which is liquid at 25°C chosen from saturated or unsatu rated, linear or branched, C_{10}-C_{26} fatty alcs.; at least one second non-volatile hydrocarbon-based oil which is liquid at 25°C chosen from ethers of formula R OR' or carbonates of formula RO(CO)OR', in which formulas, identical or not, the R and R' groups represent a saturated or unsatu rated, branched or unbranched, hydrocarbon-based group comprising at most 16 carbon atoms, preferably a C_3-C_{16} group; and also their mixtures; at least one first non-ionic hydrocarbon-based surfactant. It relates to a transparent or translucent composition in the form of an inverse emulsion comprising from 11% to 14% by weight, with respect to the total weight of the composition, of ethylcellulose; from 30% to 50% by weight, with respect to the total weight of the composition, of octyldodecanol; at least dicaprylyl ether as second oil, optionally in combination with dicaprylyl carbonate or pentaerythrityl tetrastearate; the first oil(s)/s oil(s) ratio by weight varying from 50/50 to 70/30; from 2% to 7% by weight, with respect to the total weight of the composition, of a mixture of sucrose laurate and of sucrose palmitate; from 10% to 20% by weight, with respect to the total weight of the composition, of water and of glycerol; optionally at least one water-soluble solvent chosen from saturated C_1-C_5 monoalcs.; the content of water, polyol(s), if appropriate water-soluble solvent(s) and surfactants being of between 15% and 25% by weight, with respect to the total weight of the compos ition; at least one fat-soluble or water-soluble dye. It finally relates to a method for making up and/or caring for human keratin materials which employs them.

Keywords: emulsion fatty alc number ionic sugar ester ethylcellulose

PatentPak available

Substances (51) | Reactions (0) | Citing (0)

20

Anhydrous concentrated hair care compositions in the form of a paste

30 Substances • 0 Reactions • 6 Citations

Assignee: Everist Inc.
World Intellectual Property Organization, WO2022094731 A1 2022-05-12 | Language: English, Database: CAplus

The disclosure relates to cosmetic compositions, particularly concentrated hair care compositions in the form of a paste for shampooing and/or conditioning the hair. In one aspect, a shampoo composition is provided, wherein the shampoo composition is in the form of a paste; the shampoo composition comprises a surfactant, an organic solvent and optionally a thickener and/or an emollient, wherein the shampoo composition is free of, or substantially free of, added water. In another aspect, a hair conditioner is provided, wherein the conditioner composition is in the form of a paste; the conditioner composition comprises a thickener, an organic solvent, an emulsifier and rheol. modifier, an emollient and a conditioning agent, wherein the conditioner composition is free of, or substantially free of, added water.

Keywords: anhydrous concentrated hair care paste

PatentPak available

Substances (30) | Reactions (0) | Citing (6)

21

Cosmetic compositions comprising a fatty acid dimer and trihydroxystearin and a vegetable wax and nonvolatile polar oil

11 Substances • 0 Reactions • 1 Citation

Assignee: L'Oreal
World Intellectual Property Organization, WO2022003026 A1 2022-01-06 | Language: English, Database: CAplus

The present patent application relates to a composition for making up and/or caring for the skin and/or the lips, compri sing: a dye in the form of solid particles; 1-4% by weight of glyceryl trihydroxy stearate; a polar wax; 25-60% of a liquid polyester obtained from an acid dimer, the acid being unsaturated and comprising 16-24 carbon atoms with a diol; 30-60% by weight of a nonvol atile polar oil chosen from vegetable oils, triglycerides of C_{8-60} acids, as well as their mixtures It also relates to a process for making up and/or caring for the skin and/or the lips, consisting in applying the above-mentioned composition

Keywords: cosmetic fatty acid dimer trihydroxystearin vegetable wax oil; nonvol atile polar oil vegetable cosmetic

PatentPak available

Substances (11) | Reactions (0) | Citing (1)

22

Cosmetic compositions comprising a fatty acid dimer and trihydroxystearin and a vegetable wax and nonvolatile polar oil

11 Substances • 0 Reactions • 1 Citation

Assignee: L'Oreal
France, FR3111813 A1 2021-12-31 | Language: French, Database: CAplus

The present patent application relates to a composition for making up and/or caring for the skin and/or the lips, compri sing: a dye in the form of solid particles; 1-4% by weight of glyceryl trihydroxy stearate; a polar wax; 25-60% of a liquid polyester obtained from an acid dimer, the acid being unsaturated and comprising 16-24 carbon atoms with a diol; 30-60% by weight of a nonvol atile polar oil chosen from vegetable oils, triglycerides of C8-C60 acids, as well as their mixtures It also relates to a process for making up and/or caring for the skin and/or the lips, consisting in applying the above-mentioned composition

Keywords: cosmetic fatty acid dimer trihydroxystearin vegetable wax oil; nonvolatile polar oil vegetable cosmetic

PatentPak available

Substances (11) | Reactions (0) | Citing (1)

23

Cosmetic composition comprising an oil and a polyester

5 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
France, FR3060330 A1 2018-06-22 | Language: French, Database: CAplus

The present invention relates to a composition, preferably a cosmetic composition, comprising: (a) a liquid polyester obtained by condensation of a dimer and/or trimer of unsatu rated fatty acids and of a diol; (b) a fatty acid ester of polygl ycerol which is chosen from a fatty acid ester of (poly)glycerol formed from a acid comprising an alkyl chain containing from 12 to 24 carbon atoms and from 2 to 25 glycerol units; (c) a non-volatile hydrocarbon-based oil of plant origin comprising C_{12-22} alkyl chains; and (d) an aliphatic monoalc. comprising from 2 to 8 carbon atoms; characterized in that the total content of the polyester(s) and of the fatty acid ester(s) of polyglycerol is 25-70%, preferentially 30-50% by weight The present invention also relates to a process for the cosmetic treatment of keratin materials, comprising a topical administration of the composition

Keywords: cosmetic oil polyester

PatentPak available

Substances (5) | Reactions (0) | Citing (0)

24

Cosmetic composition comprising an oil and a polyester

5 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
World Intellectual Property Organization, WO2018108871 A1 2018-06-21 | Language: English, Database: CAplus

The present invention relates to a composition, preferably a cosmetic composition, comprising: (a) a liquid polyester obtained by condensation of a dimer and/or trimer of unsatu rated fatty acids and of a diol; (b) a fatty acid ester of polygl ycerol which is chosen from a fatty acid ester of (poly)glycerol formed from a acid comprising an alkyl chain containing from 12 to 24 carbon atoms and from 2 to 25 glycerol units; (c) a non-volatile hydrocarbon-based oil of plant origin comprising C_{12-22} alkyl chains; and (d) an aliphatic monoalc. comprising from 2 to 8 carbon atoms; characterized in that the total content of the polyester (s) and of the fatty acid ester(s) of polyglycerol is 25-70%, preferentially 30-50% by weight The present invention also relates to a process for the cosmetic treatment of keratin materials, comprising a topical administration of the composition

Keywords: cosmetic oil polyester

PatentPak available

Substances (5) | Reactions (0) | Citing (0)

25

Linoleic acid derivative -encapsulated multilayer liposome composition containing cationized plant protein

31 Substances • 0 Reactions • 0 Citations

Assignee: Sunstar Inc.
Japan, JP6169240 B1 2017-07-26 | Language: Japanese, Database: CAplus

The linoleic acid composition comprises a continuous phase selected from the group consisting of a carbox yvinyl polymer and a cellulosic polymer and multilamellar liposomes includes a plant protein cation ized, linoleic acid and/or its derivative such as linoleic acid salt and linoleic acid ester dispersed in the phase above. The cellulose type polymer is chosen from hydroxyethyl cellulose, hydroxypropylcellulose, cellulose gum, and a group which consists of Me cellulose. Further, the cationized plant proteins are lauryl dimonium hydroxypropyl hydrolysis soybean protein and cocodi monium hydroxypropyl hydrolyzed soy protein selected from wheat protein, rice protein, and soybean protein. Through the present invention, it is possible to provide a constituent which improved more the stability with time of linoleic acid and/or its derivative

Keywords: linoleate derivative stability multilayer liposome cationized plant protein

PatentPak available

Substances (31) | Reactions (0) | Citing (0)

26

Cosmetic compositions comprising an oil and a polyester

13 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
World Intellectual Property Organization, WO2016110553 A1 2016-07-14 | Language: English, Database: CAplus

This invention relates to a composition, in particular for coating keratin fibers, in particular eyelashes, compri sing: an oil, a wax, and a liquid polyester obtained by condensing unsaturated fatty acid dimers and/or trimers and diol, according to a content strictly <12% by weight with respect to the total weight of the composition

Keywords: cosmetic oil wax polyester

PatentPak available

Substances (13) | Reactions (0) | Citing (0)

27

Cosmetic compositions including an aqueous phase and at least a polyester, such as dilinoleic acid/butanediol copolymers, for production of mascara

7 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
France, FR3031303 A1 2016-07-08 | Language: French, Database: CAplus

The present invention relates to a composition, in particular coating of keratinous fibers, in particular of the lashes including: - an aqueous phase, - at least a wax, and - at least a liquid polyester obtained by condensation of dimer and/or trimer of unsatu rated fatty-acids and diol. Cosmetic compos itions containing dilinoleic acid/but anediol copolymer were prepared, demonstrating stability at 45°C for two months and suitable performance as a mascara.

Keywords: mascara dilinoleic acid butanediol copolymer

PatentPak available

Substances (7) | Reactions (0) | Citing (0)

28

Cosmetic compositions comprising an oil and a polyester

13 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
France, FR3031304 A1 2016-07-08 | Language: French, Database: CAplus

This invention relates to a composition, in particular for coating keratin fibers, in particular eyelashes, compri sing: an oil, a wax, and a liquid polyester obtained by condensing unsaturated fatty acid dimers and/or trimers and diol, according to a content strictly <12% by weight with respect to the total weight of the composition

Keywords: cosmetic oil wax polyester

PatentPak available

Substances (13) | Reactions (0) | Citing (0)

29

Compositions based on polyester in an oily phase and uses thereof

2 Substances • 0 Reactions • 2 Citations

Assignee: L'Oreal
United States, US8734765 B2 2014-05-27 | Language: English, Database: CAplus

The present invention relates to a cosmetic make-up or care composition comprising an oily phase comprising at least one liquid polyester obtained by condensation of unsaturated fatty acid dimer and/or trimer and diol, said compos ition being free from lipophilic gelling agent or comprising at the most 10 weight % thereof, relative to the weight of the composition The present invention also relates to a method of make-up of the face and body comprising the use of said compos ition

Keywords: cosmetic lipstick polyester oily phase

PatentPak available

Substances (2) | Reactions (0) | Citing (2)

30

Cosmetic composition comprising a polyester and a glutamide

13 Substances • 0 Reactions • 0 Citations

Assignee: Biosynthis
World Intellectual Property Organization, WO2013004952 A1 2013-01-10 | Language: French, Database: CAplus

The invention relates to a composition comprising: (a) a polyester resulting from the reaction between a carboxylic acid dimer (C_{20-44}), an alkanediol and, optionally, a monoalc.; and (b) a glutamide such as N, N'-dialkylacylglutamide. The invention also relates to the cosmetic use of the composition for skin care and/or makeup use on the face and/or body and/or lips. Thus, a lipstick contained dibutylethylhexanoylglutamide 2.0, dibutyllauroylglutamide 3.0, diisostearyl malate 45.0, dilinoleic acid- propanediol copolymer 15.0, tocopherol 0.3, preservatives and pigments qs, and dilinoleic acid- butanediol copolymer qs to 100%.

Keywords: cosmetic polyester glutamide lipstick makeup

PatentPak available

Substances (13) | Reactions (0) | Citing (0)

31

Cosmetic composition comprising a polyester and a glutamide

10 Substances • 0 Reactions • 0 Citations

Assignee: Biosynthis
France, FR2977152 A1 2013-01-04 | Language: French, Database: CAplus

The invention relates to a composition comprising: (a) a polyester resulting from the reaction between a carboxylic acid dimer (C_{20-44}), an alkanediol and, optionally, a monoalc.; and (b) a glutamide such as N, N'-dialkylacylglutamide. The invention also relates to the cosmetic use of the composition for skin care and/or makeup use on the face and/or body and/or lips. Thus, a lipstick contained dibutylethylhexanoylglutamide 2.0, dibutyllauroylglutamide 3.0, diisostearyl malate 25.0, dilinoleic acid- propanediol copolymer 15.0, tocopherol 0.3, preservatives and pigments qs, and dilinoleic acid- butanediol copolymer qs to 100%.

Keywords: cosmetic polyester glutamide lipstick makeup

PatentPak available

Substances (10) | Reactions (0) | Citing (0)

32

Polyester-based cosmetic composition for the care of skin or lips

5 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
France, FR2958158 A1 2011-10-07 | Language: French, Database: CAplus

The present invention relates to an anhydrous liquid cosmetic composition, in particular for making up and/or caring for the skin or lips, comprising, in a physiol. acceptable medium, at least one liquid polyester obtained by conden sation of unsaturated fatty acid dimer and/or trimer and of C_2-C_{10} diol and at least one ester of C_2-C_6 carboxylic acid and of sucrose. A liquid gloss formul ation for the lips contained hydrophilic pyrogenic silica 3.5, pigments 0.3, castor oil 14.6, beeswax 2.7, polyester of hydrog enated castor oil and of dimer dilinoleic acid 19.2, shea butter 24, fragrance 0.4, sucrose diacetate hexa(2-methylpropanoate) 8.5, hydrogenated polyester of dilinoleic acid and of butanediol 26.8%.

Keywords: polyester cosmetic care skin lip lipstick

PatentPak available

Substances (5) | Reactions (0) | Citing (0)

33

Polyester-based cosmetic composition for the care of skin or lips

4 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
World Intellectual Property Organization, WO2011121527 A2 2011-10-06 | Language: English, Database: CAplus

The present invention relates to an anhydrous liquid cosmetic composition, in particular for making up and/or caring for the skin or lips, comprising, in a physiol. acceptable medium, at least one liquid polyester obtained by conden sation of unsaturated fatty acid dimer and/or trimer and of C_2-C_{10} diol and at least one ester of C_2-C_6 carboxylic acid and of sucrose. A liquid gloss formul ation for the lips contained hydrophilic pyrogenic silica 3.5, pigments 0.3, castor oil 14.6, beeswax 2.7, polyester of hydrog enated castor oil and of dimer dilinoleic acid 19.2, shea butter 24, fragrance 0.4, sucrose diacetate hexa(2-methylpropanoate) 8.5, hydrogenated polyester of dilinoleic acid and of butanediol 26.8%.

Keywords: polyester cosmetic care skin lip lipstick

PatentPak available

Substances (4) | Reactions (0) | Citing (0)

34

Cosmetic composition containing a polyester, an organic oil and water

16 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
World Intellectual Property Organization, WO2010076483 A1 2010-07-08 | Language: French, Database: CAplus

The invention relates to a cosmetic composition that contains, one or more liquid polyesters obtained by the conden sation of a dimer and/or trimer of an unsaturated fatty acid with a saturated linear diol, one or more organic oils, and water at >30 weight% relative to the total weight of the composition, as well as to a cosmetic treatment method. Thus, a hair cosmetic compos ition contained Viscoplast-14436H 2.5, octyldodecanol 6, PDMS 0.5, Salcare SC96 1, Aculyn-46 2.4, Carbomer 0.1, preservatives qs, and water qs to 100%.

Keywords: cosmetic hair polyester organic oil water

PatentPak available

Substances (16) | Reactions (0) | Citing (0)

35

Anhydrous cosmetic composition containing a polyester, a volatile oil, and a non-volatile oil

20 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
World Intellectual Property Organization, WO2010076484 A1 2010-07-08 | Language: French, Database: CAplus

The invention relates to an anhydrous cosmetic composition containing liquid polyesters resulting from the conden sation of a dimer and/or a trimer of an unsaturated fatty acid with a saturated linear diol, volatile oils and non- volatile oils, the weight ratio between the volatile oil(s) and the non-volatile oil(s) being >1.5, as well as to a cosmetic treatment method. The compos ition can used to treat keratinous materials, especially hair. Thus, a composition contained Viscoplast-14436H 5, EtOH 10, C_{12-15} alkyl benzoate 5, and isododecane 80%.

Keywords: anhydrous cosmetic hair polyester volatile nonvolatile oil

PatentPak available

Substances (20) | Reactions (0) | Citing (0)

36

Cosmetic composition including a polyester and glycerin

8 Substances • 0 Reactions • 1 Citation

Assignee: L'Oreal
France, FR2939680 A1 2010-06-18 | Language: French, Database: CAplus

The invention relates to a cosmetic hair composition including in a cosmet ically acceptable medium one or more liquid polyesters obtained by condensation of dimer and/or trimere of unsatu rated fatty-acid and diol, and glycerin, as well as a cosmetic process of treatment implementing it.

Keywords: cosmetic hair polyester glycerol formulation

PatentPak available

Substances (8) | Reactions (0) | Citing (1)

37

Compositions based on polyester in an oily phase and uses thereof

2 Substances • 0 Reactions • 5 Citations

Assignee: L'Oreal
World Intellectual Property Organization, WO2009147089 A1 2009-12-10 | Language: English, Database: CAplus

The present invention relates to a cosmetic make-up or care composition comprising an oily phase comprising at least one liquid polyester obtained by condensation of unsaturated fatty acid dimer and/or trimer and diol, said compos ition being free from lipophilic gelling agent or comprising at the most 10 weight% thereof, relative to the weight of the composition The present invention also relates to a method of make-up of the face and body comprising the use of said compos ition A lip gloss contained silica di-me silylate 2, CI 77491 (and) CI 77492 0.26, CI 77499 0.04, C115850 0.23, CI 77891 0.15, Prunus dulcis 24, pentaery thritol tetraisostearate 10, Helianthus annuus seed wax 5, dimer dilinoleyl dimer dilino leate 35, dilinoleic acid/butanediol copolymer 10, and octyldodecanol q.s. 100%.

Keywords: cosmetic lipstick polyester oily phase

PatentPak available

Substances (2) | Reactions (0) | Citing (5)

38

Cosmetic compositions containing a polyester and a colorant and uses thereof

14 Substances • 0 Reactions • 0 Citations

Assignee: L'Oreal
World Intellectual Property Organization, WO2009147088 A1 2009-12-10 | Language: English, Database: CAplus

The present invention relates to a cosmetic or skin care composition comprising an oily phase, at least one liquid polyester obtained by condensation of unsaturated fatty acid dimer and/or trimer and of diol and at least one colorant, said compos ition being free from addnl. polar oil of mol. weight below 1000, or containing at the most 15 weight % thereof relative to the weight of the compos ition it also relates to a cosmetic product comprising such a compos ition and a method of make-up or of care of the skin, lips and/or of the integumentary appendages, comprising the application of said composition or of said product on these parts. A lip gloss contained CI 15850 0.23, CI 77891 0.15, CI 77491 0.21, CI 77492 0.05, CI 77499 0.04, alkyd 26, polyvinyl laurate 6, allyl stearat e/vinyl acetate copolymer 7, dilinooleic acid/butanediol copolymer 10, tri-Me pentaphenyl trisiloxane q.s. 100%.

Keywords: cosmetic polyester colorant lipstick

PatentPak available

Substances (14) | Reactions (0) | Citing (0)

39

Cosmetic compositions containing polyesters in a fatty phase and their uses

2 Substances • 0 Reactions • 1 Citation

Assignee: L'Oreal
France, FR2931670 A1 2009-12-04 | Language: French, Database: CAplus

The present invention relates to a cosmetic make-up or care composition comprising an oily phase comprising at least one liquid polyester obtained by condensation of unsaturated fatty acid dimer and/or trimer and diol, said compos ition being free from lipophilic gelling agent or comprising at the most 10 weight% thereof, relative to the weight of the composition The present invention also relates to a method of make-up of the face and body comprising the use of said compos ition A lip gloss contained silica di-me silylate 2, CI 77491 (and) CI 77492 0.26, CI 77499 0.04, C115850 0.23, CI 77891 0.15, Prunus dulcis 24, pentaery thritol tetraisostearate 10, Helianthus annuus seed wax 5, dimer dilinoleyl dimer dilino leate 35, dilinoleic acid/butanediol copolymer 10, and octyldodecanol q.s. 100%.

Keywords: cosmetic lipstick polyester oily phase

PatentPak available

Substances (2) | Reactions (0) | Citing (1)

40

Compositions containing a polyester in a solvent and their uses

14 Substances • 0 Reactions • 3 Citations

Assignee: L'Oreal
France, FR2931672 A1 2009-12-04 | Language: French, Database: CAplus

A cosmetic make-up contains a liquid polyester, obtained by conden sation of dimer and/or trimer of unsatu rated fatty-acids, and a diol, and a volatile oil. This composition is intended to be applied on the skin and face, eyelids, lips, and the superf icial body growths like nails, eyebrows, lashes or hair. A lip gloss contained silica di-me silylate 2, CI 77491 (and) CI 77492 0.26, CI 77499 0.04, C115850 0.23, CI 77891 0.15, Prunus dulcis 24, pentaery thritol tetraisostearate 10, Helianthus annuus seed wax 5, dimer dilinoleyl dimer dilinoleate 35, dilinoleic acid/butanediol copolymer 10, and octyldodecanol q.s. 100%.

Keywords: cosmetic lipstick polyester solvent

PatentPak available

Substances (14) | Reactions (0) | Citing (3)

41

Cosmetic compositions containing a polyester and a colorant and uses thereof

14 Substances • 0 Reactions • 3 Citations

Assignee: L'Oreal
France, FR2931671 A1 2009-12-04 | Language: French, Database: CAplus

The present invention relates to a cosmetic or skin care composition comprising an oily phase, at least one liquid polyester obtained by condensation of unsaturated fatty acid dimer and/or trimer and of diol and at least one colorant, said compos ition being free from addnl. polar oil of mol. weight below 1000, or containing at the most 15 weight % thereof relative to the weight of the compos ition it also relates to a cosmetic product comprising such a compos ition and a method of make-up or of care of the skin, lips and/or of the integumentary appendages, comprising the application of said compos ition or of said product on these parts. A lip gloss contained CI 15850 0.23, CI 77891 0.15, CI 77491 0.21, CI 77492 0.05, CI 77499 0.04, alkyd 26, polyvinyl laurate 6, allyl stearat e/vinyl acetate copolymer 7, dilinooleic acid/butanediol copolymer 10, tri-Me pentaphenyl trisiloxane q.s. 100%.

Keywords: cosmetic polyester colorant lipstick

PatentPak available

Substances (14) | Reactions (0) | Citing (3)

42

Cosmetic compositions containing a polyester and a volatile oil

4 Substances • 0 Reactions • 2 Citations

Assignee: L'Oreal
France, FR2931673 A1 2009-12-04 | Language: French, Database: CAplus

A cosmetic make-up contains a liquid polyester, obtained by conden sation of dimer and/or trimer of unsatu rated fatty-acids, and a diol, and a volatile oil. This composition is intended to be applied on the skin and face, eyelids, lips, and the superf icial body growths like nails, eyebrows, lashes or hair. A lipstick contained silica di-Me silylate 3, disteardimonium hectorite and propylene carbonate 10, CI 77499 0.25, CI 15985 2.58, CI 42090 0.16, CI 15850 0.54, CI 77891 2.74, mica and CI 77891 and CI 77491 2, perfume 0.3, acrylic acid/isobutyl acrylate/isobornyl acrylate copolymer 45, trimethylsilxoyphenyl dimethicone 10, dilinoleic acid/butanediol copolymer 10, ozokerite 0.30, cera alba 2.70, bid-diglyceryl polyacryladipate-2 16, tocopheryl acetate 0.2, tri- Me pentaphenyl trisiloxane q.s., octyl dodecanol q.s. 100%.

Keywords: cosmetic lipstick polyester volatile oil

PatentPak available

Substances (4) | Reactions (0) | Citing (2)

Copyright © 2025 American Chemical Society (ACS). All Rights Reserved.
Internal use only. Redistribution is subject to the terms of your CAS SciFinder License Agreement and CAS Information Use Policies.

Bibliographic Data

Application No: 18/066,105

Foreign Priority claimed: ○ Yes ◉ No

35 USC 119 (a-d) conditions met: ☐ Yes ☑ No ☐ Met After Allowance

Verified and Acknowledged: /Brian Gulledge/ Examiner's Signature | Initials

Title: BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
12/14/2022	424	1699	GRAN-1012-U-D
RULE			

APPLICANTS

Grant Industries, Inc., Elmwood Park, NJ, UNITED STATES

INVENTORS

Anna K. CROOM, Brooklyn, NY, UNITED STATES

Ronald V. LERUM, Leonia, NJ, UNITED STATES

John GORMLEY, Midland Park, NJ, UNITED STATES

CONTINUING DATA

This application is a DIV of 16992831 08/13/2020 PAT 11534389

16992831 has PRO of 62976015 02/13/2020

16992831 has PRO of 62893968 08/30/2019

FOREIGN APPLICATIONS

IF REQUIRED, FOREIGN LICENSE GRANTED**

01/12/2023

**** SMALL ENTITY ****

STATE OR COUNTRY

UNITED STATES

ADDRESS

LUCAS & MERCANTI, LLP

30 BROAD STREET

21st FLOOR

NEW YORK, NY 10004

UNITED STATES

FILING FEE RECEIVED

$150

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (01-22)
Approved for use through 05/31/2024. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM
Art Unit	1699
Examiner Name	Brian M GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4404296	A	1983-09-13	SCHAEPEL DIETMAR	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20150197610	A1	2015-07-16	PETERSON BRUCE W, et al.	
	2	20050276770	A1	2005-12-15	FILIPPI, et al.	
	3	20090081137	A1	2009-03-26	NGUYEN KIM, et al.	
	4	20080287604	A1	2008-11-20	WIBAUX	

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]

PC 6.1.24

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM
Art Unit	1699
Examiner Name	Brian M GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

	1	2016090081	WO	A1	2016-06-09	LUBRIZOL ADVANCED MAT INC		☐
	2	2759572	EP	A1	2014-07-30	TEKNOR APEX CO, et al.		☐
	3	2008201698	JP	A	2008-09-04	LINTEC CORP	English Abstract	☒
	4	2011178693	JP	A	2011-09-15	KOSE CORP, et al.	English Abstract	☒
	5	H04320457	JP	A	1992-11-11	KUBO YASUSHI, et al.	English Abstract	☒
	6	2017114773	JP	A	2017-06-29	OREAL	English Abstract	☒
	7	2018199653	JP	A	2018-12-20	TOSHIKI PIGMENT KK, et al.	English Abstract	☒
	8	2008039466	WO	A1	2008-04-03	DU PONT, et al.		☐
	9	2380557	EP	A1	2011-10-26	KONISHI CO LTD, et al.		☐
	10	2365024	EP	A1	2011-09-14	KONISHI CO LTD		☐
	11	2008260722	JP	A	2008-10-30	DAINICHISEIKA COLOR CHEM, et al.	English Abstract	☒

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	18066105
	Filing Date	2022-12-14
	First Named Inventor	Anna K. CROOM
	Art Unit	1699
	Examiner Name	Brian M GULLEDGE
	Attorney Docket Number	GRAN-1012-U-D

	12	2008239542	JP	A	2008-10-09	DAINICHISEIKA COLOR CHEM, et al.	English Abstract	☒
	13	H05262622	JP	A	1993-10-12	NEGAMI KOGYO KK	English Abstract	☒
	14	2018122532	WO	A1	2018-07-05	LVMH RECH	English Abstract	☒
	15	3778689	EP	A1	2021-02-17	MITSUI CHEMICALS INC		☐
	16	3778690	EP	A1	2021-02-17	MITSUI CHEMICALS INC		☐

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	MUTLU et al., "Castor oil as a renewable resource for the chemical industry." Eur. J. Lipid Sci. Technol., 112: 10-30 (2010).	☐
	2	SRIVASTAVA et al., "Gel Point Prediction of Metal-filled Castor Oil-based Polyurethanes System." Polym. Adv. Technol., 13: 1055-1066 (2002).	☐
	3	International Search Report issued in International Application No. PCT/US2020/041540, mailed October 16, 2020.	☐
	4	Extended European Search Report for Corresponding European Application No. 20855942.7, November 8, 2023, 13 Pages.	☐

If you wish to add additional non-patent literature document citation information please click the Add button Add

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM
Art Unit	1699
Examiner Name	Brian M GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

EXAMINER SIGNATURE			
Examiner Signature	/Brian Gulledge/	Date Considered	03/18/2025

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(**Not for submission under 37 CFR 1.99)**

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM
Art Unit	1699
Examiner Name	Brian M GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

CERTIFICATION STATEMENT

Please see 37 CFR 1.97(e) to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached certification statement.

☒ A certification statement is not submitted herewith.

FEE

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

COPIES

☐ An identification of an earlier application pursuant to 37 CFR 1.98 (d) (1) is attached.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Michael N. Mercanti/	Date (YYYY-MM-DD)	2025-01-09
Name/Print	Michael N. Mercanti	Registration Number	33966

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (01-22)
Approved for use through 05/31/2024. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	
Filing Date	
First Named Inventor	Anna K. CROOM, et al.
Art Unit	
Examiner Name	
Attorney Docket Number	GRAN-1012-U-D

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	10035871	B2	2018-07-31	LANGER, et al.	
	2	8222363	B2	2012-07-17	LIN, et al.	
	3	9376404	B2	2016-06-28	NAKAGAWA, et al.	
	4	9610237	B2	2017-04-04	BURGO, et al.	
	5	5284897	A	1994-02-08	COLUMBUS, et al.	
	6	4661099	A	1987-04-28	VON BITTERA, et al.	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	
	First Named Inventor	Anna K. CROOM, et al.
	Art Unit	
	Examiner Name	
	Attorney Docket Number	GRAN-1012-U-D

	1	20180079852	A1	2018-03-22	HECKING, et al.	
	2	20150128335	A1	2015-05-14	DEHNI	
	3	20030092932	A1	2003-05-15	TONG, et al.	
	4	20180371149	A1	2018-12-27	LANGER, et al.	
	5	20130079486	A1	2013-03-28	HIDESAKI, et al.	
	6	20110045983	A1	2011-02-24	HEALY, et al.	
	7	20180208720	A1	2018-07-26	HASEGAWA, et al.	
	8	20110014139	A1	2011-01-20	VIALA, et al.	
	9	20120046358	A1	2012-02-23	CHENG, et al.	
	10	20090232752	A1	2009-09-17	CARSON, et al.	
	11	20190169390	A1	2019-06-06	PETERSON, et al.	

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	
	First Named Inventor	Anna K. CROOM, et al.
	Art Unit	
	Examiner Name	
	Attorney Docket Number	GRAN-1012-U-D

	12	20160067153	A1	2016-03-10	CHEN, et al.	
	13	20180311140	A1	2018-11-01	PERNER, et al.	
	14	20180369125	A1	2018-12-27	WOODLAND, et al.	

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	2013074655	WO	A1	2013-05-23	INOLEX INVESTMENT CORPORATION		
	2	2018183440	WO	A1	2018-10-04	FORD GLOBAL TECHNOLOGIES, LLC		
	3	2014167518	WO	A1	2014-10-16	STERIPAK PTY LTD		
	4	6892253	JP	B2	2021-06-23	MITSUI CHEMICALS INC	English Abstract	
	5	2021007489	WO	A1	2021-01-14	NANOMETICS LLC		
	6	2021231527	WO	A1	2021-11-18	NANOMETICS LLC		

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	
	First Named Inventor	Anna K. CROOM, et al.
	Art Unit	
	Examiner Name	
	Attorney Docket Number	GRAN-1012-U-D

	7	2021257937	WO	A1	2021-12-23	NANOMETICS LLC		
	8	1142959	EP	A1	2001-10-10	DAI ICHI KOGYO SEIYAKU CO LTD		
	9	3631542	JP	B2	2005-03-23	DAI ICHI KOGYO SEIYAKU CO LTD	English Abstract	

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	International Search Report and Written Opinion for International Application No. PCT/US2020/046170 (10 Pages) (November 18, 2020).	
	2	International Preliminary Report on Patentability for International Application No. PCT/US2020/046170 (9 Pages) (March 10, 2022).	
	3	Written Opinion corresponding to PCT/US2020/041540 (14 Pages) (October 16, 2020).	
	4	Becker et al., "Safety Assessment of Polyurethanes as Used in Cosmetics,", Cosmetic Ingredient Review, pages 1-96., 2017.	

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature	/Brian Gulledge/	Date Considered	03/18/2025

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	
	Filing Date	
	First Named Inventor	Anna K. CROOM, et al.
	Art Unit	
	Examiner Name	
	Attorney Docket Number	GRAN-1012-U-D

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99**)	Application Number	
	Filing Date	
	First Named Inventor	Anna K. CROOM, et al.
	Art Unit	
	Examiner Name	
	Attorney Docket Number	GRAN-1012-U-D

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Michael N. Mercanti/	Date (YYYY-MM-DD)	2022-12-14
Name/Print	Michael N. Mercanti	Registration Number	33966

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
18/066,105	12/14/2022	Anna K. CROOM	GRAN-1012-U-D	1563

20311 7590 04/10/2025

LUCAS & MERCANTI, LLP
30 BROAD STREET
21st FLOOR
NEW YORK, NY 10004

EXAMINER	
GULLEDGE, BRIAN M	

ART UNIT	PAPER NUMBER
1699	

NOTIFICATION DATE	DELIVERY MODE
04/10/2025	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

info@lmiplaw.com

Office Action Summary	Application No. 18/066,105	Applicant(s) CROOM et al.	
	Examiner Brian Gulledge	Art Unit 1699	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☑ Responsive to communication(s) filed on 14 March 2025.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL.** 2b) ☑ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5) ☑ Claim(s) 1-53 is/are pending in the application.

5a) Of the above claim(s) 1-27,30,36-45 and 47-53 is/are withdrawn from consideration.

6) ☐ Claim(s) _____ is/are allowed.

7) ☑ Claim(s) 28-29,33-35 and 46 is/are rejected.

8) ☑ Claim(s) 31-32 is/are objected to.

9) ☐ Claim(s) _____ are subject to restriction and/or election requirement

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to **PPHfeedback@uspto.gov.**

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☑ Notice of References Cited (PTO-892)

2) ☑ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date _____.

4) ☐ Other: _____.

DETAILED ACTION

AIA Status

The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA. In the event the determination of the status of the application as subject to AIA 35 U.S.C. 102 and 103 (or as subject to pre-AIA 35 U.S.C. 102 and 103) is incorrect, any correction of the statutory basis for the rejection will not be considered a new ground of rejection if the prior art relied upon, and the rationale supporting the rejection, would be the same under either status.

Election/Restrictions

Applicant's election with traverse of the species of polymer prepared from 1,5-pentamethylene diisocyanate trimer and dilinoleic acid/propanediol copolymer in the reply filed on 19 February 2025 is acknowledged. The traversal is on the ground(s) that the search will not be an undue burden. This is not found persuasive because the burden is present for the reasons put forth in the requirement (the inventions require a different field of search, for example, searching different classes/subclasses or electronic resources, or employing different search queries).

Applicant's election without traverse of Group II (claims 28-44 and 46-47) in the reply filed on 14 March 2025 is acknowledged. The requirements are still deemed proper and is therefore made FINAL.

Claims 1-27, 45, and 48-53 are withdrawn from further consideration pursuant to 37 CFR 1.142(b), as being drawn to a nonelected invention, there being no allowable generic or linking claim.

Claims 30, 36-44, and 47 are withdrawn from further consideration pursuant to 37 CFR 1.142(b), as being drawn to a nonelected species, there being no allowable generic or linking claim. The Examiner notes that the elected species (dilinoleic acid/propanediol copolymer) is considered to be a polymer per the instant disclosure (see page 10 of the instant specification) and not to be a polyol per the instant disclosure (see page 11 of the instant specification).

Claim Rejections - 35 USC § 112 - Indefiniteness

The following is a quotation of 35 U.S.C. 112(b):

> (b) CONCLUSION.—The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the inventor or a joint inventor regards as the invention.

Claim 33 is rejected under 35 U.S.C. 112(b) as being indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor regards as the invention.

Claim 33 recites the limitation "the diol." There is insufficient antecedent basis for this limitation in the claim. The claim depends from claim 28, and there is no diol recited by this claim.

For the purposes of claim interpretation, claim 33 will be considered to depend from and further limit claim 32, which does recite the inclusion of a diol.

Claim Rejections - 35 USC § 102

The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

> A person shall be entitled to a patent unless –
>
> (a)(1) the claimed invention was patented, described in a printed publication, or in public use, on sale, or otherwise available to the public before the effective filing date of the claimed invention.

Claims 28-29, 34-35, and 46 are rejected under 35 U.S.C. 102(a)(1) as being anticipated by Achterhof et al. (US Patent 3,192,185).

Acterhof et al. discloses polyurethane elastomers (column 1, lines 11-14). One exemplified material is prepared from a polyester and a polyisocyanate, and is crosslinked (example 2).

Allowable Subject Matter

Claims 31 and 32 are objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims.

The following is a statement of reasons for the indication of allowable subject matter. The subject matter of instant claims 31-33 is free of the prior art. The closest prior art is considered the above cited Acterhof et al. However, the use of the specific polyurethane instantly recited is not suggested therein. The specific species elected (the polyurethane prepared from DAPD polyol and PDT) is not suggested by the prior art. Also, crosslinked elastomers prepared from multifunctional crosslinkers and esterified dilinoleic acid are free of the prior art.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Brian Gulledge whose telephone number is (571) 270-5756. The examiner can normally be reached Monday - Friday 7am - 4pm.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is

encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Fereydoun Sajjadi can be reached on (571) 272-3311. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of published or unpublished applications may be obtained from Patent Center. Unpublished application information in Patent Center is available to registered users. To file and manage patent submissions in Patent Center, visit: https://patentcenter.uspto.gov. Visit https://www.uspto.gov/patents/apply/patent-center for more information about Patent Center and https://www.uspto.gov/patents/docx for information about filing in DOCX format. For additional questions, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Brian Gulledge/
Primary Examiner, Art Unit 1699

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
18/066,105	**04/18/2025 11:05:49 AM Z ET**	**GRAN-1012-U-D**

Title of Invention

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	1563	FILED BY	Carla Curado
PATENT CENTER #	70063370	FILING DATE	12/14/2022
CUSTOMER #	20311	FIRST NAMED INVENTOR	Anna K. CROOM
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Lindsay Adams

Documents

TOTAL DOCUMENTS: 1

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
Response_GRAN1012UD.pdf	11	Amendment/Request for Reconsideration-After Non-Final Rejection	138 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
Response_GRAN1012UD.pdf	573AB1E21126BF20CDC19B9EB24D8E523BA8EDF709B57770 586E1F4F548BA7FEDD0230A114A6988950EB13B13FBE79166 BEA12DE37BCE1F58AFB580A52CA8A86

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC PAYMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
18/066,105	**04/18/2025 11:05:49 AM Z ET**	**GRAN-1012-U-D**

Title of Invention

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	1563	FILED BY	Carla Curado
PATENT CENTER #	70063370	AUTHORIZED BY	Lindsay Adams
CUSTOMER #	20311	FILING DATE	12/14/2022
CORRESPONDENCE ADDRESS	-	FIRST NAMED INVENTOR	Anna K. CROOM

Payment Information

PAYMENT METHOD	PAYMENT TRANSACTION ID	PAYMENT AUTHORIZED BY
CARD / 1054	**E20254HB06315115**	**Carla Curado**

FEE CODE	DESCRIPTION	ITEM PRICE($)	QUANTITY	ITEM TOTAL($)
2202	EACH CLAIM IN EXCESS OF 20	80.00	7	560.00
			TOTAL AMOUNT:	**$560.00**

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage

submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT & TRADEMARK OFFICE

Examiner: Brian M. GULLEDGE Art Unit: 1699

Re: Application of: Anna K. CROOM, et al.

Serial No.: 18/066,105

Filed: 12/14/2022

For: **BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE**

Confirmation No.: 1563

RESPONSE

Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

April 18, 2025

SIR:

In response to the Non-Final Office Action dated April 10, 2025, please amend the above-identified patent application as follows:

Amendments to the Claims begin on page **2** of this paper.

Remarks begin on page **9** of this paper.

AMENDMENTS TO THE CLAIMS:

This listing of claims will replace all prior versions and listings of claims in the application:

1. (Withdrawn/Previously Presented) A process of preparing a non-aqueous gel composition, comprising:

a) micronizing a cross-linked polyurethane elastomer rubber composition, comprising a cross-linked polyurethane elastomer rubber and a urethanation catalyst in the presence of a cosmetic emollient wherein the cosmetic emollient forms a solvent matrix substantially surrounding the cross-linked polyurethane elastomer rubber; and optionally,

b) combining the mixture resulting from step a) with a secondary solvent whereby a non-aqueous gel composition is formed.

2. (Withdrawn) The process of claim 1, wherein the secondary solvent is the secondary solvent is selected from the group consisting of triheptanoin; undecane; tridecane; or wherein the secondary solvents are naturally derived alkanes or naturally derived esters.

3. (Withdrawn) The process of claim 1, wherein the amount of the micronized cross-linked polyurethane elastomer rubber composition in the non-aqueous gel composition is from about 30 to about 5 weight %.

4. (Withdrawn) The process of claim 1, wherein the amount of the cosmetic emollient in the non-aqueous gel composition is from about 70 to about 95 weight %.

5. (Withdrawn) The process of claim 1, further comprising combining the non-aqueous gel composition with an active composition, optionally selected from the group consisting of selected from vitamins, sunscreens, plant extracts, fragrances and mixtures thereof.

6. (Withdrawn) The process of claim 1, further comprising combining the non-aqueous gel composition with a member of the group consisting of fragrances, colorants, preservatives, active compositions, and mixtures thereof.

7. (Withdrawn) The process of claim 1, wherein the micronized cross-linked polyurethane elastomer rubber composition has a cross-sectional diameter of from about 1 to about 61 microns.

8. (Withdrawn) The process of claim 1, wherein non-aqueous gel composition has a viscosity ranging from about 15,000 cP to about 1,000,000 cP.

9. (Withdrawn) The process of claim 1, wherein the cross-linked polyurethane elastomer rubber composition has a hardness force greater than 200 g, as measured by a texture analyzer prior to any milling or dilution and the cross-linked polyurethane elastomer rubber composition has a resilience greater than or equal to 70%.

10. (Withdrawn) The process of claim 1, wherein the cross-linked polyurethane rubber composition is formed with a prepolymer having at least two free hydroxyl groups.

11. (Withdrawn) The process of claim 1, wherein the solvent matrix comprises a second cosmetic emollient.

12. (Withdrawn) The process of claim 10, wherein the polyurethane elastomer rubber is formed with from about 5 to about 25 weight percent of a prepolymer having at least two free hydroxyl groups.

13. (Withdrawn) The process of claim 1, wherein the polyurethane elastomer rubber composition is formed with from about 1 to about 20 weight percent of an isocyanate functionalized molecule and a prepolymer having OH-groups.

14. (Withdrawn/Previously Presented) The process of claim 10, wherein the prepolymer is a dimer acid/diol reaction product of a diol and a dimer acid.

15. (Withdrawn) The process of claim 1, wherein the polyurethane elastomer rubber composition is formed with a polyisocyanate, optionally containing from about 15 to about 38 weight% NCO.

16. (Withdrawn) The process of claim 15, wherein the overall molar ratio between the NCO in the polyisocyanate and the OH groups in the prepolymer is from 2:1 to 1:2.

17. (Withdrawn) The process of claim 1, wherein the amount of urethanation catalyst in the cross-linked polyurethane elastomer rubber composition is from about 0.1 to about 2.5 weight%.

18. (Withdrawn) The process of claim 1, wherein the urethanation catalyst is a bismuth, zinc, or amine catalyst.

19. (Withdrawn) The process of claim 1, wherein the cross-linked polyurethane elastomer rubber composition includes an amount of a finisher containing an alcohol or an amine sufficient to quench unreacted isocyanate groups.

20. (Withdrawn) The process of claim 1, wherein the cross-linked polyurethane elastomer rubber composition is formed with a bio-based and biodegradable prepolymer.

21. (Withdrawn) The process of claim 15, wherein the prepolymer, the polyisocyanate, and the cosmetic emollient are bio-based and biodegradable.

22. (Withdrawn) The process of claim 1, wherein the cross-linked polyurethane elastomer rubber composition is comprised of greater than about 85% renewable, bio-based feedstocks.

23. (Withdrawn) The process of claim 21, wherein the bio-based and biodegradable polyisocyanate is 1,5-pentamethylene diisocyanate trimer.

24. (Withdrawn) The process of claim 14, wherein the dimer acid/diol is a polyester reaction product of a diol and a dimer acid.

25. (Withdrawn) The process of claim 14, wherein the prepolymer is a cross-linked prepolymer.

26. (Withdrawn) The process of claim 24, wherein the polyester reaction product is a branched C_{36} dicarboxylic acid/diol copolymer.

27. (Withdrawn) The process of claim 26, wherein the branched C_{36} dicarboxylic acid/diol copolymer is dilinoleic acid/propanediol copolymer or dilinoleic acid/butanediol.

28. (Currently Amended) A cross-linked elastomer comprising a reaction product of a polyester and a multi-functional crosslinker, wherein the polyester is an esterified dilinoleic acid or a branched C_{36} dicarboxylic acid/diol copolymer.

29. (Previously Presented) The cross-linked elastomer of claim 28, wherein the multi-functional crosslinker is polyisocyanate.

30. (Withdrawn) The cross-linked elastomer of claim 28, wherein the polyester is castor oil.

31. (Cancelled).

32. (Cancelled).

33. (Previously Presented) The cross-linked elastomer of claim 28, wherein the diol is propanediol or butanediol.

34. (Previously Presented) The cross-linked elastomer of claim 28, where in the polyester is greater than 60% by weight of the total weight of the cross-linked elastomer.

35. (Previously Presented) The cross-linked elastomer of claim 28, where in the polyester is greater than 75% by weight of the total weight of the cross-linked elastomer

36. (Withdrawn) A cross-linked elastomer comprising the reaction product of a polyol and a multi-functional crosslinker.

37. (Withdrawn) The cross-linked elastomer of claim 36, wherein the multi-functional crosslinker is polyisocyanate.

38. (Withdrawn) The cross-linked elastomer of claim 36, wherein the polyol is castor oil.

39. (Withdrawn) The cross-linked elastomer of claim 36, wherein the polyol is a dimer acid/diol.

40. (Withdrawn) The cross-linked elastomer of claim 38, wherein the dimer acid/ diol is a branched C_{36} dicarboxylic acid/diol copolymer.

41. (Withdrawn) The cross-linked elastomer of claim 36, wherein the diol is propanediol or butanediol.

42. (Withdrawn) The cross-linked elastomer of claim 40, wherein the branched C_{36} dicarboxylic acid/diol copolymer is dilinoleic acid/propanediol copolymer, or dilinoleic acid/butanediol copolymer.

43. (Withdrawn) The cross-linked elastomer of claim 36, wherein the polyol is a diol or a polyol-functionalized polyester having an effective molecular weight of 280 to 3000 g/mol.

44. (Withdrawn) The cross-linked elastomer of claim 36, wherein the polyol includes glycerol or polyglycerol.

45. (Withdrawn) The process of claim 1, wherein the non-aqueous gel composition is silicone-free.

46. (Previously Presented) The cross-linked elastomer of claim 28, wherein the cross-linked elastomer is silicone-free.

47. (Withdrawn) The cross-linked elastomer of claims 36, wherein the cross-linked elastomer is silicone-free.

48. (Withdrawn) A cosmetic and personal care composition comprising the non-aqueous gel composition of claim 1.

49. (Withdrawn) The cosmetic and personal care composition of claim 48, further comprising a water phase and an oil phase.

50. (Withdrawn) A cosmetic and personal care composition comprising the cross-linked elastomer of claim 28 and a carrier fluid.

51. (Withdrawn/Currently amended) The cosmetic and personal care composition of claim 50 [[45]], further comprising a water phase and an oil phase.

52. (Withdrawn) A cosmetic and personal care composition comprising the cross-linked elastomer of claim 36 and a carrier fluid.

53. (Withdrawn) The cosmetic and personal care composition of claim 52, further comprising a water phase and an oil phase.

54. (New) The cross-linked elastomer of claim 28, wherein the branched C_{36} dicarboxylic acid/diol copolymer is dilinoleic acid/propanediol copolymer or dilinoleic acid/butanediol copolymer.

55. (New) A gel composition comprising the cross-linked elastomer of claim 28 dispersed in a carrier fluid.

56. (New) The gel composition of claim 55, the cross-linked elastomer is in micronized form.

57. (New) The gel composition of claim 56, wherein the cross-linked elastomer in micronized form has a particle size from 1 to 100 microns.

58. (New) The gel composition of claim 57, wherein the particle size is less than 60 microns.

59. (New) The gel composition of claim 55, wherein the gel has a viscosity ranging from 15,000 cP to 1,000,000 cP.

60. (New) The cosmetic and personal care composition of claim 50, wherein the composition further comprises an active selected from the group consisting of selected from vitamins, sunscreens, plant extracts, fragrances and mixtures thereof.

61. (New) The cosmetic and personal care composition of claim 50, further comprising fragrances, colorants, preservatives, or mixtures thereof.

62. (New) The cosmetic and personal care composition of claim 50, wherein the composition is a foundation, a lotion, a cream, a shampoo, a serum, or a lip care formulation.

REMARKS

Applicant has carefully considered the Non-Final Office Action dated April 10, 2025. Applicant respectfully requests reconsideration of the present application in view of the amendments to the claims and remarks presented herein. Applicant also thanks the Examiner for the indication that claims 31 and 32 contain allowable subject matter.

A. STATUS OF THE CLAIMS AND COMMENTS

Claims 1-53 were previously pending and have been examined. Claim 28 has been amended to include the subject matter of allowable claims 31 and 32, which are now cancelled. Applicant has further amended claim 51 and added new claims 54-62.

Claim 51 has been amended to correct an obvious error with claim dependency. Claim 51 incorrectly depended from claim 45. Claim 51 now depends from claim 50, which is directed to a cosmetic and personal care composition comprising the cross-linked elastomer of claim 28.

New claim 54 further limits the branched C_{36} dicarboxylic acid/diol copolymer of claim 28. Support is found in claim 42.

Claims 55-59 are directed to a gel composition incorporating the cross-linked elastomer of claim 28. Support for claim 55 is found in the specification, as filed, at paragraph [0033]. Support for claim 56 is found in paragraph [0296] and original claim 1. Support for claims 57 and 58 is found, *inter alia*, in paragraphs [0017], [0026], [0305] and original claim 7. Support for claim 59 is found, *inter alia*, in paragraph [0036] and original claim 8.

Claims 60-62 further limit the cosmetic and personal care composition of claim 50. Support for claims 60 and 61 is found, *inter alia*, in original claims 5 and 6. Support for claim 62 is found in paragraphs [0255] and [0313] to [0316].

No new matter is being added. Entry of the amendments is respectfully requested.

B. CLAIM REJECTIONS UNDER 35 U.S.C. 112(b)

Claim 33 is rejected under 35 U.S.C. 112(b) as being vague and indefinite. The Office Action states there is no antecedent basis for a "diol" in claim 28.

In response, Applicant respectfully submits that the amendment to claim 28 rectifies this issue. Applicant also thanks the Examiner for pointing out this issue

Withdrawal of the rejection is respectfully requested.

C. CLAIM REJECTIONS UNDER 35 U.S.C. 102(a)(1)

Claims 28-29, 34-35, and 46 are rejected under 35 U.S.C. 102(a)(l) as being anticipated by Achterhof et al. (US Patent 3,192,185).

In response, Applicant has amended claim 28 to include the subject matter of objected claims 31 and 32. As a result, the above-rejection is considered moot.

Withdrawal of the rejection is respectfully requested.

D. REJOINDER

Applicant hereby requests rejoinder of claims 50 and 51, and joinder of new claims 54-62, since claim 28 is now in allowable form. Claims 50 and 51 are directed to a cosmetic and personal care composition incorporating the cross-linked elastomer of claim 28. Claim 54 further limits the branched C_{36} dicarboxylic acid/diol copolymer of claim 28. Claims 55-59 are directed to a gel composition incorporating the cross-linked elastomer of claim 28. Claims 60-62 further limit the cosmetic and personal care composition of claim 50, which incorporates the cross-linked elastomer of claim 28. Due to their dependency from claim 28, rejoinder of claims 50 and 51, and joinder of new claims 54-62, is respectfully requested.

E. FEES

This response is being filed within a shortened period of reply along with the requisite fees for extra claims. No further fees are believed due. If it is determined that further fees are due, or any overpayment has been made, the Assistant Commissioner is hereby authorized to debit or credit such sum to Deposit Account No. 02-2275.

Pursuant to 37 C.F.R. 1.136(a)(3), please treat this and any concurrent or future reply in this application that requires a petition for an extension of time for its timely submission as incorporating a petition for extension of time for the appropriate length of time. The fee associated therewith is to be charged to Deposit Account No. 02-2275.

F. CONCLUSION

In view of the actions taken and arguments presented, it is respectfully submitted that each and every one of the matters raised by the Examiner has been addressed in this response and that the present application is now in condition for allowance which action is earnestly solicited.

The Examiner is asked to contact the undersigned if there are any questions regarding the response or if there are any further steps which would place the application in condition for allowance and which can be addressed by telephone.

Respectfully submitted,

LUCAS & MERCANTI, LLP

By: /Lindsay S. Adams/
Lindsay S. Adams
Registration No. 36,425

LUCAS & MERCANTI, LLP
30 Broad Street
New York, NY 10004
Phone: 212-661-8000

Espacenet

JP2000313731A ELASTIC GEL FOR MANNEQUIN

Applicants: TAKIRON CO

Inventors: SHIKINAMI YASUO,TSUTA KAORU

Classifications:
IPC ***A47F8/00; C08G18/10; C08G18/48; C08L75/08;*** (IPC1-7): A47F8/00; C08G18/10; C08G18/48; C08L75/08;

Priorities: JP12384299A 1999-04-30

Application: JP12384299A·1999-04-30

Publication: JP2000313731A·2000-11-14

Published as: JP2000313731A;**JP3614316B2**

ELASTIC GEL FOR MANNEQUIN

Abstract

PROBLEM TO BE SOLVED: To obtain an elastic gel for mannequin, preferably useful in the case of producing a soft mannequin having flexibility and elasticity approximately similar to soft tissues of human body. SOLUTION: This polyurethane gel is obtained by reacting an alkylene oxide chain-containing polyol liquid at a normal temperature and/or an alkylene oxide chain-containing polyurethane polyol prepolymer with an alkylene oxide chain- containing polyurethane polyisocyanate prepolymer liquid at a normal temperature, contains an organic dispersion medium for raising gel flexibility and has 20% modulus value in compressive deformation in the range of 50-750 g/cm2.

(19) [Publication country] JP
(12) [Kind of official gazette] A
(11) [Publication number] 2000313731
(43) [Date of publication of application] 20001114
(54) [Title of the invention] ELASTIC GEL FOR MANNEQUIN
(51) [International Patent Classification 7th Edition]
C08G 18/10 A47F 8/00 C08G 18/48 C08L 75/08
[FI]
C08G 18/10
A47F 8/00
C08G 18/48 Z
C08L 75/08

(21) [Application number] 11123842
(22) [Filing date] 19990430
(71) [Applicant]
[Name] TAKIRON CO LTD

(72) [Inventor]
[Full name] SHIKINAMI YASUO
[Full name] TSUTA KAORU

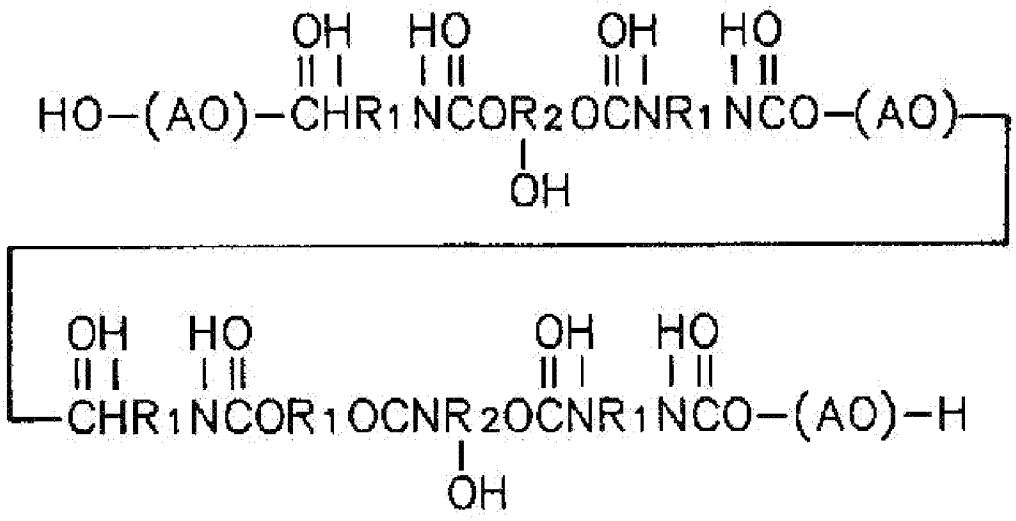
[Theme code (reference)]
4J002
4J034
[F-term (reference)]
4J002 CH052 CK041 EH036 EL106 GC00
4J034 BA03 BA07 DA01 DB01 DB03 DB05 DB07 DG02 DG03 DG04 DG05 DG06 DG08 DG10 DG12 DG14 HA01 HA02 HA07 HB12 HC03 HC12 HC13 HC17 HC22 HC46 HC52 HC61 HC64 HC67 HC71 HC73 JA42 JA44 KA01 KB04 KC17 KD02 KD12 KE02 LA22 LA33 MA12 MA24 QB13 QB14 QC06 RA03

(57) [Overview]
PROBLEM TO BE SOLVED: To obtain an elastic gel for mannequin, preferably useful in the case of producing a soft mannequin having flexibility and elasticity approximately similar to soft tissues of human body.
SOLUTION: This polyurethane gel is obtained by reacting an alkylene oxide chain-containing polyol liquid at a normal temperature and/or an alkylene oxide chain-containing polyurethane polyol prepolymer with an alkylene oxide chain- containing polyurethane polyisocyanate prepolymer liquid at a normal temperature, contains an organic dispersion medium for raising gel flexibility and has 20% modulus value in compressive deformation in the range of 50-750 g/cm2.

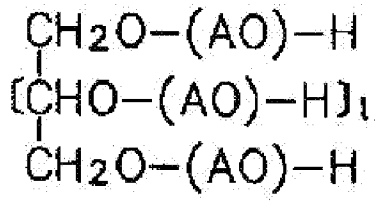
[Detailed description of the invention]
[0001]
[Technical field of invention] The present invention relates to an elastic gel for a mannequin, which is suitably used when a soft mannequin having flexibility and elasticity similar to soft tissues of a human body is manufactured.
[0002]
[Prior art] A conventional mannequin is obtained by molding a molding material such as a synthetic resin, a fiber-reinforced resin, or paper into the shape of a human body, and although the shape of the mannequin closely resembles the human body, the mannequin is a hard mannequin that is completely lacking in flexibility.
[0003]However, rigid mannequins, which are inflexible, have: For example, even when wearing underwear such as a brassiere made by three dimensional computer simulation so as to closely resemble the outer shape of a human, the shape of a part corresponding to a particularly soft human body part such as the breast, the buttocks, and the abdomen does not fit (conform to the shape of) the underwear.

To solve the problem that it is impossible to judge the true quality at the time of wearing such as how a body shape of a purchaser is changed and how the shape is changed or how underwear is fitted to the body.
[0004]Therefore, the shape adaptability of the soft tissue of the actual purchaser cannot be accurately determined from the hard mannequin wearing the high-grade underwear, and it is necessary to try on the mannequin one by one to check the change in the body shape and the quality of the fitting property. However, in view of the fact that the above-described try-on is troublesome and the underwear worn by the user becomes dirty and loses its commercial value, there has been a demand in recent years for the development of a soft mannequin having a shape and flexibility very similar to those of the human body, in particular, having flexibility of the breast, abdomen and buttocks similar to those of the human body.
[0005]
[Problem to be solved by the invention] An object of the present invention is to provide an elastic gel for a mannequin, which is suitable for use in manufacturing a soft mannequin and has flexibility and elasticity substantially equal to those of soft tissues of a human body.
[0006]
[Means for solving the problem] Solution to Problem In order to solve the above problems, an elastic gel for a mannequin according to claim 1 of the present invention includes: a polyol having an alkylene oxide chain that is liquid at normal temperature or / and a polyurethane polyol prepolymer having an alkylene oxide chain that is liquid at normal temperature; The polyurethane gel is obtained by reacting a polyurethane polyisocyanate prepolymer having an alkylene oxide chain which is liquid at normal temperature. The gel contains an organic dispersion medium for increasing the flexibility of the gel, and the value of 20% modulus at the time of compression deformation is in the range of 50-750g/cm2 .
[0007]This elastic gel makes an organic dispersion medium contain into internal penetrating [which was structurized by the three-dimensional network by the segment of the alkylene oxide chain] type (IPN:interpeneturated) segmented polyurethane It is a ratio of the functional group of an end about the reaction ratio of a polyol ingredient and a polyisocyanate component so that it may mention below, That is, the value of the 20% modulus at the time of compression deformation is controlled in the range of 50-750g/cm2 by regulating the value of OH/NCO, adjusting the segment length of the alkyleneoxide chain, adjusting the network chain concentration of the three dimensional network, or adjusting the content of the organic dispersion medium.
[0008]As the polyol component, those represented by the following structural formulae (1) to (4) are used, and as the polyisocyanate component, those represented by the following structural formulae (5) to (9) are used.
[0009]
[Chemical formula 1]

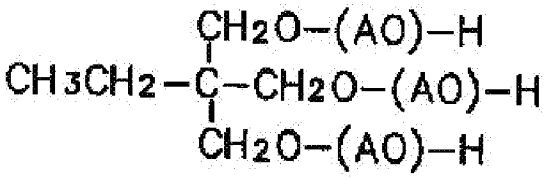
構造式（1）



構造式（2）



構造式（3）



構造式（4）



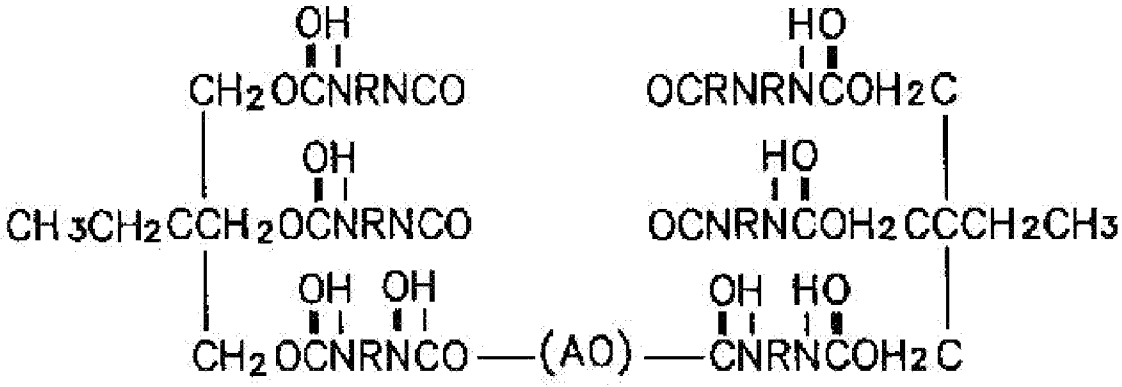
(In the structural formulae (1) to (4), R1 and R2 are any one of alkyl compounds, cycloaliphatic compounds, and aromatic compounds, (AO) is an alkyleneoxide chain, and R is hydrogen or any one of alkyl compounds, cycloaliphatic compounds, and aromatic compounds.

In the formula, 1 is an integer of 1 or 4.)

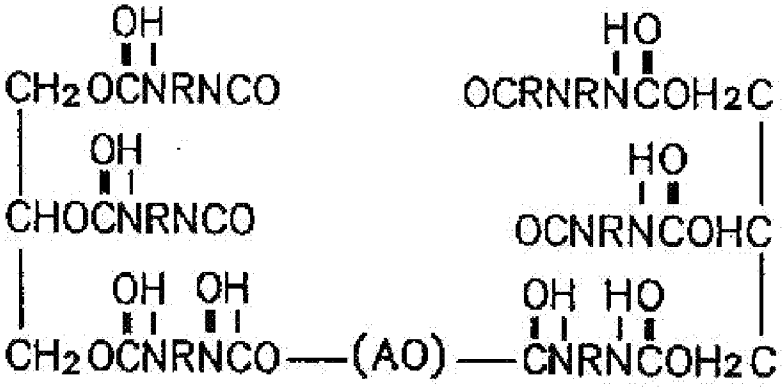
[0010]

[Chemical formula 2]

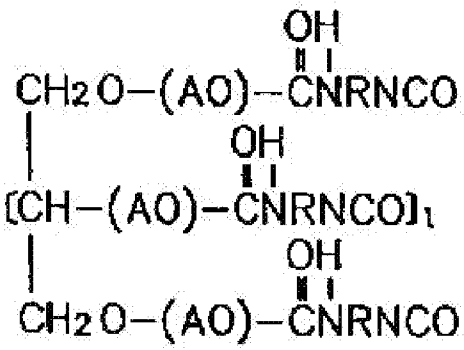
構造式（5）



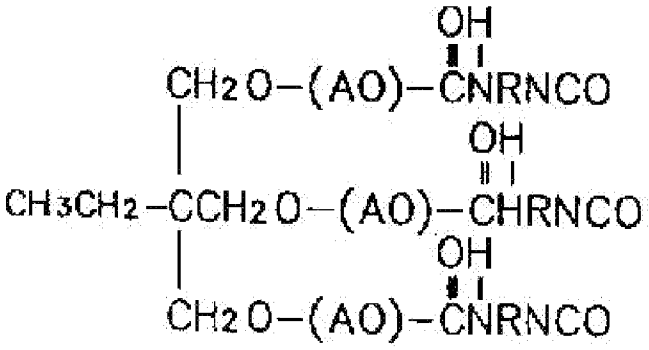
構造式（6）



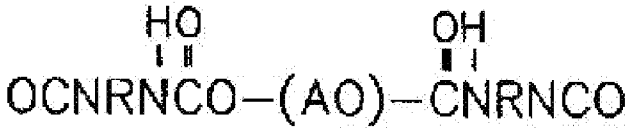
構造式（7）



構造式（8）



構造式(9)



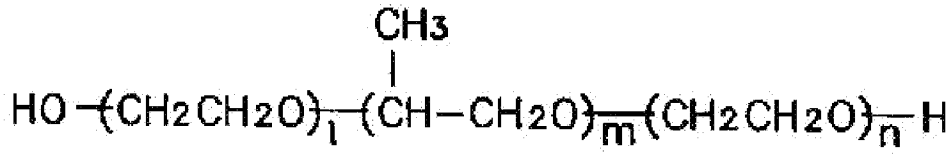
In the structural formulae (5) to (9), (AO) is an alkylene oxide chain, R is an alkyl group, an alicyclic compound or an aromatic compound, and 1 is an integer of 1 or 4.)
[0011]The structural formula (1) is a polyurethane polyol prepolymer which is a reaction product of a polyether polyol and a diisocyanate, in which both terminal components are polyether polyols and both terminals are - OH groups. The diisocyanate compound used herein is the same as that in the polyurethane polyisocyanate prepolymer described below, and examples thereof include phenylenediisocyanate, 2,2,4-tolu ylene ester diisocyanate (TDI) 4,4 ′ - diphenylmethane diisocyanate (MDI), naphthalene 1, 5-diisocyanate, hexamethylene diisocyanate (HMDI), tetramethylene diisocyanate (TMDI), lysine diisocyanate

Silylene diisocyanate (XDI), hydrogenated TDI, hydrogenated MDI, dicyclohexyldimethylmethane p, p ′ - diisocyanate, diethyl fumarate diisocyanate, isophorone diisocyanate (IPDI) and the like can be optionally used.
[0012]In the structural formula (2), polyether polyol is added to glycerol (l = 1) or sorbitol (l = 4).
[0013]Similarly, adducts of polyhydric alcohols such as 1,2,6-hexanetriol , trimethylolethane, pentaerithritol, polyglycerine and partial esters thereof with polyetherpolyols can also be used.
[0014]The structural formula (4) is a polyether polyol having an alkylene oxide chain, both terminals of which are - O

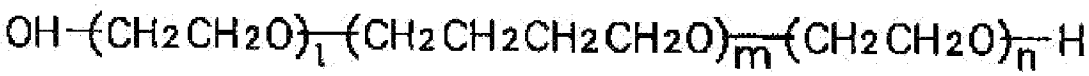
There are a case of an H group and a case in which one terminal is blocked with an alkyl group, an aromatic group, or the like, and are easily available as commercial products.
[0015]The structural formula (5) is a tetrafunctional tetraisocyanate obtained by dimerizing two molecules of a triisocyanate obtained by reacting trimethylolpropane with diisocyanate with one molecule of (AO), and the tetraisocyanate of the structural formula (6) is obtained by using glycerol instead of trimethylolpropane. Since this type of tetraisocyanate cannot be obtained by the reaction of two or three molecules of (AO) with two molecules of triisocyanate, it is necessary to finely control the reaction by reducing the amount of (AO) to less than the chemical equivalent amount. When the unreacted triisocyanate reacts with the polyol, the size of the segmented polyurethane molecule varies, which may be advantageous in controlling the elasticity of the elastic gel.
[0016]Formula (7) is a polyol of Formula (2)

Similarly, the structural formula (8) is obtained by reacting the polyol of the structural formula (3) with a diisocyanate, and is trifunctional. Structural formula (9) is a reaction product of a polyether polyol and a diisocyanate, and is bifunctional.
[0017]Examples of the compound constituting the alkylene oxide chain (AO) include polymethylene glycol, polyethylene glycol, polypropylene glycol, and mixtures thereof. Examples thereof include polybutylene glycol, polytetramethylene glycol, polypentamethylene glycol, polyhexamethylene glycol, and polyheptamethylene glycol. Among these, polyethylene glycol, polypropylene glycol, and low molecular weight polytetramethylene glycol are easily available as liquid substances at normal temperature. Further, copolymers thereof, for example, polymers represented by the following structural formulae (10) and (11) can also be used.
[0018]
[Chemical formula 3]

構造式 (10)



構造式 (11)



Where l, m, and n are each an integer of 1 or more.
[0019]These copolymers may be either block copolymers or random copolymers, and segments in one prepolymer may be composed of different kinds of alkylene oxide chains.
[0020]The ranges of the molecular weights of the polyol component and the polyisocyanate component as described above vary in a wide range depending on the kinds and molecular shapes of the alkylene oxide and the isocyanate, whether (AO) is a homopolymer or a copolymer, and the like. The weight average molecular weight is about 700 to 10000 for polyurethane-polyol prepolymers, about 150 to 6000 for polyols, and about 500 to 10000 for polyurethane-polyisocyanate prepolymers, and preferably each can be selected in the range of about 1000-6000,200-3000,800-5000 .
[0021]The flexibility and elasticity of the polyurethane gel can be controlled by regulating the reaction ratio of the polyol component and the polyisocyanate component by the ratio of the terminal functional groups, that is, the value of OH / NCO.

In general, the higher the OH/NCO value, the lower the deformation modulus value. When the value of OH/NCO is less than 1, a post-reaction occurs due to unreacted - NCO, and when the value of OH/NCO is more than 5, it is difficult to form a gel. In order to obtain a polyurethane gel having flexibility and elasticity similar to those of soft tissues of the human body, the value of OH / NCO is preferably adjusted to the range of 1.3 to 4.0, more preferably 1.5 to 3.5.
[0022]In addition, the flexibility and elasticity of the polyurethane gel vary depending on the segment length of the alkylene oxide chain (AO), and in general, as the segment length increases, the flexibility increases. Therefore, by adjusting the molecular weight of the compound constituting the alkylene oxide chain (AO), it is possible to bring the flexibility of the polyurethane gel close to that of the soft tissue of the human body. Mw:150-800 , preferably Mw:200-600 , and in the case of polypropylene glycol, Mw:200-3000 , preferably

, preferably from Mw:1000-2000 , and in the case of polytetramethylene glycol By using Mw:200-1000 , preferably Mw:400-800 , it is possible to obtain a polyurethane gel with flexibility and elasticity which closely resembles the soft tissue of the human body.
[0023]Further, the flexibility and elasticity of the polyurethane gel also vary depending on the network chain concentration of the three dimensional network, and in general, the higher the network chain concentration, the lower the flexibility. In order to obtain a polyurethane gel of a three dimensional network, one of the polyol component and the polyisocyanate component has two or more functional groups. A combination in which the other has a functionality of 3 or more may be employed, but if both components each have a functionality of 5 or more, the network chain concentration becomes

too high, making it difficult to obtain a polyurethane gel having flexibility and elasticity that closely resemble the soft tissue of the human body. It is preferable to use a combination in which one of the components has a functionality of 2 to 4 and the other component has a functionality of 3 to 4.
[0024]The organic dispersion medium contained in the polyurethane gel serves to enhance the flexibility of the gel, and examples thereof include oligomers of polyethylene glycol or polypropylene glycol in which the terminal of alkylene oxide is blocked with methoxy or ethoxy, or copolymers (which may be block or random) of both; High-boiling solvents which do not react with the components of the polyurethane, such as cyclic carbonates (e.g., propylene carbonate) and esters of higher alcohols (e.g., hexaacetate n-octyl and hexaacetate n-decyl), can be used.
[0025]The content of the organic dispersion medium is required to be in the range of 30 to 90% by weight, and when the content is less than 30% by weight, the flexibility of the polyurethane gel becomes insufficient. On the other hand, when the amount exceeds 90% by weight, gelation becomes difficult and a polyurethane gel having shape retention is not formed. The content of the organic dispersion medium is preferably 40 to 70% by weight, depending on the type of the dispersion medium.
[0026]In the organic dispersion medium-containing polyurethane gel constituting the elastic gel for a mannequin of the present invention, as described above, the reaction ratio of the polyol component and the polyisocyanate component is set to satisfy the relationship between the ratio of the terminal functional groups and That is, the value of the 20% modulus at the time of compression deformation is controlled in the range of 50-750g/cm2 by regulating the value of OH/NCO, adjusting the segment length of the alkyleneoxide chain, adjusting the network chain concentration of the three dimensional network, or adjusting the content of the organic dispersion medium.
[0027]As described above, the polyurethane gel containing an organic dispersion medium having a 20% modulus value in the range of 50-750g/cm2 has It is preferably used because it has flexibility and elasticity similar to those of soft tissues of the human body, does not change into a hard xerogel with time due to scattering of water as a dispersion medium from a gel by air drying like a hydrogel, and maintains its flexibility and elasticity.

[0028]In particular, an organic dispersion medium-containing polyurethane gel having a value of 20% modulus at the time of compression deformation in the range of 50-350g/cm2 has flexibility and elasticity very similar to that of a very flexible fatty part of a human body such as a mamma, and is a very flexible polyurethane gel which contains an organic dispersion medium and is likely to flow. Due to the network chain structure of the three dimensional network, when an external force is applied and removed, the deformed polyurethane gel has a repulsive force of a low modulus capable of instantaneously (within 0.5 seconds) restoring the original shape, and exhibits a restoring behavior very similar to that of a fatty site such as a breast. Therefore, the elastic gel is suitably used as a material for manufacturing parts of a mannequin, such as the breast, the abdomen, and the buttocks, which are strongly required to have flexibility.
[0029]On the other hand, an organic dispersion medium-containing polyurethane gel having a value of 20% modulus at the time of compressive deformation in the range of 250-750g/cm2 has the following properties: The polyurethane gel has flexibility and elasticity similar to those of human muscles, and when an external force is applied and removed, the deformed polyurethane gel has a repulsive force capable of instantaneously (within 0.5 seconds) restoring its original shape, and shows a restoring behavior similar to that of muscles. Therefore, the elastic gel is suitably used as a material for manufacturing muscular parts of a mannequin, which do not require high flexibility, except for the breast, abdomen, buttocks, and the like.
[0030]The organic dispersion medium-containing polyurethane gel can be easily obtained by casting a mixture of a polyol component, a polyisocyanate component and an organic dispersion medium, and reacting the polyol component with the polyisocyanate component under heating or at room temperature. In this case, an appropriate amount (about 0.01 to 1.0% by weight) of a tertiary amine such as dibutyltin dilaurate, trialkylamine, or triethylenediamine may be added as a catalyst to adjust the reaction rate.
[0031]While the above examples describe an elastic gel using a polyurethane gel, other elastic gels may also be used. For example, a dispersion medium having affinity for an acrylic gel or a polyvinyl alcohol gel, such as water or an alcohol, is added to the gel. It is also theoretically possible to prepare and use a gel in which the value of the 20% modulus at the time of compression deformation is defined as 50-750g/cm2 , and the time to restore the original shape when the external pressure is

removed is instantaneous (within 0.5 seconds). However, in the case of using such a gel, there is a possibility that a dispersion medium such as water is scattered, and it is necessary to prevent the dispersion medium from being scattered by covering the surface of the gel with an outer skin film when the mannequin is produced. Nevertheless, the scattering of water is inevitable for a long period of time, and there remains a high risk of hardening by xerogel formation. Further, silicone gel can be used, but it is not practical because the cost is very high.
[0032]Next, a method for producing a mannequin (a front image of a woman's upper body) using the elastic gel for a mannequin of the present invention will be described.

It describes, while referring to * and Fig.1.
[0033]First, a first material 30 (a mixture of unreacted polyols, polyisocyanate components, and an organic dispersion medium) for forming an organic dispersion medium-containing polyurethane gel (having a 20% modulus value at the time of compressive deformation in the 250-750g/cm2 range) having flexibility and elasticity similar to human muscles is prepared. To provide a polyurethane gel containing an organic dispersion medium, having flexibility and elasticity closely resembling a fatty part such as the breast of a human body. A second material 40 (a mixture of unreacted polyols, polyisocyanate components, and an organic dispersion medium) for forming (a material having a value of 20% modulus at the time of compressive deformation which is smaller than that of the gel and is in the range of 50-350g/cm2) is prepared.
[0034]Then, as shown in FIG. 1 (a), a soft outer skin film 1 previously formed into a shape imitating the front shape of the upper body of a woman is set in a mold 5 for the front image of the upper body of the woman, and a previously formed hard core material 2 made of a plastic is set inside the outer skin film 1 by changing the thickness of the gel layer.
[0035]Next, as shown in FIG. 1 (b), a second material 40 is injected into a portion corresponding to a flexible breast and heated and cured to form a gel layer of a second organic dispersion medium-containing polyurethane gel 4 having flexibility and elasticity very similar to those of the breast.
[0036]Further, as shown in FIG. 1 (c), a first material 30 is injected between the core material 2 and the outer skin film 1 and between the core material 2 and the second organic dispersion medium-containing polyurethane gel 4 and cured by heating to form a gel layer of the first organic dispersion medium-containing polyurethane gel 3 having flexibility and elasticity very similar to muscle.
[0037]When the gel layer of the second organic dispersion medium-containing polyurethane gel 4 and the gel layer of the first organic dispersion medium-containing polyurethane gel 3 are formed as described above, the outer skin film 1 and the core material 2 are adhered and integrated by the adhesive force of these gels 3 and 4, and as shown in FIG. 1 (d), 1 (d), a mannequin M of a front image of the upper half of a woman's body is obtained.
[0038]As the soft outer skin film 1, soft synthetic resins having a torsional rigidity of 100-1100kgf/cm2 (JIS K 6730), such as low-density or medium-density polyethylene, ethylen-hexaacetate vinyl , polyurethane, and silicone, and having thicknesses of about 50 to 500 μ m are preferably used.
[0039]When the brassiere is attached to the mannequin M of the upper body front image of the woman, the shape change of the part corresponding to the breast and its peripheral part is very similar to the change of the breast of the woman and its peripheral part when the brassiere is attached. By observing the shape change of the mannequin M, the change of the bust shape when the woman wears the brassiere and the quality of the fitting property of the brassiere can be considerably accurately predicted.

The real flesh texture which could not be obtained at the bottom is obtained, and the appropriateness of the size, shape, etc., of the underwear can be grasped as reality.
[0040]
[Embodiment of invention] Next, Examples and Comparative Examples of the elastic gel for mannequin according to the present invention will be described.
[0041][Example 1] To polypropylene glycol (Mw: 1500) as a polyol component, a trifunctional triisocyanate (Mw: 3100) obtained by adding polypropylene glycol to trimethylolpropane and allowing hexamethylene diisocyanate to react therewith was added as a polyisocyanate component. The components were blended at a ratio such that the value of OH/NCO was 1.5, and 60% by weight of tetraglyme in which both ends of tetraethylene oxide were blocked with methoxy groups was further contained as an organic dispersion medium to prepare a gel-forming material. The gel forming

material was filled in a mold and reacted at 55 ° C. for 5 hours to obtain an elastic gel for a mannequin.

[0042]A sample obtained by cutting the elastic gel into 5 × 5 × 5cm was subjected to a compression deformation test (JIS K 7208) under the condition of a compression rate of 10mm / min using a probe having a 5mm size to obtain a stress-compression deformation curve, and a curve (a) shown in the graph of FIG. 2 was obtained. When the 20% modulus value was calculated based on the curve (A), it was about 550g / cm2.

[0043]This elastic gel had flexibility and elasticity similar to those of human muscles when pressed with a fingertip, and had a repulsive force such that the elastic gel was compressed and deformed by 20% with a probe having a 10mm size and then instantaneously (within 0.5 seconds) restored when the probe was removed.

[0044]The polypropylene glycol and triisocyanate used in Example 1 were blended at a ratio such that the value of OH / NCO was 2.0, and 65% by weight of tetraglyme was further contained to prepare a gel-forming material. The gel forming material was filled in a mold and reacted under the same conditions as in Example 1 to obtain an elastic gel for a mannequin.

[0045]When the stress-compressive deformation curve of this elastic gel was determined in the same manner as in Example 1, the curve (b) shown in the graph of FIG. 2 was obtained. The 20% modulus value calculated based on the curve (b) was about 125g / cm2.

[0046]This elastic gel had flexibility and elasticity similar to those of a fatty site such as a woman's breast when pressed with a finger tip, and had a flexible repulsive force of being instantaneously (within 0.5 seconds) restored when a probe having a 10mm size was removed after 20% compressive deformation with the probe in spite of being extremely flexible.

[0047]The polypropylene glycol and triisocyanate used in Example 1 were blended at a ratio such that the value of OH / NCO was 2.0 to prepare a gel-forming material. Filling a mold with the gel-forming material;

The reaction was carried out under the same conditions as in Example 1 to obtain an elastic gel.

[0048]When the stress-compressive deformation curve of this elastic gel was determined in the same manner as in Example 1, the curve (c) shown in the graph of FIG. 2 was obtained. When the 20% modulus value was calculated based on the curve (c), it was about 1000g/cm2 .

[0049]This elastic gel had the same OH/NCO value of 2.0 as was the same as that of the elastic gel of Example 2, but did not contain tetraglyme for increasing flexibility, so that it felt considerably hard when pressed with a fingertip, and when the probe was removed after 20% compressive deformation with a 10mm probe, it slowly recovered to its original shape in 1.7 seconds.

[0050]The polypropylene glycol and triisocyanate used in Example 1 were blended at a ratio such that the value of OH / NCO was 3.0 to prepare a gel-forming material. This gel-forming material was filled in a mold and reacted under the same conditions as in Example 1 to obtain an elastic gel.

[0051]When the stress-compressive deformation curve of this elastic gel was determined in the same manner as in Example 1, the curve (d) shown in the graph of FIG. 2 was obtained. When the 20% modulus value was calculated based on this curve (d), it was about 350g / cm2.

[0052]Since the elastic gel had an OH/NCO value of 3.0, the elastic gel was very soft even when it did not contain tetraglyme, which increases the softness of the elastic gel, and when the elastic gel was pressed with a fingertip, the elastic gel had intermediate softness and elasticity between those of muscles and fatty parts of the human body. However, since tetraglyme was not contained, when the specimen was compressed and deformed by 20% with a probe having a 10mm size and then the probe was removed, the specimen was gradually restored to the original shape in 7.5 seconds, and showed a restoration behavior considerably different from that of muscles or fatty sites.

[0053][Example 3] To a mixture (at a weight ratio of 5:1) of polypropylene glycol (Mw: 1000) and a triol (Mw: 3000) obtained by adding polypropylene glycol to glycerin as a polyol component The triisocyanate used in Example 1 was blended at a ratio of OH / NCO of 2.5, and 55% by weight of octaethylene glycol dimethyl ether was further added as an organic dispersion medium to prepare a gel-forming material. This gel-forming material was filled in a mold and reacted under the same conditions as in Example 1 to obtain an elastic gel.

[0054]The pressure-compression deformation curve of this elastic gel was obtained in the same manner as in Example 1, and the 20% modulus value was calculated to be about 660g / cm2.

[0055]This elastic gel is a human body if pressing it by a fingertip.

The sample had flexibility and elasticity similar to those of muscles, and had a repulsive force such that the sample was compressed and deformed by 20% with a probe having a 10mm size and then instantaneously (within 0.5 seconds) restored when the probe was removed.

[0056][Example 4] With respect to PEG-PPG-PEG block copolymers (molar ratio 1:2:1,Mw:2000) in which polyethylene glycols (PEGs) are bonded to both ends of polypropylene glycol (PPG) The triisocyanate used in Example 1 was blended at a ratio such that the value of OH / NCO was 1.8, and 65% by weight of diethylene glycol dimethyl ether was further added as an organic dispersion medium to prepare a gel-forming material. This gel-forming material was filled in a mold and reacted under the same conditions as in Example 1 to obtain an elastic gel.

[0057]The pressure-compression deformation curve of this elastic gel was obtained in the same manner as in Example 1, and the 20% modulus value was calculated to be about 100g / cm2.

[0058]This elastic gel had flexibility and elasticity similar to those of a fatty part of a human body when pressed with a fingertip, and had a repulsive force such that it was compressed and deformed by 20% with a probe having a 10mm size and then instantaneously (within 0.5 seconds) restored when the probe was removed.

[0059]

[Effect of the Invention] If the elastic gel for mannequins of the present invention equips with underwear the mannequin manufactured by this elastic gel since the flexibility, the elasticity, and the restoration action similar to the tissue of the human body are shown so that clearly from the above description, The elastic gel is deformed in almost the same way as the soft tissue of the human body to show a flesh texture as if it is a living body, and from the state, a remarkable effect that the change of the body shape when the underwear is worn on the human body and the quality of the fitting property of the underwear can be easily estimated is obtained.

[Patent Claims]
[Claim 1] The polyurethane gel is obtained by reacting a polyol having an alkylene oxide chain which is liquid at normal temperature or / and a polyurethane polyol prepolymer having an alkylene oxide chain which is liquid at normal temperature with a polyurethane polyisocyanate prepolymer having an alkylene oxide chain which is liquid at normal temperature. The elastic gel for the mannequin contains an organic dispersion medium for enhancing the flexibility of the gel and has a 20% modulus value in compression deformation in the range of 50-750g/cm2 .
[Claim 2] The elastic gel for a mannequin according to claim 1, wherein the organic dispersion medium is contained in an amount of 30 to 90% by weight.
[Claim 3] Polyethylene glycol in which a terminal of alkylene oxide is blocked with methoxy or ethoxy; The elastic gel for a mannequin according to claim 1 or 2, which is any one of an oligomer such as polypropylene glycol or a copolymer thereof, a cyclic carbonate such as propylene carbonate, or an ester of a higher alcohol.
[Claim 4] The elastic gel for a mannequin according to claim 1, wherein a 20% modulus value at the time of compression deformation is in a 250-750g/cm2 range, and the elastic gel has flexibility and elasticity similar to human muscles.
[Claim 5] The elastic gel for a mannequin according to claim 1, wherein a 20% modulus value at the time of compression deformation is in a 50-350g/cm2 range, and the elastic gel has flexibility and elasticity similar to those of fatty parts of a human body such as a breast.
[Claim 6] An elastic gel for a mannequin, wherein a value of 20% modulus at the time of compression deformation is 50-750g/cm2 , and the elastic gel is restored to an original shape within 0.5 seconds when an external pressure is removed.

[Brief Description of the Drawings]
[Fig. 1]FIG. 1 is a schematic view of a method for manufacturing a mannequin using the elastic gel for a mannequin of the present invention.
[Fig. 2]FIG. 3 is a graph showing the relationship between stress and compressive deformation of elastic gels for mannequins obtained in Examples 1 and 2 of the present invention and elastic gels obtained in Comparative Examples 1 and 2.
[Explanation of letters or numerals]
1 Film for Envelopes
2 Core Material
3 first organic dispersion medium-containing polyurethane gel (elastic gel for mannequin)
4 second organic dispersion medium-containing polyurethane gel (elastic gel for mannequin)
M Mannequin of upper body front view of woman

(19)日本国特許庁（ＪＰ）　(12) **公開特許公報（Ａ）**　(11)特許出願公開番号
特開2000－313731
（P2000－313731A）
(43)公開日　平成12年11月14日(2000.11.14)

(51)Int.Cl.[7]	識別記号	ＦＩ		ﾃｰﾏｺｰﾄﾞ(参考)
Ｃ０８Ｇ　18/10		Ｃ０８Ｇ	18/10	４Ｊ００２
Ａ４７Ｆ　8/00		Ａ４７Ｆ	8/00	４Ｊ０３４
Ｃ０８Ｇ　18/48		Ｃ０８Ｇ	18/48	Ｚ
Ｃ０８Ｌ　75/08		Ｃ０８Ｌ	75/08	

審査請求　未請求　請求項の数６　ＯＬ　（全 10 頁）

(21)出願番号　特願平11－123842

(22)出願日　平成11年４月30日(1999.4.30)

(71)出願人　000108719
タキロン株式会社
大阪府大阪市中央区安土町２丁目３番13号
(72)発明者　敷波　保夫
大阪市中央区安土町２丁目３番13号　タキロン株式会社内
(72)発明者　蔦　薫
大阪市中央区安土町２丁目３番13号　タキロン株式会社内
(74)代理人　100090608
弁理士　河▲崎▼　眞樹

最終頁に続く

(54)【発明の名称】　マネキン用弾性ゲル

(57)

(2)

1 2

2

2

10

20

2

2

30

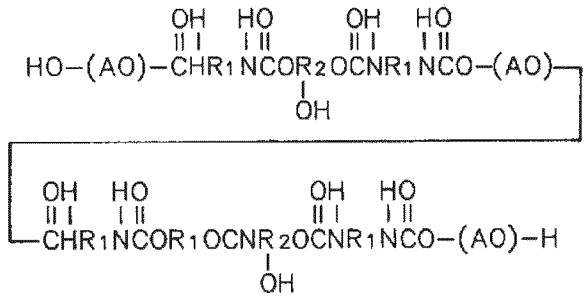
interpeneturated

2

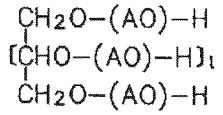
40

3 4

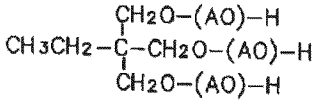
構造式（1）



構造式（2）



構造式（3）



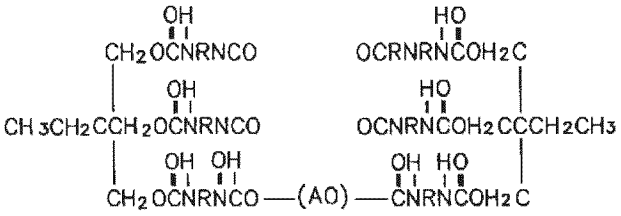
構造式（4）



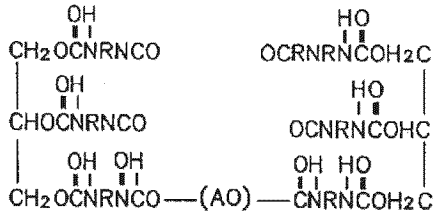
1 2

5 6

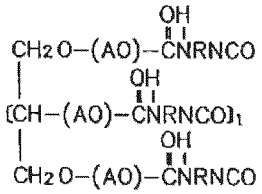
構造式（5）



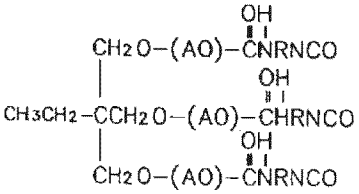
構造式（6）



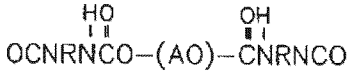
構造式（7）



構造式（8）

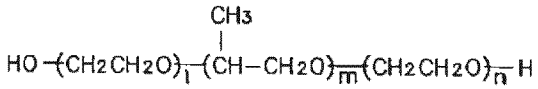


構造式（9）

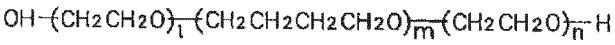


10

構造式 (10)



構造式 (11)



40

50

^{2}

(6)

9 10

^{2}

10 ^{2}

20

^{2}

30

40

^{2}

50

(7)

11 12

2

2

2

2

10

20

30

2

40

50

(8)

13

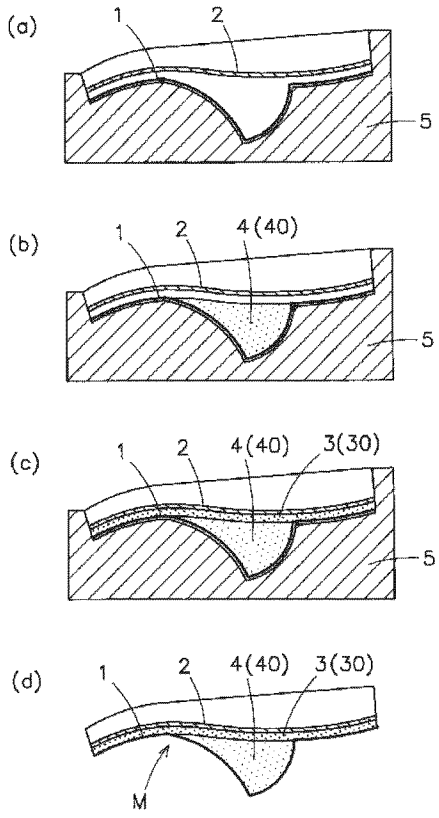
14

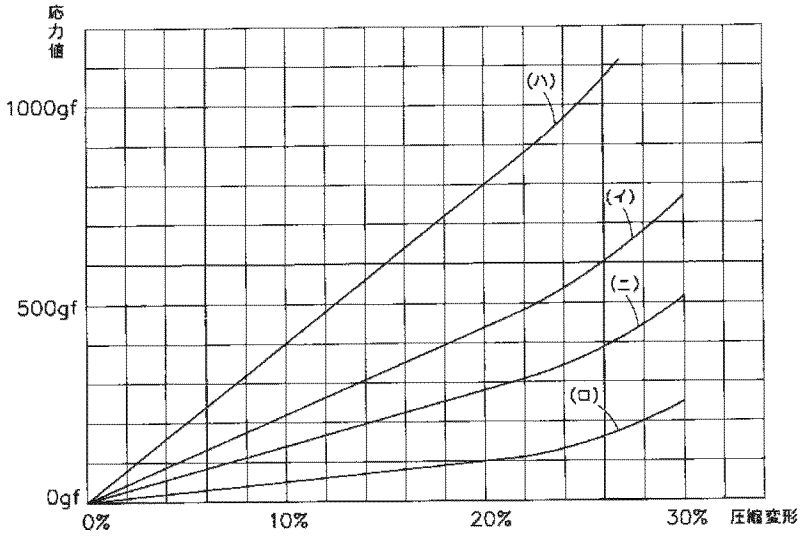
10

20

30

40


(a)
1
2
5
(b)
1
2
4(40)
5
(c)
1
2
4(40)
3(30)
5
(d)
1
2
4(40)
3(30)
M


応力値
1000gf
500gf
0gf
(ハ)
(イ)
(ニ)
(ロ)
0%
10%
20%
30%
圧縮変形

(

4J002 CH052 CK041 EH036 EL106
GC00
4J034 BA03 BA07 DA01 DB01 DB03
DB05 DB07 DG02 DG03 DG04
DG05 DG06 DG08 DG10 DG12
DG14 HA01 HA02 HA07 HB12
HC03 HC12 HC13 HC17 HC22
HC46 HC52 HC61 HC64 HC67
HC71 HC73 JA42 JA44 KA01
KB04 KC17 KD02 KD12 KE02
LA22 LA33 MA12 MA24 QB13
QB14 QC06 RA03

PTO/SB/08 (01-25)
Approved for use through 11/30/2027. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM, et al.
Art Unit	1699
Examiner Name	Brian M. GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

U.S. PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Inventor of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
	1					

If you wish to add additional U.S. Patent citation information, please click the Add button. Add

U.S. PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Inventor or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
	1					

If you wish to add additional U.S. Published Application citation information, please click the Add button Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2]	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	2000313731	JP	A	2000-11-14	TAKIRON CO LTD	English Abstract, English Machine Translation	☐

If you wish to add additional Foreign Patent Document citation information, please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT		
	Application Number	18066105
	Filing Date	2022-12-14
	First Named Inventor	Anna K. CROOM, et al.
	Art Unit	1699
	Examiner Name	Brian M. GULLEDGE
	Attorney Docket Number	GRAN-1012-U-D

	1		☐

If you wish to add additional non-patent literature document citation information, please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered and whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM, et al.
Art Unit	1699
Examiner Name	Brian M. GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

TIMING STATEMENT

Please see 37 CFR 1.97(e) to make the appropriate selection(s):

☒ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☒ See attached timing statement under 37 CFR 1.97(e).

☐ A timing statement under 37 CFR 1.97(e) is not submitted herewith.

TIMING FEE

☐ The fee set forth in 37 CFR 1.17(p) has been submitted herewith.

COPIES

☐ An identification of an earlier application pursuant to 37 CFR 1.98(d)(1) is attached.

SIZE FEE ASSERTION

Please see 37 CFR 1.17(v) and the IDS Auto-Load Instructions for completing this form to make the appropriate selection of an assertion under 37 CFR 1.98. For the information disclosure statement (IDS) submitted herewith, the applicant or patent owner certifies the following with respect to the cumulative number of applicant-provided or patent-owner provided items of information submitted to date including those in the accompanying IDS (select only one):

☒ No IDS size fee is required under 37 CFR 1.17(v) at this time.

☐ The IDS is accompanied by the IDS size fee under 37 CFR 1.17(v)(1).

☐ The IDS is accompanied by the IDS size fee under 37 CFR 1.17(v)(2).

☐ The IDS is accompanied by the IDS size fee under 37 CFR 1.17(v)(3).

SIGNATURE

A signature of the applicant or representative is required in accordance with 37 CFR 1.33 and 11.18. Please see 37 CFR 1.4(d) for the form of the signature.

Signature	/Michael N. Mercanti/	Date (YYYY-MM-DD)	2025-04-30
Name/Print	Michael N. Mercanti	Registration Number	33966

PC.1.19.25

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM, et al.
Art Unit	1699
Examiner Name	Brian M. GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
18/066,105	**04/30/2025 03:56:18 PM Z ET**	**GRAN-1012-U-D**

Title of Invention

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	1563	FILED BY	Carla Curado
PATENT CENTER #	70234067	FILING DATE	12/14/2022
CUSTOMER #	20311	FIRST NAMED INVENTOR	Anna K. CROOM
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Michael Mercanti

Documents

TOTAL DOCUMENTS: 2

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
Suppl_IDSSB08_GRAN1012UD.pdf	5	Information Disclosure Statement (IDS) Form (SB08)	1314 KB
JP2000313731A.pdf	25	Foreign Reference	1384 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
Suppl_IDSSB08_GRAN1012UD.pdf	B54F17AF6E75BA6AB2643DF85FFE7C9A51D37703C63DBB488B27133253B3B429541B92AC06E916D226F1B2F68357934719EE2DF972263825DD9AEF9B6D855357
JP2000313731A.pdf	422BFB7F839329F92D85ED677507D27EFEF21890C246F0BAA88E05B2BF956AA075F702E3D301EE2CFBB423CE2F16F95AB5

70F2BA15CAB7044CCED40562720F6C

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	18/066,105	CROOM et al.
	Examiner	Art Unit
	Brian Gulledge	1699

CPC - Searched*		
Symbol	Date	Examiner
A61K 8/042 (limited as in SEARCH transcript)	04/22/2025	BMG

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	Date	Examiner
Inventor search performed in PDP	03/18/2025	BMG
SciFinder search performed: see attached transcripts	03/18/2025	BMG
Inventor search updated in PDP	04/22/2025	BMG
SEARCH search performed: see attached transcript	04/22/2025	BMG
SciFinder search updated	04/22/2025	BMG

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner
A61K	8/042 (limited as in SEARCH transcript)	04/22/2025	BMG

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	18/066,105	CROOM et al.
	Examiner	**Art Unit**
	Brian Gulledge	1699

CPC						
Symbol					**Type**	**Version**
A61K	/	8	/	87	F	2013-01-01
A61K	/	8	/	042	I	2013-01-01
A61Q	/	19	/	008	I	2013-01-01
A61Q	/	17	/	04	I	2013-01-01
A61K	/	2800	/	54	A	2013-01-01
A61K	/	2800	/	10	A	2013-01-01

CPC Combination Sets							
Symbol					**Type**	**Set**	**Ranking**	**Version**
	/		/					

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	17	
/Brian Gulledge/ Primary Examiner, Art Unit 1699	22 April 2025	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	28	None

U.S. Patent and Trademark Office — Part of Paper No.: 20250422A

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	18/066,105	CROOM et al.
	Examiner	**Art Unit**
	Brian Gulledge	1699

INTERNATIONAL CLASSIFICATION				
CLAIMED				
A61K	/	8	/	02
A61K	/	8	/	06
A61K	/	8	/	19
	/		/	

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	**SUBCLASS**

CROSS REFERENCES(S)						
CLASS	**SUBCLASS (ONE SUBCLASS PER BLOCK)**					

NONE (Assistant Examiner) (Date)	**Total Claims Allowed:** 17	
/Brian Gulledge/ Primary Examiner, Art Unit 1699 (Primary Examiner) 22 April 2025 (Date)	O.G. Print Claim(s) 28	O.G. Print Figure None

U.S. Patent and Trademark Office Part of Paper No.: 20250422A

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	18/066,105	CROOM et al.
	Examiner	**Art Unit**
	Brian Gulledge	1699

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
	1		10		19	1	28		37	6	46	13	55		
	2		11		20	2	29		38		47	14	56		
	3		12		21		30		39		48	15	57		
	4		13		22		31		40		49	16	58		
	5		14		23		32		41	8	50	17	59		
	6		15		24	3	33		42	9	51	10	60		
	7		16		25	4	34		43		52	11	61		
	8		17		26	5	35		44		53	12	62		
	9		18		27		36		45	7	54				

NONE (Assistant Examiner)	(Date)	**Total Claims Allowed:** 17	
/Brian Gulledge/ Primary Examiner, Art Unit 1699 (Primary Examiner)	22 April 2025 (Date)	O.G. Print Claim(s) 28	O.G. Print Figure None

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08 (01-25)
Approved for use through 11/30/2027. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM, et al.
Art Unit	1699
Examiner Name	Brian M. GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

U.S. PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Inventor of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
	1	3627719	A	1971-12-14	SELLET	

If you wish to add additional U.S. Patent citation information, please click the Add button. Add

U.S. PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Inventor or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
	1					

If you wish to add additional U.S. Published Application citation information, please click the Add button Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							☐

If you wish to add additional Foreign Patent Document citation information, please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM, et al.
Art Unit	1699
Examiner Name	Brian M. GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

	1	Hamid YEGANEH, et al., "Preparation and properties of novel biodegradable polyurethane networks based on castor oil and poly(ethylene glycol)" Polymer Degradation and Stability, vol. 92, pp. 480-489, 2007.	☐

If you wish to add additional non-patent literature document citation information, please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature	/Brian Gulledge/	Date Considered	04/22/2025

*EXAMINER: Initial if reference considered and whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM, et al.
Art Unit	1699
Examiner Name	Brian M. GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

TIMING STATEMENT

Please see 37 CFR 1.97(e) to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☐ See attached timing statement under 37 CFR 1.97(e).

☒ A timing statement under 37 CFR 1.97(e) is not submitted herewith.

TIMING FEE

☐ The fee set forth in 37 CFR 1.17(p) has been submitted herewith.

COPIES

☐ An identification of an earlier application pursuant to 37 CFR 1.98(d)(1) is attached.

SIZE FEE ASSERTION

Please see 37 CFR 1.17(v) and the IDS Auto-Load Instructions for completing this form to make the appropriate selection of an assertion under 37 CFR 1.98. For the information disclosure statement (IDS) submitted herewith, the applicant or patent owner certifies the following with respect to the cumulative number of applicant-provided or patent-owner provided items of information submitted to date including those in the accompanying IDS (select only one):

☐ No IDS size fee is required under 37 CFR 1.17(v) at this time.

☒ The IDS is accompanied by the IDS size fee under 37 CFR 1.17(v)(1).

☐ The IDS is accompanied by the IDS size fee under 37 CFR 1.17(v)(2).

☐ The IDS is accompanied by the IDS size fee under 37 CFR 1.17(v)(3).

SIGNATURE

A signature of the applicant or representative is required in accordance with 37 CFR 1.33 and 11.18. Please see 37 CFR 1.4(d) for the form of the signature.

Signature	/Michael N. Mercanti/	Date (YYYY-MM-DD)	2025-04-07
Name/Print	Michael N. Mercanti	Registration Number	33966

PC.1.19.25

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM, et al.
Art Unit	1699
Examiner Name	Brian M. GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

PE2E SEARCH - Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	British Equivalents	Time Stamp
L1	14228	(grant ADJ indust$)	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB)	OR	ON	ON	2022/08/10 12:39 PM
L2	15	(grant ADJ indust$).as.	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB)	OR	ON	ON	2022/08/10 12:39 PM
L3	4	L2 AND polyurethane	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB)	OR	ON	ON	2022/08/10 12:48 PM
L5	33680	polyurethane AND emollient	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY,	OR	ON	ON	2022/08/10 01:42 PM

			CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB)				
L6	1347	polyurethane.ab. AND emollient	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB)	OR	ON	ON	2022/08/10 01:42 PM
L7	809	L6 AND A61K8$.cpc.	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB)	OR	ON	ON	2022/08/10 01:43 PM
L8	1241	polyurethane.ab. AND (gel.ab. OR gel.clm.) AND A61K8$.cpc.	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH,	OR	ON	ON	2022/08/10 01:43 PM

			TN, TR, TW, UA, VN, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB)				
L9	229	polyurethane.ab. AND (gel.ab. OR gel.clm.) AND A61K8/042.cpc.	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB)	OR	ON	ON	2022/08/10 01:44 PM
L10	119	polyurethane.ab. AND (gel.ab. OR gel.clm.) AND A61K8/042.cpc.	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO)	OR	ON	ON	2022/08/10 01:44 PM
L11	74	L10 AND cross$	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO)	OR	ON	ON	2022/08/10 01:45 PM
L12	3867	polyurethane ADJ ("32" OR "34" OR "35" OR "48")	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV,	OR	ON	ON	2022/08/10 02:51 PM

			MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB)				
L13	124	L12 WITH cross	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB)	OR	ON	ON	2022/08/10 02:51 PM
L14	113	L12 WITH cross	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS)	OR	ON	ON	2022/08/10 02:52 PM
L15	13	L12 WITH cross	(US-PGPUB; USPAT; USOCR)	OR	ON	ON	2022/08/10 02:52 PM
L16	20	(("polyurethane-34") WITH particle) AND (particle WITH size)	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB)	OR	ON	ON	2022/08/10 03:34 PM

L17	6	("10035871" OR "20180079852" OR "5284897" OR "8222363" OR "9376404" OR "9610237").pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/08/10 03:46 PM
L18	5	("20030092932" OR "20110045983" OR "20130079486" OR "20150128335" OR "20180371149").pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/08/10 03:49 PM
L19	1055	(viscosity WITH gel).clm. AND A61K8/042.cpc.	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO)	OR	ON	ON	2022/08/11 11:41 AM
L20	215	(viscosity WITH gel WITH cP).clm. AND A61K8/042.cpc.	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO)	OR	ON	ON	2022/08/11 11:41 AM
L21	53	(viscosity WITH gel WITH cP).clm. AND A61K8/042.cpc.	(US-PGPUB; USPAT; USOCR)	OR	ON	ON	2022/08/11 11:41 AM
L22	240	polyurethane.ab. AND (gel.ab. OR gel.clm.) AND A61K8/042.cpc.	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO;	OR	ON	ON	2022/10/26 02:02 PM

			JPO; DERWENT; IBM_TDB)				
L23	291	polyurethane.ab. AND (gel.ab. OR gel.clm.) AND A61K8/042.cpc.	(US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB)	OR	ON	ON	2025/04/22 02:46 PM

PE2E SEARCH - Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	British Equivalents	Time Stamp
N1	21	polyurethane.ab. AND (gel.ab. OR gel.clm.) AND A61K8/042.cpc.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/26 02:02 PM
N2	29	polyurethane.ab. AND (gel.ab. OR gel.clm.) AND A61K8/042.cpc.	(US-PGPUB; USPAT)	OR	ON	ON	2025/04/22 02:46 PM

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08 (01-25)
Approved for use through 11/30/2027. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM, et al.
Art Unit	1699
Examiner Name	Brian M. GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

U.S. PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Inventor of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
	1					

If you wish to add additional U.S. Patent citation information, please click the Add button. Add

U.S. PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Inventor or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
	1					

If you wish to add additional U.S. Published Application citation information, please click the Add button Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	2000313731	JP	A	2000-11-14	TAKIRON CO LTD	English Abstract, English Machine Translation	☐

If you wish to add additional Foreign Patent Document citation information, please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT		
	Application Number	18066105
	Filing Date	2022-12-14
	First Named Inventor	Anna K. CROOM, et al.
	Art Unit	1699
	Examiner Name	Brian M. GULLEDGE
	Attorney Docket Number	GRAN-1012-U-D

	1		☐

If you wish to add additional non-patent literature document citation information, please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature	/Brian Gulledge/	Date Considered	05/04/2025

*EXAMINER: Initial if reference considered and whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM, et al.
Art Unit	1699
Examiner Name	Brian M. GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

TIMING STATEMENT

Please see 37 CFR 1.97(e) to make the appropriate selection(s):

☒ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☒ See attached timing statement under 37 CFR 1.97(e).

☐ A timing statement under 37 CFR 1.97(e) is not submitted herewith.

TIMING FEE

☐ The fee set forth in 37 CFR 1.17(p) has been submitted herewith.

COPIES

☐ An identification of an earlier application pursuant to 37 CFR 1.98(d)(1) is attached.

SIZE FEE ASSERTION

Please see 37 CFR 1.17(v) and the IDS Auto-Load Instructions for completing this form to make the appropriate selection of an assertion under 37 CFR 1.98. For the information disclosure statement (IDS) submitted herewith, the applicant or patent owner certifies the following with respect to the cumulative number of applicant-provided or patent-owner provided items of information submitted to date including those in the accompanying IDS (select only one):

☒ No IDS size fee is required under 37 CFR 1.17(v) at this time.

☐ The IDS is accompanied by the IDS size fee under 37 CFR 1.17(v)(1).

☐ The IDS is accompanied by the IDS size fee under 37 CFR 1.17(v)(2).

☐ The IDS is accompanied by the IDS size fee under 37 CFR 1.17(v)(3).

SIGNATURE

A signature of the applicant or representative is required in accordance with 37 CFR 1.33 and 11.18. Please see 37 CFR 1.4(d) for the form of the signature.

Signature	/Michael N. Mercanti/	Date (YYYY-MM-DD)	2025-04-30
Name/Print	Michael N. Mercanti	Registration Number	33966

PC.1.19.25

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

Application Number	18066105
Filing Date	2022-12-14
First Named Inventor	Anna K. CROOM, et al.
Art Unit	1699
Examiner Name	Brian M. GULLEDGE
Attorney Docket Number	GRAN-1012-U-D

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /BG/

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

20311 7590 05/14/2025

LUCAS & MERCANTI, LLP
30 BROAD STREET
21st FLOOR
NEW YORK, NY 10004

EXAMINER	
GULLEDGE, BRIAN M	
ART UNIT	PAPER NUMBER
1699	

DATE MAILED: 05/14/2025

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
18/066,105	12/14/2022	Anna K. CROOM	GRAN-1012-U-D	1563

TITLE OF INVENTION: BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$516	$0.00	$0.00	$516	08/14/2025

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 40% the amount of undiscounted fees, and micro entity fees are 20% the amount of undiscounted fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Maintenance fees are due in utility patents issuing on applications filed on or after Dec. 12, 1980. It is patentee's responsibility to ensure timely payment of maintenance fees when due. More information is available at www.uspto.gov/PatentMaintenanceFees.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via the USPTO patent electronic filing system.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications. **Because electronic patent issuance may occur shortly after issue fee payment, any desired continuing application should preferably be filed prior to payment of this issue fee in order not to jeopardize copendency.**

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

20311 7590 05/14/2025
LUCAS & MERCANTI, LLP
30 BROAD STREET
21st FLOOR
NEW YORK, NY 10004

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via the USPTO patent electronic filing system or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
18/066,105	12/14/2022	Anna K. CROOM	GRAN-1012-U-D	1563

TITLE OF INVENTION: BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$516	$0.00	$0.00	$516	08/14/2025

EXAMINER	ART UNIT	CLASS-SUBCLASS
GULLEDGE, BRIAN M	1699	424-401000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

❑ Change of correspondence address (or Change of Correspondence Address form PTO/AIA/122 or PTO/SB/122) attached.

❑ "Fee Address" indication (or "Fee Address" Indication form PTO/AIA/47 or PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 _____
2 _____
3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. Fees submitted: ❑ Issue Fee ❑ Publication Fee (if required)

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

❑ Electronic Payment via the USPTO patent electronic filing system ❑ Enclosed check ❑ Non-electronic payment by credit card (Attach form PTO-2038)

❑ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. _____

5. **Change in Entity Status** (from status indicated above)

❑ Applicant certifying micro entity status. See 37 CFR 1.29

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.

❑ Applicant asserting small entity status. See 37 CFR 1.27

NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.

❑ Applicant changing to regular undiscounted fee status.

NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
18/066,105	12/14/2022	Anna K. CROOM	GRAN-1012-U-D	1563

20311 7590 05/14/2025

LUCAS & MERCANTI, LLP
30 BROAD STREET
21st FLOOR
NEW YORK, NY 10004

EXAMINER	
GULLEDGE, BRIAN M	
ART UNIT	PAPER NUMBER
1699	

DATE MAILED: 05/14/2025

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. The United States Patent and Trademark Office (USPTO) collects the information in this record under authority of 35 U.S.C. 2. The USPTO's system of records is used to manage all applicant and owner information including name, citizenship, residence, post office address, and other information with respect to inventors and their legal representatives pertaining to the applicant's/ owner's activities in connection with the invention for which a patent is sought or has been granted. The applicable Privacy Act System of Records Notice for the information collected in this form is COMMERCE/PAT-TM-7 Patent Application Files, available in the Federal Register at 78 FR 19243 (March 29, 2013).
https://www.govinfo.gov/content/pkg/FR-2013-03-29/pdf/2013-07341.pdf

Routine uses of the information in this record may include disclosure to:

1) law enforcement, in the event that the system of records indicates a violation or potential violation of law;
2) a federal, state, local, or international agency, in response to its request;
3) a contractor of the USPTO having need for the information in order to perform a contract;
4) the Department of Justice for determination of whether the Freedom of Information Act (FOIA) requires disclosure of the record;
5) a Member of Congress submitting a request involving an individual to whom the record pertains, when the individual has requested the Member's assistance with respect to the subject matter of the record;
6) a court, magistrate, or administrative tribunal, in the course of presenting evidence, including disclosures to opposing counsel in the course of settlement negotiations;
7) the Administrator, General Services Administration (GSA), or their designee, during an inspection of records conducted by GSA under authority of 44 U.S.C. 2904 and 2906, in accordance with the GSA regulations and any other relevant (i.e., GSA or Commerce) directive, where such disclosure shall not be used to make determinations about individuals;
8) another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c));
9) the Office of Personnel Management (OPM) for personnel research purposes; and
10) the Office of Management and Budget (OMB) for legislative coordination and clearance.

If you do not furnish the information requested on this form, the USPTO may not be able to process and/or examine your submission, which may result in termination of proceedings, abandonment of the application, and/or expiration of the patent.

Notice of Allowability	Application No. 18/066,105	Applicant(s) CROOM et al.	
	Examiner Brian Gulledge	Art Unit 1699	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to the submission received 18 April 2025.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

3. ☑ The allowed claim(s) is/are See Continuation Sheet . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some* c) ☐ None of the:

   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☑ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____.
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____.
5. ☐ Examiner's Amendment/Comment
6. ☑ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/Brian Gulledge/
Primary Examiner, Art Unit 1699

Continuation of 3. The allowed claim(s) is/are: 28-29,33-35,46,50-51 and 54-62

DETAILED ACTION

Previous Rejections

Applicants' arguments, filed 18 April 2025, have been fully considered. In particular, the rejections are withdrawn in view of the amendment to the claims (see the response starting at page 9).

Examiner's Amendment

An examiner's amendment to the record appears below. Should the changes and/or additions be unacceptable to applicant, an amendment may be filed as provided by 37 CFR 1.312. To ensure consideration of such an amendment, it MUST be submitted no later than the payment of the issue fee.

Authorization for this examiner's amendment was given in an interview with Lindsay Adams on 25 April 2025.

The application has been amended as follows:

1) Claims 1-27, 45, 48-49, and 52-53 have been cancelled without prejudice thereto.

Reasons for Allowance

The following is an examiner's statement of reasons for allowance. The closest prior art is considered previously cited Acterhof et al. (US Patent 3,192,185). Acterhof et al. discloses polyurethane elastomers (column 1, lines 11-14). One exemplified material is prepared from a polyester and a polyisocyanate, and is crosslinked (example 2). However, the use of the specific polyurethane instantly recited is not suggested therein. The specific species elected (the

polyurethane prepared from DAPD polyol and PDT) is not suggested by the prior art. Also, crosslinked elastomers prepared from multifunctional crosslinkers and esterified dilinoleic acid are free of the prior art.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Brian Gulledge whose telephone number is (571) 270-5756. The examiner can normally be reached Monday - Friday 7am - 4pm.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Fereydoun Sajjadi can be reached on (571) 272-3311. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of published or unpublished applications may be obtained from Patent Center. Unpublished application information in Patent Center is available to registered users. To file and manage patent submissions in Patent Center, visit: https://patentcenter.uspto.gov. Visit https://www.uspto.gov/patents/apply/patent-center for more information about Patent Center

and https://www.uspto.gov/patents/docx for information about filing in DOCX format. For additional questions, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Brian Gulledge/
Primary Examiner, Art Unit 1699

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
18/066,105	**05/21/2025 03:25:59 PM Z ET**	**GRAN-1012-U-D**

Title of Invention

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	1563	FILED BY	Carla Curado
PATENT CENTER #	70528589	FILING DATE	12/14/2022
CUSTOMER #	20311	FIRST NAMED INVENTOR	Anna K. CROOM
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Michael Mercanti

Documents

TOTAL DOCUMENTS: 1

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
IssueFee_GRAN1012UD.pdf	1	Issue Fee Payment (PTO-85B)	209 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
IssueFee_GRAN1012UD.pdf	C02745E68CB70028CF75ADACDE7075CA4BCBDBE83A221CD 7DCF9DE14A76FEBAE6F074647DD528632324920E0DFE0B955 2F99D5C3780DCA6E5589657E2787935E

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC PAYMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
18/066,105	**05/21/2025 03:25:59 PM Z ET**	**GRAN-1012-U-D**

Title of Invention

BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	1563	FILED BY	Carla Curado
PATENT CENTER #	70528589	AUTHORIZED BY	Michael Mercanti
CUSTOMER #	20311	FILING DATE	12/14/2022
CORRESPONDENCE ADDRESS	-	FIRST NAMED INVENTOR	Anna K. CROOM

Payment Information

PAYMENT METHOD	PAYMENT TRANSACTION ID	PAYMENT AUTHORIZED BY
CARD / 1054	**E20255KF26298209**	**Carla Curado**

FEE CODE	DESCRIPTION	ITEM PRICE($)	QUANTITY	ITEM TOTAL($)
2501	UTILITY ISSUE FEE	516.00	1	516.00
			TOTAL AMOUNT:	**$516.00**

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via the USPTO patent electronic filing system.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications. **Because electronic patent issuance may occur shortly after issue fee payment, any desired continuing application should preferably be filed prior to payment of this issue fee in order not to jeopardize copendency.**

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

20311 7590 05/14/2025
LUCAS & MERCANTI, LLP
30 BROAD STREET
21st FLOOR
NEW YORK, NY 10004

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via the USPTO patent electronic filing system or by facsimile to (571) 273-2885, on the date below.

Michael N. Mercanti	(Typed or printed name)
/Michael N. Mercanti/	(Signature)
05/21/2025	(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
18/066,105	12/14/2022	Anna K. CROOM	GRAN-1012-U-D	1563

TITLE OF INVENTION: BIO-BASED AND BIODEGRADABLE ELASTOMER FOR COSMETIC AND PERSONAL CARE

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$516	$0.00	$0.00	$516	08/14/2025

EXAMINER	ART UNIT	CLASS-SUBCLASS
GULLEDGE, BRIAN M	1699	424-401000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

☐ Change of correspondence address (or Change of Correspondence Address form PTO/AIA/122 or PTO/SB/122) attached.

☐ "Fee Address" indication (or "Fee Address" Indication form PTO/AIA/47 or PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 LUCAS & MERCANTI, LLP
2
3

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: GRANT INDUSTRIES, INC

(B) RESIDENCE: (CITY and STATE OR COUNTRY): ELMWOOD PARK, NEW JERSEY

Please check the appropriate assignee category or categories (will not be printed on the patent) : ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. Fees submitted: ☒ Issue Fee ☐ Publication Fee (if required)

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

☒ Electronic Payment via the USPTO patent electronic filing system ☐ Enclosed check ☐ Non-electronic payment by credit card (Attach form PTO-2038)

☒ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. 02-2275

5. **Change in Entity Status** (from status indicated above)

☐ Applicant certifying micro entity status. See 37 CFR 1.29

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.

☐ Applicant asserting small entity status. See 37 CFR 1.27

NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.

☐ Applicant changing to regular undiscounted fee status.

NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature /Michael N. Mercanti/ Date 05/21/2025

Typed or printed name Michael N. Mercanti Registration No. 33966

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
18/066,105	06/24/2025	12337057	GRAN-1012-U-D	1563

20311 7590 06/11/2025

LUCAS & MERCANTI, LLP
30 BROAD STREET
21st FLOOR
NEW YORK, NY 10004

ISSUE NOTIFICATION

The projected patent number and issue date are specified above. The patent will issue electronically. The electronically issued patent is the official patent grant pursuant to 35 U.S.C. § 153. The patent may be accessed on or after the issue date through Patent Center at https://patentcenter.uspto.gov/. The patent will be available in both the public and the private sides of Patent Center. Further assistance in electronically accessing the patent, or about Patent Center, is available by calling the Patent Electronic Business Center at 1-888-217-9197.

The USPTO is implementing electronic patent issuance with a transition period, during which period the USPTO will mail a ceremonial paper copy of the electronic patent grant to the correspondence address of record. Additional copies of the patent (i.e., certified and presentation copies) may be ordered for a fee from the USPTO's Certified Copy Center at https://certifiedcopycenter.uspto.gov/index.html. The Certified Copy Center may be reached at (800)972-6382.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 273 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Center (https://patentcenter.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Patents Stakeholder Experience (OPSE), Stakeholder Support Division (SSD) at (571)-272-4200.

INVENTOR(s) (Please see PATENT CENTER site https://patentcenter.uspto.gov for additional inventors):

Anna K. CROOM, Brooklyn, NY;
Ronald V. LERUM, Leonia, NJ;
John GORMLEY, Midland Park, NJ;

APPLICANT(s) (Please see PATENT CENTER site https://patentcenter.uspto.gov for additional applicants):

Grant Industries, Inc., Elmwood Park, NJ;

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The USA offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to encourage and facilitate business investment. To learn more about why the USA is the best country in the world to develop technology, manufacture products, and grow your business, visit SelectUSA.gov.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
18/066,105	12/14/2022	Anna K. CROOM	GRAN-1012-U-D	1563

20311 7590 06/24/2025

LUCAS & MERCANTI, LLP
30 BROAD STREET
21st FLOOR
NEW YORK, NY 10004

EXAMINER	
GULLEDGE, BRIAN M	

ART UNIT	PAPER NUMBER
1699	

NOTIFICATION DATE	DELIVERY MODE
06/24/2025	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

info@lmiplaw.com

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	ISSUE DATE	PATENT NO.
18/066,105	24-Jun-2025	12337057

LUCAS & MERCANTI, LLP
30 BROAD STREET
NEW YORK, NY 10004

EGRANT NOTIFICATION

Your electronic patent grant (eGrant) is now available, which can be accessed via Patent Center at https://patentcenter.uspto.gov

The electronic patent grant is the official patent grant under 35 U.S.C. 153. For more information, please visit https://www.uspto.gov/electronicgrants