

present invention.

FIG. 1B is a sectional schematic view showing a layer configuration of the light-shielding sheet and the container of the present invention.

FIG. 1C is a sectional schematic view showing a layer configuration of the light-shielding sheet and the container of the present invention.

FIG. 1D is a sectional schematic view showing a layer configuration of the light-shielding sheet and the container of the present invention.

FIG. 1E is a sectional schematic view showing a layer configuration of the light-shielding sheet and the container of the present invention.

FIG. 1F is a sectional schematic view showing a layer configuration of the light-shielding sheet and the container of the present invention.

FIG. 1G is a sectional schematic view showing a layer configuration of the light-shielding sheet and the container of the present invention.

Description of Embodiments

[0033] Hereinafter, preferred embodiments of a light-shielding sheet and a light-shielding container according to the present invention will be described.

[0034] FIGS. 1A to 1G are sectional schematic views showing combinations of layer configurations of a light-shielding sheet and a light-shielding container according to embodiments of the present invention.

[0035] Although not shown in the drawings, one of or two or more of an adhesive layer, a gas barrier layer, and a water vapor barrier layer can be provided between the layers as required.

[0036] In the container of the present invention, an innermost layer refers to a layer which is in direct contact with contents to be stored in the container when the sheet of the present invention is formed into a container.

[0037] In the container of the present invention, an outermost layer refers to a layer which is the outermost layer of the container and comes into contact with the outside of the container when the sheet of the present invention is formed into a container.

[0038] The light-shielding sheet and the container of the present invention are a light-shielding sheet that has a multilayer structure of three or more layers including one or more of the group consisting of one or more light-shielding layers and one or more eluate-blocking layers, and a container produced using the light-shielding sheet. When the total light transmittance of the sheet and the container at a wavelength of 380 nm or shorter is set to 1% or lower, a near ultraviolet ray portion of a wavelength of 380 nm to 200 nm, which is thought to be the most harmful, can be shielded and the effect of enhancing the storage stability of contents is obtained.

[0039] In addition, when the total light transmittance at a wavelength of 380 nm to 400 nm is set to 30% or lower and preferably set to 1% or lower, the ultraviolet ray portion near to visible light can be shielded and the storage stability of contents can be further enhanced. Even when the total light transmittance is in a range of higher than 1% and lower than 30%, a certain degree of a light-shielding effect is obtained and thus the sheet and the container can be used for most contents such as pharmaceutical products, cosmetics, foods and the like.

[0040] When the total light transmittance at a wavelength of 450 nm is set to 15% or higher and more preferably set to 55% or higher, the contents in the multilayer sheet and the container are visible from the outside and foreign substances and defective products can be eliminated in a step of visual inspection and the effect of enhancing quality can be obtained. The total light transmittance at a wavelength of 450 nm of 15% or higher is a level in which visual inspection is possible and thus it is necessary to set the minimum to 15% or higher, preferably 30% or higher, and more preferably 55% or higher. When the total light transmittance is 55% or higher, the container can satisfy transparency test standards in the testing method for pharmaceutical containers of the Japanese Pharmacopoeia, Sixteenth Edition, described in the Pharmaceutical Affairs Law and can be easily applied to containers for injections, infusion solutions and liquid medicines among containers for liquid pharmaceutical products. In many of the light-shielding containers that have been suggested, the importance of transmission at 450 nm is not mentioned. A total light transmittance of 15% or lower is not preferable because visual inspection of contents is not easy and a risk of omission occurrence in the inspection of defective products is high.

[0041] When the sheet is formed into a container, a light-shielding layer is provided as at least one layer of an intermediate layer portion other than the outermost layer and the innermost layer in the light-shielding sheet of the present invention.

[0042] The light-shielding layer is a resin layer containing at least one of an ultraviolet absorber, an organic or inorganic pigment, an inorganic substance, a colored pigment, a fluorescent brightening agent, and a dye, and as long as the light-shielding layer is the light-shielding sheet and a layer (intermediate layer) of the container other than the outermost layer and the innermost layer, the layer may be provided at any position in the multilayer structure. The light-shielding layer may be provided as a single layer or multiple layers. The number of layers is not limited as long as a light-shielding

effect can be obtained.

[0043] In the case of using a transparent thermoplastic resin as the resin for the light-shielding layer, when a linear low-density polyethylene-based resin having a density of 0.905 to 0.95, a high-density polyethylene-based resin having a density of 0.94 to 0.98, or a polypropylene-based resin having a density of 0.88 to 0.91 is used, flexibility can be enhanced and the discharge efficiency of liquid contents is improved to improve drop impact strength. Thus, this case is preferable. Additionally, for example, resins such as an acid-modified polyolefin-based resin obtained by modifying a polyolefin-based resin such as low-density polyethylene, medium-density polyethylene, high-density polyethylene, a random copolymer of ethylene and propylene, a block copolymer, a polyethylene-based elastomer, a polypropylene-based elastomer, a styrene-based elastomer, an ethylene-vinyl acetate copolymer, methyltenpen, polybutene, polyethylene, or polypropylene, with acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, and other unsaturated carboxylic acids, and a urethane-based resin, can be used. In addition, when an adhesive resin layer for adhesion with other resin layers is used as a multilayer, the resin layer can be used as a light-shielding layer. A known adhesive resin can be used as the adhesive resin and for example, an ADMER resin produced by Mitsui Chemicals, Inc., Modic produced by Mitsubishi Chemical Corporation, DLZ produced by Tosoh Corporation, a metalocene-based linear low-density polyethylene having a density of 0.91 or lower, a polyamide-based resin, copolymers of a polyamide-based resin and other resins, substituents thereof, modifications thereof, and the like can be used. When the light-shielding layer is provided as a single layer or multiple layers, the total thickness thereof is in a range of 10 μm to 200 μm and preferably in a range of 20 μm to 100 μm . When the thickness is 10 μm or less, the light-shielding effect is reduced and an appropriate level of stability of liquid contents cannot be maintained. Further, when the thickness is 200 μm or more, the multilayer sheet and the container have increased thickness and thus are not practical. Thus, this case is not preferable.

[0044] The melting point of the linear low-density polyethylene is a value of a melting peak temperature measured according to JIS K 7121 (DSC) and is preferably 105°C to 130°C and particularly preferably 110°C to 130°C. The melting point of the high-density polyethylene is a value of a melting peak temperature measured according to JIS K 7121 (DSC) and is preferably 120°C to 145°C and particularly preferably 130°C to 140°C. The melting point of the polypropylene is a value of a melting peak temperature measured according to JIS K 7121 (DSC) and is preferably 118°C to 170°C and particularly preferably 123°C to 165°C. In addition, a polymer blend containing the aforementioned linear low-density polyethylene, high-density polyethylene, or polypropylene as a main component may also be employed. Further, to the aforementioned polyethylene-based resin and polypropylene-based resin, known additives such as an antioxidant, a photo-stabilizer, a neutralizing agent, an α -nucleating agent, a β -nucleating agent, an anti-blocking agent, and a lubricant may be added in such an amount that the object of the invention is not impaired.

[0045] In the present invention, the term "main component" refers to a component having a content of 60% by weight or more.

[0046] The resin for the light-shielding layer forms a layer containing any one of a cyclic polyolefin-based resin, a fluorine-based resin and a polyester-based resin as a main component. Thus, a higher effect of preventing light-shielding substances (an ultraviolet absorber, an organic or inorganic pigment, an inorganic substance, a colored pigment, a fluorescent brightening agent, a dye, and the like) used for the light-shielding layer from being eluted into contents or liquid contents or bleeding out of the container through interlayer movement of these substances when the light-shielding sheet and the container are stored at a high temperature of 50°C or higher or subjected to a heat treatment represented as hot filling at 70°C to 95°C, an inactivation treatment of viruses or the like by heat of 60°C to 70°C, a sterilization treatment with high pressure steam at a temperature of 100°C or higher, or the like can be obtained and this case is preferable. The cyclic polyolefin-based resin, fluorine-based resin and polyester-based resin may form a layer alone or in combination of two or more thereof.

[0047] In the sheet of the present invention, an eluate-blocking layer is provided on one surface of the sheet or between one surface and the light-shielding layer. In the case in which a container is produced using the sheet, when the one surface is provided on the content side, substances eluted into liquid contents by interlayer moving substances (an ultraviolet absorber, an organic or inorganic pigment, an inorganic substance, a colored pigment, a fluorescent brightening agent, a dye and the like), which are eluted from the light-shielding layer, can be blocked (hereinafter, the eluate-blocking layer in this embodiment is referred to as an eluate-blocking layer A). On the other hand, in the case in which a container is produced using the sheet, when the one surface is provided on the outer side of the container, other containers or production lines can be prevented from being contaminated due to bleeding out of interlayer moving substances (an ultraviolet absorber, an organic or inorganic pigment, an inorganic substance, a colored pigment, a fluorescent brightening agent, a dye and the like), which are eluted from the light-shielding layer, to the outside of the container (hereinafter, the eluate-blocking layer in this embodiment is referred to as an eluate-blocking layer B).

[0048] The eluate-blocking layer A may be provided on the side closer to contents than the light-shielding layer when the sheet is formed into a container, may be directly laminated on the light-shielding layer, or may be laminated though an adhesive layer and other layers.

[0049] The eluate-blocking layer B may be provided on the outer side of the light-shielding layer, may be directly

laminated on the light-shielding layer, or may be laminated through an adhesive layer and other layers.

[0050] When the eluate-blocking layer A and the eluate-blocking layer B are formed to have a layer containing any one of a cyclic polyolefin-based resin, a fluorine-based resin, a polyester-based resin, and a polyamide-based resin as a main component, an ultraviolet absorber, an organic or inorganic pigment, an inorganic substance, a colored pigment, a fluorescent brightening agent, a dye and the like used for the light-shielding layer can be prevented from being eluted into liquid contents or bleeding out of the container through interlayer movement of these light-shielding substances when the light-shielding sheet and the container are stored at a high temperature of 50°C or higher or subjected to a heat treatment represented as hot filling at 70°C to 95°C, an inactivation treatment of viruses or the like by heat of 60°C to 70°C, a sterilization treatment with high pressure steam at a temperature of 100°C or higher, or the like. In addition, when a resin containing any one of a cyclic polyolefin-based resin, a fluorine-based resin and a polyester-based resin as a main component is used as the resin for the light-shielding layer, a higher interlayer moving substance-blocking effect by the eluate-blocking layers A and B is obtained and thus this case is preferable. The cyclic polyolefin-based resin, the fluorine-based resin, the polyester-based resin and the polyamide-based resin may form a layer alone or in combination of two or more thereof. The eluate-blocking layers A and B may be provided as a single layer respectively or plural layers. The thickness of each single layer is in a range of 5 μm to 300 μm and preferably in a range of 10 μm to 200 μm . When the thickness is 5 μm or less, the eluate-blocking effect is small and an appropriate level of stability of liquid contents cannot be maintained. Further, when the thickness is 300 μm or more, the multilayer sheet and the container have an increased thickness and thus are not practical. Thus, this case is not preferable. When the thickness is in a range of 10 μm to 200 μm , a sufficient eluate-blocking effect can be obtained and sufficient flexibility can be imparted to the sheet and the container. Thus, this case is more preferable.

[0051] The cyclic polyolefin-based resin used for the light-shielding layer, the eluate-blocking layer A and the eluate-blocking layer B has a glass transition temperature of 60°C or higher, preferably 110°C or higher, and more preferably 126°C or higher. In the case in which the glass transition temperature is 60°C or lower, the polymer molecular motion is promoted when the sheet and the container are stored at a high temperature of 50°C or higher or subjected to a heat treatment represented as hot filling at 70°C to 95°C, an inactivation treatment of viruses or the like by heat of 60°C to 70°C, a sterilization treatment with high pressure steam at a temperature of 100°C or higher, or the like, and interlayer movement of an ultraviolet absorber, a pigment, and an inorganic substance easily occurs. Thus, this case is not preferable. Further, in the case in which the glass transition temperature is 110°C or higher, even when sterilization is carried out at a high pressure steam sterilization temperature of 105°C, interlayer movement of an ultraviolet absorber, an organic or inorganic pigment, an inorganic substance, a colored pigment, and the like does not occur and the substances can be prevented from being eluted into liquid contents or bleeding out of the container. Thus, this case is preferable. Further, in the case in which the glass transition temperature is 126°C or higher, a range, in which interlayer movement of an ultraviolet absorber, an organic or inorganic pigment, an inorganic substance, a colored pigment, and the like does not occur even when sterilization is carried out at a high pressure steam sterilization temperature of 121°C, and the substances can be prevented from being eluted into liquid contents or bleeding out of the container, is widened and particularly, overkill sterilization that is internally accepted for injection for infusion solutions and liquid medicine is possible. Thus, this case is preferable.

[0052] Rotational motion of polymer chains occurs by polymer molecular motion represented as micro brownian motion at the level of a molecule in a polymeric material. When the light-shielding sheet and the container are placed under an environment of the glass transition temperature or higher, the micro brownian motion of the molecular chains is promoted and thus the polymeric material becomes soft. The interlayer movement in which the ultraviolet absorber, the organic or inorganic pigment, the inorganic substance, the colored pigment, the fluorescent brightening agent, the dye and the like used for the light-shielding layer are easily transferred to other layers easily occurs and thus contamination of other containers and lines resulting from a problem of elution of the substances into the container or bleeding out of the substances to the outside of the container occur.

[0053] Particularly, the glass transition temperature is a temperature at which micro-Brownian motion of polymer chains starts and therefore reflects the ease of polymer chain motion. Thus, the glass transition temperature is very important. Since movement of polymers is determined by internal rotation of the polymer chains and steric hindrance, it is important to select a resin in which a large number of aromatic rings or heterocyclic rings, which impart steric hindrance, are incorporated or introduced into a main chain and side chains, a resin in which molecules of halogenides and the like are present in a main chain and side chains, or a resin in which a distance between molecules by a hydrogen bond is short in addition to the glass transition temperature as a method of easily preventing interlayer movement of the ultraviolet absorber, the organic or inorganic pigment, the inorganic substance, the colored pigment, the fluorescent brightening agent, the dye and the like used for the light-shielding layer to other layers.

[0054] It is found that the best method of preventing and solving a problem of contamination of other containers or lines resulting from the problem of elution of the substances into the container or bleeding out of the substances to the outside of the container is to design the container material which is determined under the consideration of the temperature and environment in which the light-shielding sheet and the container are placed or treated while taking such points into

consideration by preventing or blocking interlayer movement without transfer of the ultraviolet absorber, the organic or inorganic pigment, the inorganic substance, the colored pigment and the like used for the light-shielding layer into other layers.

[0055] Particularly, it is necessary for the eluate-blocking layer to select a resin from resins in which the glass transition temperature can be set to be high under the temperature and environment in which the light-shielding sheet and the container are placed or treated such that the rotational motion of polymer chains does not occur by micro-Brownian motion, or a large number of aromatic rings or heterocyclic rings, which impart steric hindrance, are incorporated or introduced into a main chain and side chains, molecules of halogenides and the like are present in a main chain and side chains, and in which a distance between molecules by hydrogen bond is short. As the most suitable resins to be used for the sheet and the container among these resins, there are a cyclic polyolefin-based resin, a fluorine-based resin, a polyester-based resin, and a polyamide-based resin. It is necessary to form the eluate-blocking layer using these resins as main components. In addition, by forming the light-shielding layer using such a cyclic polyolefin-based resin, a fluorine-based resin, and a polyester-based resin in combination as a main component, the effect can be further enhanced.

[0056] Examples of the cyclic polyolefin-based resin include polymers of various cyclic olefin monomers, copolymers of cyclic olefin monomers and monomers such as ethylene and hydrogen additives thereof. Examples of the cyclic polyolefin monomers include bicyclic cycloolefins such as norbornene, norbornadiene, methylnorbornene, dimethylnorbornene, ethylnorbornene, chlorinated norbornene, chloromethylnorbornene, trimethylsilylnorbornene, phenylnorbornene, cyanonorbornene, dicyanonorbornene, methoxycarbonylnorbornene, pyridylnorbornene, nadic anhydride, and nadic acid imide; tricyclic cycloolefins such as dicyclopentadiene, dihydrodicyclopentadiene, and alkyl, alkenyl, alkylidene and aryl substitutes thereof; tetracyclic cycloolefins such as dimethanohexahydronaphthalene and dimethanooctahydronaphthalene, and alkyl, alkenyl, alkylidene and aryl substituents thereof; pentacyclic cycloolefins such as tricyclopentadiene; and hexacyclic cycloolefins such as hexacycloheptadecene. Also included are compounds containing the norbornene ring, such as dinorbornene and compounds obtained by bonding two norbornene rings via hydrocarbon chains or ester groups and the like, alkyl and aryl substituents thereof, and the like.

[0057] As the polyolefin-based resin of the present invention, preferred are polynorbornene-based resins obtained by polymerizing one or two or more of norbornene-based monomers containing the norbornene skeleton in their molecular skeletons, such as dicyclopentadiene, norbornene and tetracyclododecene; hydrogen additives thereof; one of or mixtures of two or more of these polynorbornene-based resins and hydrogenation products thereof; and the like. From the viewpoint of strength and flexibility when the sheet is formed into as a liquid storing container, these resins are preferable.

[0058] The polymerization method or polymerization mechanism of monomer molecules of each cyclic polyolefin-based resin in the present invention may be either ring-opening polymerization or addition polymerization. As the polymerization method and the polymerization mechanism when a plurality of monomers are used in combination, known methods can be used. For example, a plurality of monomers can be combined together while the plural monomers are monomers, and then copolymerization may be performed. As an alternative, after being polymerized to some extent, the monomers may be combined together into a block copolymer.

[0059] For example, as a specific structure of the cyclic polyolefin-based resin, a structural formula expressed by the following formula (1) or (2) can be used. When the polyolefin-based resin particularly expressed by the following formula (1) of these formulae is used, the occurrence of fracturing and cracks of the layer itself due to an impact or pressure from the outside and the like is reduced. Particularly, the storage stability of a drug is improved and thus, it is found that a higher effect can be exhibited.

[Chem. 1]

[0060] (in the formula, R^1 , R^2 , R^3 and R^4 , which may be identical to or different from each other, each represent an organic group having 1 to 20 carbon atoms, and R^1 and R^2 and/or R^3 and R^4 each may form a ring. m and p each represent an integer of 0 or 1 or more. 1 and n each represent an integer of 1 or more.)

[0061] More specific examples of the organic group having 1 to 20 carbon atoms include alkyl groups such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, t-butyl, i-pentyl, t-pentyl, n-hexyl, n-heptyl, n-octyl, t-octyl (1,1-dimethyl-3,3-dimethylbutyl), 2-ethylhexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and icosyl; cycloalkyl groups such as cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl; alkylcycloalkyl groups such as 1-methylcyclopentyl, 1-methylcyclohexyl and 1-methyl-4-i-propylcyclohexyl; alkenyl groups such as allyl, propenyl, butenyl, 2-butenyl, hexenyl and cyclohexenyl; aryl groups such as a phenyl group, a naphthyl group, a methylphenyl group, a methoxyphenyl group, a biphenyl group, a phenoxy phenyl group, a chlorophenyl group and a sulfofenyl group; and aralkyl groups such as a benzyl group, 2-phenylethyl group (phenethyl group), α -methyl benzyl group and α,α -dimethyl benzyl group, but are not limited thereto. In addition, one of the above-described organic groups may be used alone or a combination of two or more thereof may be used.

[0062] The glass transition temperature of such cyclic polyolefins can be appropriately adjusted by appropriately

selecting values of 1, m, n and p in the above formulae (1) and (2), or substituents. The glass transition temperature of polycycloolefins other than the polycycloolefins expressed by formulae (1) and (2) may be arbitrarily adjusted to obtain a desired value by appropriately selecting the species, blending ratio, and sequence of monomers to be used, the type of substituents, and the like.

[0063] The cyclic polyolefin expressed by formula (1) may be a commercially available product. For example, Zeonex and Zeonox (products of Nippon Zeon Co., Ltd.) are suitably used. The polycycloolefin represented by formula (2) also may be a commercially available product. For example, Apel (product of Mitsui Chemicals Inc.) and TOPAS (product of TICONA) are suitably used.

[0064] As the cyclic polyolefin of the present invention, it is most preferable to use the cyclic polyolefin expressed by the above formula (1) and it is more preferable to use the resin expressed by the above formula (1) alone without including other resins. However, other resins can be added in a range of 40% or less. As other resins, polyethylene-based resins are preferable. However, the resins are not particularly limited as long as the resins are resins which are commonly used.

[0065] The fluorine-based resin used for the light-shielding layer, the eluate-blocking layer A and the eluate-blocking layer B is a synthetic resin obtained by polymerization of olefin including fluorine and known fluorine-based resins including copolymers of other resins and monomers, modifications, and substituents can be used. The resin is not particularly limited as long as the density is 1.3 g/cm³ or higher. When the density is lower than 1.3 g/cm³, interlayer movement of light-shielding substances and the blocking effect cannot be sufficiently obtained and this case is not preferable. Examples of the fluorine-based resin include polytetrafluoroethylene (abbreviation: PTFE), polychlorotrifluoroethylene (abbreviation: PCTFE, CTFE), polyvinylidene fluoride (abbreviation: PVDF), polyvinyl fluoride (abbreviation: PVF), perfluoroalkoxy fluororesin (abbreviation: PFA), an ethylenetetrafluoride-propylenehexafluoride copolymer (abbreviation: FEP), an ethylene-tetrafluoroethylene copolymer (abbreviation: ETFE), an ethylene-chlorotrifluoroethylene copolymer (abbreviation: ECTFE), a tetrafluoroethylene-perfluoroalkylvinyl ether copolymer resin, a perfluoroethylene-propene copolymer (FEP), polyvinylidene fluoride (PVdF), a perfluoroethylene-propylene copolymer, a perfluoroethylene-propene copolymer, polyvinylidene fluoride, polychlorotrifluoroethylene, a tetrafluoroethylene-perfluorodioxole copolymer, polyvinyl fluoride, EFEP having improved adhesion, and a tetrafluoroethylene/perfluoro(alkylvinylether)/chlorotrifluoroethylene copolymer (CPT).

[0066] The polyester-based resin used for the light-shielding layer, the eluate-blocking layer A, and the eluate-blocking layer B is a copolymer of dicarboxylic acid and diol. Known polyester-based resins including copolymers of other resins and monomers, modifications, and substituents, polymers including an elastomer component, and mixtures can be used and there is no particular limitation thereto.

[0067] Examples of the dicarboxylic acid include succinic acid, adipic acid, terephthalic acid, isophthalic acid, suberic acid, sebacic acid, itaconic acid, dodecanedioic acid, cellulose acetate, naphthalene-2,6-dicarboxylic acid, and succinic acid. As other acid components, diphenylsulfone dicarboxylic acid, hexahydro terephthalic acid, hexahydro isophthalic acid, azelaic acid or the like can be selected. One of these acids may be used alone or a combination of two or more thereof may be used. Examples of the diol include glycols such as 1,4-butanediol, 1,3-propanediol, 1,4-cyclohexane dimethanol, 2,3-butanediol, 1,3-butanediol, 1,4-pentanediol, 2,4-pentanediol, 1,6-hexanediol, neopentyl glycol, ethylene glycol, diethylene glycol, propylene glycol, and butylene glycol, and polyoxyalkylene glycols such as polyethylene glycol, polypropylene glycol, and polytetramethylene glycol, neopentyl glycol, diethylene glycol, 1,4-cyclohexane dimethylol, 2,2-bis(4- β -hydroxyethoxyphenyl)propane, and 1,4-bis(β -hydroxyethoxy)benzene. One of these diols may be used alone or a combination of two or more thereof may be used.

[0068] Particularly, a copolymer including terephthalic acid of a first main component and isophthalic acid of a second main component as dicarboxylic acid components and ethylene glycol of a main component as a diol component exhibits a high interlayer moving substance-blocking effect and thus is preferable. The sum of copolymerization ratios of terephthalic acid and isophthalic acid of the dicarboxylic acid components is preferably 95% by mole to 100% by mole, and more preferably 99% by mole to 100% by mole. In addition, the copolymerization ratio of ethylene glycol of the diol component is preferably 95% by mole to 100% by mole and more preferably 99% by mole to 100% by mole. The intrinsic viscosity (IV) is preferably 0.60 dl/g to 0.85 dl/g. The intrinsic viscosity in the present invention is a value that is measured at a temperature of 30°C using a mixture solvent of a phenol and 1,1,2,2-tetrachloroethane (mass ratio 1/1) according to JIS K 7367-5. When the intrinsic viscosity is lower than 0.60 dl/g, the molecular weight of the resin is excessively reduced and a sufficient interlayer moving substance-blocking effect is hardly obtained. When the intrinsic viscosity is higher than 0.85 dl/g, the viscosity at the time of thermofusion is excessively increased and extrusion is difficult. However, in this case, the productivity is lowered and it is therefore not preferable.

[0069] Further, the polyester-based resin may contain an aliphatic oxycarboxylic acid unit. At this time, specific examples of the aliphatic oxycarboxylic acid to which an aliphatic oxycarboxylic acid is imparted include lactic acid, glycolic acid, 2-hydroxy-n-butyric acid, 2-hydroxy caproic acid, 6-hydroxy caproic acid, 2-hydroxy-3,3-dimethyl butyric acid, 2-hydroxy-3-methyl butyric acid, 2-hydroxy isocaproic acid, or lower alkyl esters thereof, or intramolecular esters. In the case in which these have an optical isomer resin, the optical isomer resin may be any of D-resin, L-resin and racemic resin, and the morphology may be a solid, a liquid or an aqueous solution. One of these aliphatic oxycarboxylic acids

may be used alone or in a mixture of two or more thereof.

[0070] The polyester-based resin may be a resin obtained by copolymerizing "a trifunctional or higher functional aliphatic polyhydric alcohol", "a trifunctional or higher functional aliphatic polyvalent carboxylic acid or an acid anhydride thereof", or "a trifunctional or higher functional aliphatic polyvalent oxycarboxylic acid". Specific examples of the trifunctional or higher functional aliphatic polyhydric alcohol include trimethylolpropane and glycerol. These polyhydric alcohols may be used alone or a mixture of two or more thereof may be used. Specific examples of tetrafunctional aliphatic polyhydric alcohol include pentaerythritol. Specific examples of the trifunctional or higher functional aliphatic polyvalent carboxylic acid or an acid anhydride thereof include propanetricarboxylic acid and an acid anhydride thereof. Specific examples of tetrafunctional polyvalent carboxylic acid or an acid anhydride thereof include cyclopentane tetracarboxylic acid and an acid anhydride thereof. These acids may be used alone or a mixture of two or more thereof may be used. The trifunctional aliphatic oxycarboxylic acid is classified into (i) a type having two carboxyl groups and one hydroxyl group in the same molecule and (ii) a type having one carboxyl group and two hydroxyl groups in the same molecule, and either type may be used. Specifically, malic acid and the like are preferably used. Also, the tetrafunctional aliphatic oxycarboxylic acid is classified into (i) a type having three carboxyl groups and one hydroxyl group together in the same molecule, (ii) a type having two carboxyl groups and two hydroxyl groups together in the same molecule, and (iii) a type having three hydroxyl groups and one carboxyl group together in the same molecule, and any type may be used. Specific examples thereof include citric acid and tartaric acid. These acids may be used alone or a mixture of two or more thereof may be used.

[0071] The polyamide-based resin used for the light-shielding layer, the eluate-blocking layer A and the eluate-blocking layer B is composed of a crystalline polymer having an amide bond [-NHCO-] as repeating units in the molecule. Examples of the polyamide-based resin include a resin composed of crystalline polymer in which an amide bond is bonded with an aliphatic structure or alicyclic structure, so-called nylon resin. Examples of the nylon resin include nylon 6, nylon 11, nylon 12, nylon 610, nylon 612, nylon 6/66, nylon 66/12, and a blend of at least two or more of these resins. However, the nylon resin is not particularly limited as long as the nylon resin is a resin which is commonly used. In addition, examples of polyamide-based elastomers [TPAE] include a nylon 6/polyester copolymer, a nylon 6/polyether copolymer, a nylon 12/polyester copolymer, and a nylon 12/polyether copolymer but are not limited thereto.

[0072] In the case in which the polyolefin-based resin and/or the fluorine-based resin are used for the light-shielding layer, the eluate-blocking layer A and the eluate-blocking layer B to form a sheet, if a total thickness of a layer made of the polyolefin-based resin and a layer made of the fluorine-based resin is 80 μm or more, the dampproofness of the sheet against water vapor can be improved and thus this case is preferable.

[0073] One of an ultraviolet absorber, an organic or inorganic pigment, an inorganic substance, a colored pigment and the like used for the light-shielding layer may be used alone or a combination of two or more thereof may be used and the type and number are not limited. Further, a known ultraviolet absorber, organic or inorganic pigment, inorganic substance, colored pigment, fluorescent brightening agent, dye, and the like, which are commonly used, may be used.

[0074] As the ultraviolet absorber, the organic or inorganic pigment, the inorganic substance, the colored pigment, and the like, for example, an organic ultraviolet absorbers and light-shielding agent such as benzophenone-based compounds, oxybenzone-based compounds, benzoylmethane-based compounds, butyl-methoxybenzoylmethane-based compounds, benzotriazole-based compounds, triazole-based compounds, benzoate-based compounds, hydroxyphenyl triazine-based compounds, salicylate-based compounds, triaryl triazine-based compounds, cinnamic acid-based compounds, 2-ethylhexyl para-methoxycinnamate, para-amino benzoic acid-based compounds, octyl para-dimethylamino benzoate, camphor-based compounds, and methylbenzylidene camphor. The above-described ultraviolet absorber and light-shielding agent have an advantage of having better transparency than an inorganic ultraviolet absorber and light-shielding agent. Among these, a benzophenone-based ultraviolet absorber and a benzotriazole-based ultraviolet absorber are most preferable from the viewpoint of light-shielding performance and visibility inspection properties at 450 nm.

[0075] Specific examples of the benzophenone-based ultraviolet absorber include, 2,4-dihydroxy benzophenone, 2,2',4,4'-tetrahydroxy benzophenone, 2-hydroxy-4-(β -hydroxyethoxy)-benzophenone, bis(5-benzoyl-4-hydroxy-2-methoxyphenyl)methane, 2-hydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone, 2-hydroxy-4-octyloxybenzophenone, and 2-hydroxy-4-n-octyloxybenzophenone. Among these, an ultraviolet absorber having good heat resistance is preferable and bis(5-benzoyl-4-hydroxy-2-methoxyphenyl)methane and 2,2',4,4'-tetrahydroxy benzophenone is particularly preferable.

[0076] Specific examples of the benzotriazole-based ultraviolet absorber include 2-(5-chloro-2-benzotriazol)-6-tert-butyl-p-cresol, 2-(5-methyl-2-hydroxyphenyl)benzotriazol, 2-[3,5-bis(2,2-dimethylpropyl)-2-hydroxyphenyl] benzotriazol, 2-(3-tertiary butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzotriazol, 2-(3,5-ditertiary butyl-2-hydroxyphenyl)-5-chlorobenzotriazol, 2-[2-hydroxy-3,5-bis(α,α -dimethylbenzyl)phenyl]-2H-benzotriazol, 2,2-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-(2H-benzotriazol-2-yl)phenol], 2-(3-tert-butyl-2-hydroxy-5-methylphenyl)-5-chloro-2H-benzotriazol, 2,2'-methylenebis [4-(1,1,3,3-tetramethylbutyl)-6-[(2H-benzotriazol-2-yl) phenol]], 2-(2'-hydroxy-5'-methylphenyl)benzotriazol, 2(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazol, and 2-(2-hydroxy-5-methylphenyl)benzotriazol.

Among these, 2-[2-hydroxy-3,5-bis(α,α -dimethylbenzyl)phenyl]-2H-benzotriazol, 2,2-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-(2H-benzotriazol-2-yl)phenol], and 2-[5-chloro(2H)-benzotriazol-2-yl]-4-methyl-6-(tert-butyl)phenol having good heat resistance are preferable.

[0077] Specific examples of the triazine-based ultraviolet absorber include 2,4,6-tris(2-hydroxy-4-hexyloxy-3-methylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(hexyloxy)phenol]-4,6-diphenyl-1,3,5-triazine, and 2-(4,6-diphenyl-1,3,5-triazine-2-yl)-5-[2-(2-ethyl hexyloxy)ethoxy]phenol. Among these, 2,4-bis(2,4-dimethylphenyl)-6-(2-hydroxy-4-n-octyloxyphenyl)-1,3,5-triazine having good heat resistance is preferable.

[0078] In addition, as the inorganic ultraviolet absorber and light-shielding agent, titanium oxide, zinc oxide, iron oxide, cerium oxide, zirconium oxide, nickel oxide, magnesium oxide, mica, kaolin, sericite, or modifications thereof can be used.

[0079] A colorant or pigment such as an organic pigment such as an organic pigment such as phthalocyanine or inorganic pigment can be used. The pigments having colors of yellow, blue, green, orange, red, brown, black, white and the like may be used alone or a mixture of two or more thereof may be used.

[0080] Specific examples of the fluorescent brightening agent and the dye include diaminostilbene-based materials, imidazole-based materials, thiazole-based materials, oxazole-based materials, 2,5-thiophenediyl(5-tert-butyl-1,3-benzoxazole) [Tinopal OB (product of BASF)] and the like), triazole-based materials, oxadiazole-based materials, thiadiazole-based materials, coumarin-based materials, naphthalimide-based materials, pyrazoline-based materials, pyrene-based materials, imidazolone-based materials, benzidine-based materials, diaminocarbazole-based materials, oxacyanin-based materials, methine-based materials, pyridine-based materials, anthrapyridazine-based materials, distyryl-based materials, carbostyryl-based materials, indole-based materials, and quinolinone-based materials and oxazole-based materials are preferably used.

[0081] The amount of the light-shielding substances such as the above-described ultraviolet absorber, organic or inorganic pigment, inorganic substance, and colored pigment added is preferably 0.01% by weight to 30% by weight with respect to the resin. When the amount of the light-shielding substances added is less than 0.01% by weight, a desired light-shielding function cannot be sufficiently exhibited. On the other hand, when the amount of the light-shielding substances added is more than 30% by weight, the light-shielding function is not significantly improved and not only is an increase in cost caused but also there is a high possibility of elution and bleeding out. Thus, this case is not preferable.

[0082] The light-shielding sheet and the container of the present invention are used for a sheets and a container for pharmaceutical products, such as drugs stored in soft bags such as PTP packaging and blister packaging, obtained by thermoforming a blister sheet, and an infusion solution and liquid medicine bag, and a plastic ampoule and vial, and a syringe, and medical supplies, various cosmetics, or foods.

[0083] The light-shielding sheet of the present invention has a multilayer structure of three or more layers including at least one light-shielding layer and eluate-blocking layer. Examples of the production method include known methods such as dry lamination, extrusion coating, extrusion lamination, co-extrusion lamination such as a co-extrusion inflation method or co-extrusion T-die method, co-extrusion water-cooling inflation, and heat lamination. These methods may be used alone or in combination. When co-extrusion lamination such as co-extrusion blowing or co-extrusion T-die method, co-extrusion water-cooled blowing, and heat lamination are particularly used, a multilayer sheet can be produced without using an organic adhesive such as a two-pack curing type polyester urethane-based adhesive or polyether urethane-based adhesive, or epoxy-based adhesive and these methods are preferable from the viewpoint of safety and hygiene of contents. Further, since gas barrier properties and water vapor barrier properties are imparted to the sheet, several layers may be laminated as barrier layers. As the material to be laminated on the barrier layer, a silica- or alumina-deposited PET film, silica- or alumina- deposited nylon film, aluminum-deposited PET film, aluminum-deposited nylon, aluminum foil, EVOH, PVA, PVDC, MXD nylon, organic or inorganic hybrid type barrier film, and the like can be used. When the multilayer is formed using different material resins and films, an adhesive resin can be used without causing a problem in safety and hygiene. As a resin, known resins can be used as long as the resins have excellent adhesion with different materials. These resins may be used alone or in combination of two or more thereof. Examples of the adhesive resin include an acid modified polyolefin resin and metallocene-based LLDPE. Preferred specific examples of the acid modified polyolefin resin include metal-cross-linked polyethylene (ionomer), an ethylene-acrylic acid copolymer (EAA), an ethylene-methacrylic acid copolymer (EMAA), an ethylene-ethyl acrylate copolymer (EEA), maleic anhydride-modified polyethylene, and maleic anhydride-modified polypropylene. Examples of unsaturated carboxylic acids to be graft-polymerized with the raw material for the acid modified polyolefin resin include acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, acid anhydride thereof, and derivatives of esters, amides, imides, and metal salts. The metallocene-based LLDPE is a linear low-density polyethylene (LLDPE) obtained by polymerization using a metallocene catalyst. Examples thereof include ADMER produced by Mitsui Chemicals, Inc., Modic produced by Mitsubishi Chemical Corporation, DLZ produced by Tosoh Corporation, and a metallocene-based linear low-density polyethylene having a density of 0.91 or lower.

[0084] The light-shielding container of the present invention is produced using the light-shielding sheet of the present invention. The light-shielding container of the present invention has a multilayer structure of three or more layers including at least one light-shielding layer and eluate-blocking layer. Examples of the production method include known methods

such as extrusion direct blow molding, extrusion drawing blow molding, multidimensional blow molding, exchange blow molding, injection blow molding, injection drawing blow molding (hot parison and cold parison), multilayer blow molding, and multilayer injection blow molding. These methods may be used alone or in combination. In addition, since the container has a multilayer structure, the adhesive resin can be used.

[0085] The light-shielding container of the present invention can be produced into a pouch or a soft bag through a typical method including cutting two light-shielding sheets and stacking the sheets such that each seal layer is disposed inside, and heat-sealing the periphery of the stacked sheets. In addition, after the seal layers of the light-shielding sheets are disposed inside to form a tubular shape, the periphery thereof may be heat-sealed for molding. The heat sealing of the light-shielding sheets may be carried out in a temperature range of 150°C to 250°C. Further, it is more preferable to provide a discharge outlet (port) for discharging liquid contents at a part of the heat-sealed periphery from the viewpoint of improving discharge efficiency. The container may be sealed by welding a rubber plug to the port after the container is filled with liquid contents, or by welding a rubber plug to the port in advance or attaching a rubber plug to the port by insert injection molding. In the latter case, when the container is filled with liquid contents, methods of providing an opening at a part of the heat-sealed periphery or opening a part of the heat-sealed periphery at the time of filling and sealing the opened part by heat sealing after the container is filled with the liquid contents can be used.

[0086] In the present invention, the thickness of the barrier layer is preferably 5 μm to 200 μm and more preferably 10 μm to 100 μm from the viewpoint of the storage stability and flexibility of the light-shielding sheet and the container.

[0087] In the present invention, the total thickness of the light-shielding sheet and the container is preferably 50 μm to 2000 μm and more preferably 100 μm to 1200 μm although an appropriate range thereof varies depending on use of the container. When the total thickness is 50 μm or smaller, there is a possibility of lowering of strength for a sheet and a container. On the other hand, when the total thickness is larger than 2000 μm , a thickness of larger than 2000 μm is not required for a sheet and a container and an increase in cost is caused. Thus, this case is not preferable.

[0088] The light-shielding sheet and the container of the present invention are applicable to a sheet and a container in which pharmaceutical products and medical supplies, such as a blister sheet, an infusion solution and liquid medicine bag, a plastic ampoule and vial, and a plastic syringe, and drugs, various cosmetics, or foods can be stored. Although the contents are not particularly limited, the sheet and container can be used for contents such as powders, capsules, tablets, granules, oral disintegration tablets, and liquids and liquid contents. Among these, when the contents are contents that are approved by regulations for plastic pharmaceutical containers of the Japanese Pharmacopoeia, a higher effect is obtained and this case is preferable. The contents are liquids for pharmaceutical or medical use, and particularly for injections such as an infusion solution and a liquid medicine, from the viewpoint of the safety and hygiene of the contents, the light-shielding sheet and the container of the present invention by which various problems resulting from elution from light-shielding substances are solved are suitable. In the present invention, a liquid for pharmaceutical or medical use, as contents, is poured into a pouch, a soft bag, an ampoule, or a vial container and the container is sealed. Then, it is possible to solve a problem of elution or bleeding out of light-shielding substances when the container is stored at a high temperature of 50°C or higher or subjected to a heat treatment represented as hot filling at 70°C to 95°C, an inactivation treatment of viruses and the like at 60°C to 70°C, a high pressure steam sterilization treatment at a temperature of 100°C or higher, or the like. Particularly, even when the container is subjected to high pressure steam sterilization at a temperature of 110°C or higher and then used, there is a high possibility of the above problem arising and thus the light-shielding sheet and the container of the present invention are most suitable.

[0089] A drug to which the light-shielding sheet and the container of the present invention are applicable is not particularly limited as long as the drug is a known drug in which deterioration and lowering of titer occur by ultraviolet rays. Examples thereof include diltiazem, nifedipine, nisoldipine, carbamazepine, nitrendipine verapamil, azasetron, paclitaxel, thiamine, amlodipine, olopatadine, palonosetron, irinotecan, epoprostenol, riboflavin, cyanocobalamin, pyridoxine, nicotinic acid amide, panthenol, biotin, ascorbic acid, cholecalciferol, tocopherol, phytonadione, ozagrel hydrochloride, olopatadine, ketoprofen, somatropin, menatetrenone, benidipine, and mecobalamin. Particularly, the application of the sheet and the container to levofloxacin which is deteriorated by ultraviolet rays and a derivative or modification thereof (ofloxacin, tosufloxacin, sparfloxacin, norfloxacin, enoxacin, ciprofloxacin, lomefloxacin, nalidixic acid, pipemidic acid, piromidic acid, and the like), palonosetron hydrochloride and a derivative or modification thereof is most preferable from the viewpoint of preventing drug deterioration.

[Examples]

[0090] Hereinafter, the present invention will be described in detail by way of Examples and Comparative Examples, which should not be construed as limiting the invention thereto.

[Examples and Comparative Examples]

[0091] According to the configurations shown in FIGS. 1A to 1G, multilayer sheets having three or more layers of a

light-shielding layer, an eluate-blocking layer A, and an eluate-blocking layer B and containers were formed. The detailed configurations are specifically shown in Table 1.

[0092] As the resins for forming the sheets and containers, the following a to j were used for the light-shielding layer and the following I to XII were used for the eluate-blocking layers A and B.

- a: Linear low-density polyethylene having a density of 0.908 and linear low-density polyethylene having a melting point of 105°C (Harmolex, produced by Japan Polyethylene Corporation)
- b: Metallocene-based linear low-density polyethylene having a density of 0.924 and a melting point of 120°C (Umerit, produced by Ube-Maruzen polyethylene)
- c: High-density polyethylene having a density of 0.953 and a melting point of 132°C (Novatec, produced by Japan Polyethylene Corporation)
- d: Ziegler-based linear low-density polyethylene having a density of 0.923 and a melting point of 120°C (Moretec, produced by Prime Polymer)
- e: Polypropylene having a density of 0.90 and a melting point of 135°C (Wintec, produced by Japan Polypropylene Corporation)
- f: Cyclic polyolefin having a glass transition temperature of 136°C (Zeonex, produced by Nippon Zeon Co., Ltd.)
- g: Cyclic polyolefin having a glass transition temperature of 135°C (Apel, produced by Mitsui Chemicals Inc.)
- h: Fluorine-based resin having a density of 2.12 (Neofuron, produced by Daikin Kogyo Co., Ltd.)
- i: Polyester-based resin having a density of 1.34 (isophthalic acid-modified polyester)
- j: Cyclic polyolefin having a glass transition temperature of 75°C (Apel, produced by Mitsui Chemicals Inc.)

[0093]

- I: Cyclic polyolefin having a glass transition temperature of 136°C (Zeonex, produced by Nippon Zeon Co., Ltd.)
- II: Cyclic polyolefin having a glass transition temperature of 135°C (Apel, produced by Mitsui Chemicals Inc.)
- III: Cyclic polyolefin having a glass transition temperature of 165°C (Zeonox, produced by Nippon Zeon Co., Ltd.)
- IV: Cyclic polyolefin having a glass transition temperature of 105°C (Zeonox, produced by Nippon Zeon Co., Ltd.)
- V: Cyclic polyolefin having a glass transition temperature of 75°C (Zeonox, produced by Nippon Zeon Co., Ltd.)
- VI: Fluorine-based resin having a density of 2.12 (Neofuron, produced by Daikin Kogyo Co., Ltd.)
- VII: Cyclic polyolefin having a glass transition temperature of 138°C (Topas, produced by Daicel Polymer Ltd.)
- VIII: Fluorine-based resin having a density of 2.1 (polychloro trifluoro ethylene)
- IX: Fluorine-based resin having a density of 1.74 (Neofuron, produced by Daikin Kogyo Co., Ltd.)
- X: Polyester-based resin having a density of 1.34 (copolymer of terephthalic acid, isophthalic acid, and ethylene glycol: isophthalic acid-modified polyester)
- XI: Cyclic polyolefin having a glass transition temperature of 80°C (Apel, produced by Mitsui Chemicals Inc.)
- XII: Cyclic polyolefin having a glass transition temperature of 75°C (Apel, produced by Mitsui Chemicals Inc.)

[0094] Since different resins are used for each layer as resins for forming the films and the containers, an adhesive resin may be used. The following α to ε were used. The following α to ε were used as light-shielding layers by incorporating light-shielding substances into the adhesive resin layer.

- α : Admer (produced by Mitsui Chemicals Inc.)
- β : Modic (produced by Mitsubishi Plastics, Inc.)
- γ : Polyamide-based elastomer (produced by Daicel-Degussa, Ltd.)
- δ : Polyamide-based resin nylon 12 (produced by Ube Industries, Ltd.)
- ε : Resin obtained by mixing Harmolex (produced by Japan Polyethylene Corporation) and Wintec (produced by Japan Polypropylene Corporation) at 2:8

[0095] As resins for forming the films and the containers, an innermost layer, or an outermost layer, and other resin layers may be laminated and the above a to j, I to XII, and α to ε were used.

[0096] As the light-shielding substances used for the light-shielding layer, the following (1) to (9) were used.

[0097] The concentration used herein refers to % by weight of the following components incorporated into the light-shielding layer.

(1):

First component:

EP 3 000 750 A1

2-[5-chloro(2H)-benzotriazol-2-yl]-4-methyl-6-(tert-butyl)phenol

(concentration: 0.9%)

Second component:

2,4-bis(2,4-dimethylphenyl)-6-(2-hydroxy-4-n-octyloxyphenyl)-1,3,5-triazine

(concentration: 0.25%)

Third component: 2,2',4,4'-tetrahydroxy benzophenone (concentration: 0.25%)

(2):

First component:

2-[5-chloro(2H)-benzotriazol-2-yl]-4-methyl-6-(tert-butyl)phenol

(concentration: 0.5%)

Second component:

2,4-bis(2,4-dimethylphenyl)-6-(2-hydroxy-4-n-octyloxyphenyl)-1,3,5-triazine

(concentration: 0.5%)

Third component: 2,2',4,4'-tetrahydroxy benzophenone (density: 0.5%)

(3):

First component:

2-[5-chloro(2H)-benzotriazol-2-yl]-4-methyl-6-(tert-butyl)phenol

(concentration: 0.9%)

Second component: Zinc oxide (concentration: 0.9%)

(4):

First component:

2-[5-chloro(2H)-benzotriazol-2-yl]-4-methyl-6-(tert-butyl)phenol

(concentration: 0.75%)

Second component: YELLOW #021 (PEX MASTER COROR, produced by TOKYO PRINTING INK MFG.CO.,LTD.) (concentration: 6%)

(5):

First component:

2-[5-chloro(2H)-benzotriazol-2-yl]-4-methyl-6-(tert-butyl)phenol

(concentration: 1.8%)

Second component: 2-hydroxy-4-n-octyloxybenzophenone (concentration: 0.5%)

Third component: 2,5-thiophenediyl(5-tert-butyl-1,3-benzoxazole) (concentration: 0.3%)

(6):

First component:

2-[5-chloro(2H)-benzotriazol-2-yl]-4-methyl-6-(tert-butyl)phenol

(concentration: 0.3%)

Second component: 2-hydroxy-4-n-octyloxybenzophenone (concentration: 0.25%)

Third component: 2,5-thiophenediyl(5-tert-butyl-1,3-benzoxazole) (concentration: 0.05%)

Fourth component:

2(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazol

(concentration: 0.3%)

(7):

First component:

2-[5-chloro(2H)-benzotriazol-2-yl]-4-methyl-6-(tert-butyl)phenol

(concentration: 0.3%)

Second component:

2,4-bis(2,4-dimethylphenyl)-6-(2-hydroxy-4-n-octyloxyphenyl)-1,3,5-triazine

(concentration: 0.3%)

Third component: 2,5-thiophenediyl(5-tert-butyl-1,3-benzoxazole) (concentration: 0.05%)

(8):

First component:

2-[5-chloro(2H)-benzotriazol-2-yl]-4-methyl-6-(tert-butyl)phenol

(concentration: 0.15%)

Second component: Zinc oxide (concentration: 10%)

(9):

First component:

2-[5-chloro(2H)-benzotriazol-2-yl]-4-methyl-6-(tert-butyl)phenol (concentration: 0.075%)

Second component: 2-hydroxy-4-n-octyloxybenzophenone (concentration: 0.25%)

Third component: 3,5-di-tert-butyl-4-hydroxybenzoate 2,4-di-tert-butylphenyl (concentration: 0.075%)

[Table 1]

		Example																										Comparative Example				
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	1	2	3	4	
5	Outermost layer	Type of resin	b	a	b	b	c	b	c	c	b	b	c	b	b	-	-	c	c	c	b	b	c	c	c	c	b	b	b	c	b	b
	Thickness (μm)	60	60	80	70	40	70	40	40	70	80	60	130	200	-	-	50	50	60	95	45	30	15	20	15	95	350	60	60	130	200	
	Adhesive layer	Type of resin	-	-	-	-	α	-	β	α	-	-	α	-	-	-	-	-	-	-	-	e	-	-	-	-	-	-	α	-	-	
	Thickness (μm)	-	-	-	-	-	20	-	15	20	-	-	20	-	-	-	-	-	-	-	-	20	-	-	-	-	-	-	20	-	-	
	Eluate-blocking layer B	Type of resin	I	II	I	III	I	I	I	IV	-	-	-	-	I	X	VI	-	-	-	I	I	VII	XII	XI	-	-	I	V	-	-	e
	Thickness (μm)	25	25	15	10	25	10	15	25	-	-	-	-	100	20	20	-	-	-	10	15	10	45	30	-	-	150	25	-	-	100	
10	Adhesive layer	Type of resin	-	-	-	-	-	-	-	-	-	-	-	-	α	γ	α	α	β	-	-	-	-	-	-	-	-	-	-	-	-	
	Thickness (μm)	-	-	-	-	-	-	-	-	-	-	-	-	-	20	20	20	20	25	-	-	-	-	-	-	-	-	-	-	-	-	
	Light-shielding layer	Type of resin	a	a	c	b	b	f	g	b	f	g	f	g	b	b	h	γ	γ	i	f	b	b	j	b	j	f	b	a	b	c	b
	Light-shielding substance	(1)	(2)	(3)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(2)	(1)	(3)	(1)	(1)	(1)	(5)	(6)	(7)	(8)	(9)	(8)	(5)	(1)	(1)	(4)	(2)	(1)	
15	Adhesive layer	Type of resin	-	-	-	-	-	-	-	-	-	-	-	-	-	γ	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
	Thickness (μm)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
	Eluate-blocking layer A	Type of resin	I	II	I	III	I	I	I	IV	I	III	III	III	I	I	VI	VI	IX	X	I	I	VII	XII	XI	-	-	I	V	V	a	e
	Thickness (μm)	25	25	15	10	25	10	15	25	20	20	20	30	100	20	20	20	20	10	10	15	10	45	30	-	-	150	25	20	30	100	
20	Adhesive layer	Type of resin	-	-	-	-	α	-	β	α	-	-	α	-	-	-	γ	δ	β	-	-	e	-	-	-	-	-	-	α	-	-	
	Thickness (μm)	-	-	-	-	20	-	15	20	-	-	20	-	-	-	-	20	20	25	-	-	20	-	-	-	-	-	-	20	-	-	
	Adhesive layer	Type of resin	-	-	-	-	-	-	-	-	-	-	-	-	-	-	α	α	-	-	-	-	-	-	-	-	-	-	-	-	-	
	Thickness (μm)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	20	20	-	-	-	-	-	-	-	-	-	-	-	-	-	
	Innermost layer	Type of resin	b	a	b	d	e	b	c	c	b	b	c	-	-	b	-	c	c	e	b	b	c	c	c	c	b	-	b	c	-	-
	Thickness (μm)	60	60	80	70	40	70	40	40	70	80	60	-	-	80	-	50	50	60	95	45	30	15	20	15	95	-	60	60	-	-	

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* When the column of the resin for the innermost layer of the eluate-blocking layer A is blank, the eluate-blocking layer is the innermost layer.

* When the column of the resin for the outermost layer of the eluate-blocking layer B is blank, the eluate-blocking layer is the outermost layer.

* The mark “-” indicates that the layer with “-” is not used in the configurations of the sheets and the containers.

[Production Method 1]

[0098] As structures shown in Table 1, in Examples 1 to 4, 10, 14, 19, 20, and 25 and Comparative Example 1, a multilayer sheet was prepared by a co-extrusion T-die method. Then, the innermost layers of two sheets were stacked to be opposite to each other as a seal layer and the periphery thereof was welded twice at a die temperature 175°C for 3 seconds. At this time, a metallocene-based linear low-density polyethylene having a density of 0.935 and a melting point of 125°C was used at a part of the periphery to form a discharge outlet (port) through an injection molding method. The discharge outlet was attached by welding which was carried out twice at a die temperature 200°C for 3 seconds to prepare a soft bag for storing liquid having a volume of 100 ml.

[Production Method 2]

[0099] As the configuration shown in Table 1, in Examples 6 and 9, a multilayer sheet was prepared in the same manner as in Production method 1 except that a co-extrusion water-cooling inflation method was used and then a soft bag for storing liquid having a volume of 200 mL was prepared in the same manner as in Production Method 1.

[Production Method 3]

[0100] As the configuration shown in Table 1, in Examples 5, 7, 11, 16, 17, and 18, a multilayer sheet was prepared in the same manner as in Production Method 1 except that the die temperature at the time of welding the periphery was changed to 195°C and the material for the discharge outlet was changed to polypropylene having a density of 0.90 and

a melting point of 135°C to carry out welding twice at 220°C for 3 seconds. Thus, a soft bag having a volume of 100 mL was prepared.

[Production Method 4]

[0101] As the configuration shown in Table 1, in Examples 8 and 15, a multilayer sheet was prepared in the same manner as in Production Method 1 to form a sheet for blister molding for storing oral pharmaceutical products (tablets).

[Production Method 5]

[0102] As the configuration shown in Table 1, in Example 12, a multilayer sheet was prepared in the same manner as in Production Method 1 except that the die temperature at the time of welding the periphery was changed to 195°C for 4 seconds and the material for the discharge outlet was changed to cyclic polyolefin having a glass transition temperature of 136°C to carry out welding twice at 225°C for 6 seconds. Thus, a soft bag having a volume of 100 mL was prepared.

[Production Method 6]

[0103] As the configuration shown in Table 1, in Example 13, a molten resin (parison) extruded from a circular die was interposed between two dies while putting air into the dies and thus an ampoule container was prepared by a co-extrusion direct blow molding method.

[Production Method 7]

[0104] As the configuration shown in Table 1, in Examples 21 to 24, a multilayer sheet was prepared in the same manner as in Production Method 1 to form a sheet for blister molding for storing oral pharmaceutical products (tablets).

[Production Method 8]

[0105] As the configuration shown in Table 1, in Example 26, a molten resin (parison) extruded from a circular die was interposed between two dies while putting air into the dies and thus a vial container for storing powder and liquid was prepared by a co-extrusion direct blow molding method.

[Production Method 9]

[0106] As the configuration shown in Table 1, in Comparative Examples 1 and 3, a soft bag for storing liquid was prepared in the same manner as in Production Method 1.

[Production Method 10]

[0107] As the configuration shown in Table 1, in Comparative Example 2, a soft bag for storing liquid was prepared in the same manner as in Production Method 3.

[Production Method 11]

[0108] As the configuration shown in Table 1, in Comparative Example 4, an ampoule container was prepared in the same manner as in Production Method 6.

[Evaluation Method]

[0109] The following evaluation was performed on the light-shielding sheet and the container of the present invention.

[0110] In order to evaluate light-shielding properties, a part of each sheet and container of the above Examples and Comparative Examples was cut and evaluated using an ultraviolet and visible spectrophotometer.

[0111] The testing method for pharmaceutical containers of the Japanese Pharmacopoeia, Sixteenth Edition, was carried out by cutting some of the sheets and containers of the above Examples and Comparative Examples. In an eluate test, soft bags having different volumes were prepared and filled with purified water as liquid contents. After the bags were sealed, extraction at 100°C for 2 hours was carried out and then evaluation was carried out. The results are shown in Table 2.

[Table 2]

		Example																										Comparative Example					
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	1	2	3	4		
Light-shielding performance	380 nm (%)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	2	3	4	
	400 nm (%)	13	7	27	15	12	17	16	10	18	20	17	15	8	24	18	14	15	19	6	8	4	28	25	25	0	6	14	0	29	9		
	450 nm (%)	69	56	77	75	68	75	75	69	73	73	72	70	57	75	75	74	75	74	82	83	84	56	79	81	80	57	70	0	78	58		
Test of pharmaceutical containers of Japanese Pharmacopoeia, Sixteenth Edition	1. Heavy metal	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O		
	2. Lead	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O		
	3. Cadmium	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O		
	4. Fluoride	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	x	x	x	x	
	(i) Foaming	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O		
	(ii) pH	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O		
	(iii) Potassium permanganate reducing substance	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	x	x	x	x	
	(iv) Ultraviolet absorption spectrum	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	x	x	x	x	
	220 nm or longer and shorter than 240 nm	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	x	x	x	x
	241 nm or longer and 350 nm or shorter	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	x	x	x	x
	(v) Evaporation residue	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	x	x	x	x
Cytotoxicity test	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	-	-	-	-		

* The mark "O" means that the result is adequate.

* The mark "X" means the result is inadequate.

* The mark "-" means that the test is not carried out.

[0112] In Examples 1 to 26, regarding light-shielding performance, light transmittance at 380 nm was 0% to 0.9%, the light transmittance at 400 nm was 0.2% to 28%, and the light transmittance at 450 nm was 56% to 84%. In addition, the results satisfied a total light transmittance of 55% or higher at 450 nm, prescribed in the Japanese Pharmacopoeia and there was no problem in the results of the elution test.

[0113] In addition, in Examples 1 to 8, 13 to 15, 19 to 23, and 26 (configurations having the eluate-blocking layer B), there was no stickiness on the outside of the sheets and containers and bleeding out could be prevented. In addition, in Examples 9 to 12, 16 to 18, 24, and 25, since a resin layer which hardly allows elution of light-shielding substances to the light-shielding layer was provided, there was no stickiness on the outside of the sheet and containers and bleeding out could be prevented without the eluate-blocking layer B.

[0114] On the other hand, in Comparative Examples 1 to 4, irrespective of selection of light-shielding substances, all the containers were determined to be inadequate in the elution test.

[0115] Further, there was stickiness on the outside of the containers and bleeding out could not be prevented.

Reference Signs List

[0116]

- 1 LIGHT-SHIELDING LAYER
- 2 ELUATE-BLOCKING LAYER A
- 3 INNERMOST LAYER
- 4 OUTERMOST LAYER
- 5 ELUATE-BLOCKING LAYER B

Claims

1. A light-shielding sheet that has a multilayer structure of three or more layers comprising one or more of the group consisting of one or more light-shielding layers and one or more eluate-blocking layers, wherein the light-shielding layer is made of a resin containing at least one of an ultraviolet absorber, an organic pigment, an inorganic pigment, an inorganic substance, a colored pigment, a fluorescent brightening agent, and a dye, and is provided in an intermediate layer of the sheet, and the eluate-blocking layer is provided on at least one surface of the sheet or between at least one surface of the sheet and the light-shielding layer.

2. The light-shielding sheet according to claim 1,
wherein a total light transmittance of the sheet having the multilayer structure at a wavelength of 380 nm or shorter
is 1% or lower and a total light transmittance at a wavelength of 380 nm to 400 nm is 30% or lower.
- 5 3. The light-shielding sheet according to claim 1,
wherein the eluate-blocking layer has any one of a cyclic polyolefin-based resin, a fluorine-based resin, a polyester-
based resin, and a polyamide-based resin as a main component.
- 10 4. The light-shielding sheet according to claim 1,
wherein the light-shielding layer has any one of a cyclic polyolefin-based resin, a fluorine-based resin, and a polyester-
based resin as a main component.
- 15 5. The light-shielding sheet according to claim 1,
wherein the light-shielding layer has at least any one of a linear low-density polyethylene-based resin having a
density of 0.905 or higher, a high-density polyethylene-based resin having a density of 0.94 or higher, and a poly-
propylene-based resin having a density of 0.88 or higher as a main component.
- 20 6. The light-shielding sheet according to claim 1,
wherein a cyclic polyolefin-based resin is used for the eluate-blocking layer and the light-shielding layer and a glass
transition temperature thereof is 60°C or higher.
7. The light-shielding sheet according to claim 6,
wherein the glass transition temperature of the cyclic polyolefin-based resin is 110°C or higher.
- 25 8. The light-shielding sheet according to claim 1,
wherein the eluate-blocking layer and the light-shielding layer have a fluorine-based resin as a main component, and
a density of the fluorine-based resin is 1.3 g/cm³ or higher.
- 30 9. The light-shielding sheet according to claim 1,
wherein a total light transmittance at a wavelength of 450 nm or longer is 15% or higher.
10. The light-shielding sheet according to claim 9,
wherein the total light transmittance at a wavelength of 450 nm or longer is 55% or higher.
- 35 11. A light-shielding container that is produced using the light-shielding sheet according to claim 1.
12. A container
wherein a solution for pharmaceutical and medical use is stored in the light-shielding container according to claim
11 as contents and
40 the container is sterilized with high pressure steam at a temperature of 101°C or higher.
13. The container according to claim 11,
wherein the solution for pharmaceutical and medical use is a liquid drug in which at least one of deterioration,
lowering of titer, and impurity formation is caused by one or more of the group consisting of ultraviolet light and
45 visible light at a wavelength range of 220 nm to 450 nm.
14. The container according to claim 13,
wherein the drug includes one of the group consisting of levofloxacin, a derivative thereof, and a modification thereof.
- 50 15. The container according to claim 13,
wherein the drug includes one of the group consisting of palonosetron hydrochloride, a derivative thereof, and a
modification thereof.
- 55 16. A method of producing a light-shielding container comprising:

producing a container using the light-shielding sheet according to claim 1 by one or more methods selected
from the group consisting of extrusion direct blow molding, extrusion drawing blow molding, multidimensional
blow molding, exchange blow molding, injection blow molding, injection drawing blow molding, multilayer blow

molding, and multilayer injection blow molding.

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FIG. 1A

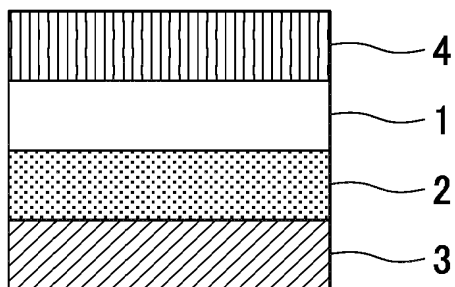


FIG. 1B

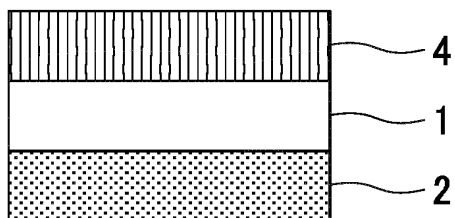


FIG. 1C

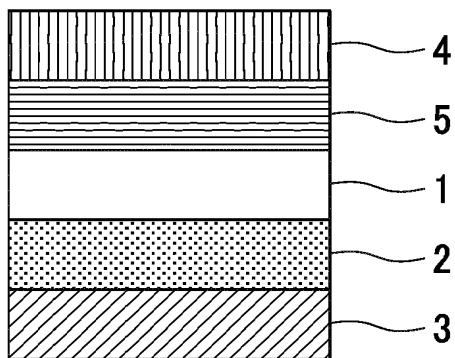


FIG. 1D

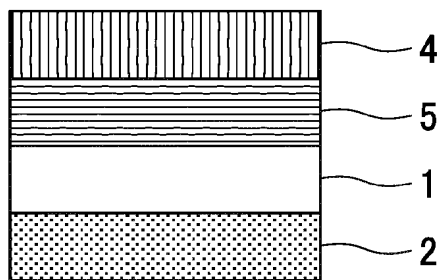


FIG. 1E

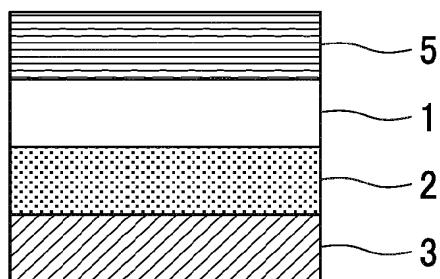


FIG. 1F

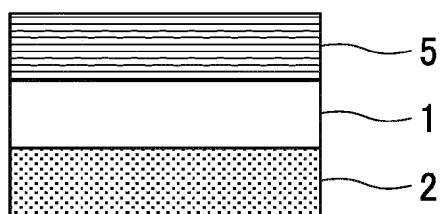
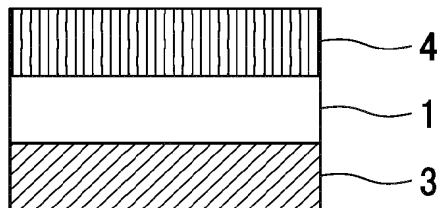


FIG. 1G



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/063297

A. CLASSIFICATION OF SUBJECT MATTER

B65D81/30(2006.01)i, B32B27/00(2006.01)i, B32B27/18(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)

B65D81/30, B32B27/00, B32B27/18

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 1996-2014

Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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.
X	JP 2005-305745 A (Toppan Printing Co., Ltd.), 04 November 2005 (04.11.2005), paragraphs [0005] to [0006], [0016] to [0024]; fig. 1 to 2 (Family: none)	1-2, 5, 9-11, 16
X	JP 2011-203400 A (Nippon Zeon Co., Ltd.), 13 October 2011 (13.10.2011), paragraphs [0011] to [0012], [0021], [0027], [0048] to [0053] (Family: none)	1, 3-4, 6-7

☒ 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
19 August, 2014 (19.08.14)Date of mailing of the international search report
09 September, 2014 (09.09.14)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/063297

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 2012-206514 A (Saint-Gobain Performance Plastics Corp.), 25 October 2012 (25.10.2012), paragraphs [0016] to [0036], [0039], [0054]; fig. 1 & BR PI0620991 A2 & CN 101360605 A & CN 103009737 A & JP 2009-523625 A & MX 2008008999 A & US 2007/0166562 A1 & WO 2007/087055 A1	1, 3-4, 8-10
X Y	JP 2008-174304 A (Otsuka Pharmaceutical Factory, Inc.), 31 July 2008 (31.07.2008), paragraphs [0017], [0037], [0068] to [0073]; tables 5, 6; fig. 3 (Family: none)	1-3, 9-11, 16 12-15
Y	JP 2012-135621 A (Otsuka Pharmaceutical Factory, Inc.), 19 July 2012 (19.07.2012), paragraphs [0081] to [0087] & AU 2004231389 B2 & CA 2526902 A1 & DK 1616549 T3 & EP 1616549 A1 & ES 2397136 T3 & JP 4939054 B2 & KR 10-2006-0003896 A & PT 1616549 E & TW I253929 B & US 2006/0229583 A1 & WO 2004/093775 A1	12-15
A	JP 2006-289070 A (Santen Pharmaceutical Co., Ltd.), 26 October 2006 (26.10.2006), paragraphs [0009] to [0013] (Family: none)	13-14

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/063297

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:

The invention of claim 1 does not have novelty, since the invention is disclosed in, for example, the document: JP 2005-305745 A (Toppan Printing Co., Ltd.), 04 November 2005 (04.11.2005), paragraphs [0005] to [0006], [0016] to [0024], fig. 1 to 2.

Therefore, the matter set forth in claim 1 is not a special technical feature within the meaning of PCT Rule 13.2, second sentence.
(Continued to 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.:

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 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/063297

Continuation of Box No.III of continuation of first sheet(2)

Since there is no other common matter which is considered to be a special technical feature within the meaning of PCT Rule 13.2, second sentence among the inventions of claims 1-16, it is not considered that there is a technical relationship involving one or more of the same or corresponding special technical features among those different inventions.

Consequently, the inventions of claims 1-16 do not comply with the requirement of unity of invention.

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 2003275280 A [0013]
- JP 2008230112 A [0013]
- JP 2007302328 A [0013]
- JP H8193149 A [0013]
- JP 2008104868 A [0013]

(19)



(11)

EP 3 112 384 B1

(12)

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(22) Date of filing: **30.06.2015**

(54) **ETHYLENE POLYMERS HAVING HIGH DENSITY**

ETHYLENPOLYMERE MIT HOHER DICHT

POLYMÈRES D'ÉTHYLÈNE AYANT UNE DENSITÉ ÉLEVÉE

(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**

(43) Date of publication of application:
04.01.2017 Bulletin 2017/01

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6160 GA GELEEN (NL)

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6160 GA Geleen (NL)

(56) References cited:
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Description

[0001] The present invention relates to ethylene polymers having a high density and high purity. The invention further relates to the production of such ethylene polymers. The invention further relates to the use of such ethylene polymers.

[0002] Ethylene polymers are well known in the art. There are a great variety of applications in which ethylene polymers find their field of application. A great variety of ethylene polymers are available, having properties rendering them suitable for specific applications. The family of ethylene polymers comprises for example low-density polyethylenes (also referred to as LDPE), linear low-density polyethylenes (also referred to as LLDPE), and high-density polyethylenes (also referred to as HDPE). These types of ethylene polymers are well known in the art. The production processes of these ethylene polymers are for example described in "Handbook of Polyethylene" by Andrew Peacock (2000; Dekker; ISBN 0824795466) at pages 43-66.

[0003] One type of ethylene polymers is high-density polyethylene. High-density polyethylenes are polymers that have amongst others certain low permeability to oxygen and water vapour. High-density polyethylenes are commonly produced in catalytic polymerisation processes. The catalyst systems that may be applied in such catalytic polymerisation processes are for example catalyst systems of the Ziegler type, of the Phillips type, and/or of the single-site type. These types of catalyst systems are well known in the art and for example described in Lloyd, L., 'Olefin Polymerization Catalysts', in 'Handbook of Industrial Catalysts', p. 311-350, ISBN: 978-0-387-24682-6, 2011. High-density polyethylenes may for example have a density as measured according to ISO 1183-1 (2012), method A of ≥ 935 and ≤ 970 kg/m³.

[0004] High-density polyethylenes produced via catalytic polymerisation processes have certain drawbacks. For example, such high-density polyethylenes may contain traces of undesirable compounds originating from the catalyst system used in the production of such high-density polyethylenes.

[0005] High-density polyethylenes produced via catalytic polymerisation processes in the presence of catalyst systems of the Ziegler type commonly contain traces of tetrahydrofuran. High-density polyethylenes produced via catalytic polymerisation processes in the presence of catalyst systems of the Phillips type commonly contain traces of chromium. High-density polyethylenes produced via catalytic polymerisation processes in the presence of catalyst systems of the single-site type commonly contain traces of zirconium and/or hafnium.

[0006] Chromium is known to have detrimental effects. Chromium compounds, in particular those containing chromium (VI), are suspected carcinogenic and mutagenic, and may cause health problems such as for example allergic reactions, skin rash, nose irritations and nose bleed, ulcers, weakened immune system, and damage to internal organs such as liver and kidney. Both tetrahydrofuran and chromium are undesirable to be present in polymer materials that are intended for use in food contact applications for health reasons. The use of tetrahydrofuran and chromium in the production process of high density polyethylene is also undesirable in view of workers health. This is for example presented in US Dept. of Labor report OSHA 3373-10 2009 'Hexavalent Chromium', which presents the hazards of workers exposed to chromium (VI), and in US Dept. of Labor OSHA report 'Occupational Health Guideline for Tetrahydrofuran', Feb. 1978, which present the hazards of workers exposed to tetrahydrofuran. Tetrahydrofuran is also suspected carcinogenic.

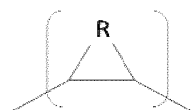
[0007] In the context of the present invention, essentially free of tetrahydrofuran means that the ethylene polymer comprises for example at most 40 ppm of tetrahydrofuran, alternatively at most 20 ppm, alternatively at most 10 ppm, alternatively at most 5 ppm, alternatively at most 2 ppm. In the context of the present invention, essentially free of chromium means that the ethylene polymer comprises for example at most 20 ppm of chromium or compounds comprising chromium atoms, alternatively at most 10 ppm, alternatively at most 5 ppm, alternatively at most 2 ppm. In the context of the present invention, essentially free of zirconium means that the ethylene polymer comprises for example at most 20 ppm of zirconium or compounds comprising zirconium atoms, alternatively at most 10 ppm, alternatively at most 5 ppm, alternatively at most 2 ppm. In the context of the present invention, essentially free of hafnium means that the ethylene polymer comprises for example at most 20 ppm of hafnium or compounds comprising hafnium atoms, alternatively at most 10 ppm, alternatively at most 5 ppm, alternatively at most 2 ppm. In the context of the present invention, 'ppm' is to be understood to be the parts per million of weight, being the number of weight units per million weight units of the ethylene polymer.

[0008] Such traces may be detrimental for the long-term stability of the ethylene polymer. Also, such traces may render the ethylene polymer unsuitable for certain areas of application where a high purity is required. Such areas of application include for example certain food packaging applications, such as flexible films for packaging of fresh foods such as for example fruit juices, dairy products, meat, cheese, fish, fruits, vegetables and/or baked goods. High-density polyethylenes produced via catalytic polymerisation processes may lack the level of purity that is required for such applications. Increasingly stringent regulations in the field of product health and safety require an ever increasing need for reduction of impurities present in materials to be used in such applications.

[0009] Therefore, it is apparent that there is an ongoing need for the development of ethylene polymers having a high density, a low oxygen permeability and a low water vapour permeability, and also having a high purity.

[0010] This objective has now been achieved according to the present invention by an ethylene polymer comprising

in the polymer chain recurring units according to formula I:



Formula I

wherein R may for example be a moiety comprising ≥ 1 and ≤ 10 carbon atoms; wherein

- the ethylene polymer may for example have a molecular weight distribution defined as the ratio between the weight average molecular weight M_w and the number average molecular weight M_n , (M_w/M_n) as determined according to ASTM D-6474 (2012) of ≥ 3.0 and ≤ 13.0 ;
- the ethylene polymer may for example have a melting temperature as determined according to ISO 11357-3 (2011) at a heating rate of 10 K of ≥ 115 °C;
- the ethylene polymer may for example have a density as measured according to ISO 1183-1 (2012), method A of ≥ 935 and ≤ 960 kg/m³;
- the ethylene polymer may for example be essentially free from chromium, hafnium, zirconium and tetrahydrofuran;
- for the fraction of the ethylene polymer having a molecular weight > 100 kg/mol, the intrinsic viscosity of the ethylene polymer may for example be related to the molecular weight according to the inequality:

$$\log I.V. < 0.65 * \log M - 3.10$$

wherein I.V. is the intrinsic viscosity, expressed in dl/g, of a fraction of the ethylene polymer having a molecular weight M, the molecular weight M expressed in kg/mol;

wherein the molecular weight may be determined via Size Exclusion Chromatography (SEC) according to ISO 16014-1 (2012);

and wherein the intrinsic viscosity may be determined via differential viscometry of the fractions obtained from SEC, in accordance with ASTM D5225 (2014).

[0011] Ethylene polymers according to the invention may for example have improved barrier properties, such as for example low oxygen permeability and water vapour permeability. Such ethylene polymers for example have a high Vicat softening temperature. For example, such ethylene polymers have a high purity. Such ethylene polymers have an advantageous balance of processability and barrier properties, such as for example low oxygen permeability and water vapour permeability. Such advantageous balance of processability and barrier properties may for example result from a certain degree of long-chain branching in the ethylene polymers. Such ethylene polymers may for example have a high purity as they are essentially free from chromium, zirconium, hafnium and tetrahydrofuran.

[0012] Ethylene polymers according to the invention having such relation of the intrinsic viscosity to the molecular weight may for example have a high melt elasticity, low sagging, a low energy consumption in melt processing, a good bubble stability in blow film production, and good processability.

[0013] Alternatively, the present invention relates to an ethylene polymer wherein for the fraction of the ethylene polymer having a molecular weight > 100 kg/mol, alternatively > 200 kg/mol, alternatively > 300 kg/mol, alternatively > 400 kg/mol, alternatively > 500 kg/mol, the intrinsic viscosity of the ethylene polymer is related to the molecular weight according to the inequality:

$$\log I.V. < 0.60 * \log M - 2.85$$

[0014] In the context of the present invention, recurring units are to be understood to be units of the polymer molecule that together form the polymer chain. Such units may for example be originating from unsaturated monomers comprising at least one carbon-carbon double bond capable of reacting in free-radical polymerisation reactions. For example, such unsaturated monomers may be olefinic monomers. Such free-radical addition polymerisation mechanisms are well known in the art and for example described in 'Introduction to Polymer', Young et al, Chapman & Hall, 1995, p. 43-68.

[0015] The molecular weight may be determined via Size Exclusion Chromatography (SEC) using for example a

Polymer Laboratories PL-GPC220 high-temperature GPC/SEC system, to obtain fractions of the ethylene polymer having a certain molecular weight. For example, as column set may be used three Polymer Laboratories 13 μ m PLgel Olexis, 300 x 7.5 mm. For example, the calibration for the molar mass may be performed with a linear polyethylene as standard. The molecular weight may be determined according to ISO 16014-1 (2012).

[0016] The intrinsic viscosity of the obtained fractions may be determined using a Polymer Laboratories BV-400 viscometer. Refractive index detector: Polymer Char IR5 infrared detector. The intrinsic viscosity may be determined in accordance with ASTM D5225 (2014).

[0017] In an embodiment, the ethylene polymers comprising recurring units derived from cyclic olefin comonomers according to the present invention may for example be produced in a high-pressure free-radical polymerisation process.

[0018] In an embodiment, the present invention relates to an ethylene polymer wherein R may for example be a moiety selected from linear alkanes, branched alkanes, cyclic alkanes, linear alkenes, branched alkenes or cyclic alkenes.

[0019] For example, R may be a linear alkane having 4 carbon atoms. Alternatively, R may be a linear alkane having 6 carbon atoms.

[0020] The present invention further relates to an ethylene polymer wherein R may for example be a moiety selected from $-C_2H_4-$, $-C_3H_6-$, $-C_4H_8-$, $-C_5H_{10}-$, $-C_6H_{12}-$.

[0021] The present invention also relates to an ethylene polymer wherein the ethylene polymer may for example be produced by reacting a reaction mixture comprising ethylene and one or more cyclic olefin comonomers.

[0022] The present invention also relates to an ethylene polymer wherein the ethylene polymer may for example comprise $\geq 0.05\%$ and $\leq 6.00\%$ of moieties according to formula I compared to the total number of recurring moieties in the ethylene copolymer.

[0023] For example, the ethylene comprises $\geq 0.05\%$, alternatively $\geq 0.10\%$, alternatively $\geq 0.20\%$, alternatively $\geq 0.30\%$, alternatively $\geq 0.50\%$ of moieties according to formula I compared to the total number of recurring moieties in the ethylene copolymer.

[0024] For example, the ethylene comprises $\leq 6.00\%$, alternatively $\leq 4.00\%$, alternatively $\leq 3.00\%$, alternatively $\leq 2.00\%$, alternatively $\leq 1.00\%$ of moieties according to formula I compared to the total number of recurring moieties in the ethylene copolymer.

[0025] For example, the ethylene comprises $\geq 0.05\%$ and $\leq 6.00\%$, alternatively $\geq 0.10\%$ and $\leq 3.00\%$, alternatively $\geq 0.20\%$ and $\leq 2.00\%$, of moieties according to formula I compared to the total number of recurring moieties in the ethylene copolymer.

[0026] In an embodiment, the ethylene polymers according to the present invention are produced using at least ethylene and at least one cyclic olefin comonomer as feeds.

[0027] The cyclic olefin comonomers that may be used in the production of the ethylene polymers according to the present invention may for example be selected from compounds represented by the molecular structure of formula II:



Formula II

[0028] In which R is a moiety comprising ≥ 1 and ≤ 10 carbon atoms;

[0029] In an embodiment, the present invention relates to an ethylene polymer wherein the cyclic olefin comonomer may for example be one or more selected from cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclooctadiene, cyclononene, cyclodecene, 1-methyl cyclohexene, 3-methyl cyclohexene, α -pinene, and/or norbornene.

[0030] In an embodiment, the present invention relates to an ethylene wherein reaction mixture may for example comprise ≥ 0.10 and ≤ 2.00 mol% of the cyclic olefin comonomer compared to the total molar composition of the reaction mixture.

[0031] For example, the reaction mixture may comprise ≥ 0.10 mol%, alternatively ≥ 0.20 mol%, alternatively ≥ 0.30 mol% of the cyclic olefin comonomer, compared to the total molar composition of the reaction mixture.

[0032] For example, the reaction mixture may comprise ≤ 2.00 mol%, alternatively ≤ 1.00 mol%, alternatively ≤ 0.50 mol% of the cyclic olefin comonomer, compared to the total molar composition of the reaction mixture.

[0033] For example, the reaction mixture may comprise ≥ 0.10 mol% and ≤ 2.00 mol%, alternatively ≥ 0.20 mol% and ≤ 1.00 mol%, alternatively ≥ 0.30 mol% and ≤ 0.50 mol% of the cyclic olefin comonomer, compared to the total molar composition of the reaction mixture.

[0034] The reaction mixture is to be understood to be the total quantity of olefin monomers fed to the polymerisation reaction.

[0035] In an embodiment, such cyclic olefin comonomers may be monocyclic olefin comonomers. Examples of such monocyclic olefin comonomers include unsubstituted monocyclic olefins such as cyclobutene, cyclopentene, cyclohex-

ene, cycloheptene, cyclooctene, cyclononene, and cyclodecene.

[0036] Examples of such monocyclic olefin comonomers include substituted monocyclic olefins. For example, such substituted monocyclic olefins may be monosubstituted, disubstituted or trisubstituted. For example, such substituted monocyclic olefins may comprise as substituents one or more of each a methyl, ethyl and/or butyl group.

[0037] Alternatively, such cyclic olefin comonomers may be multicyclic olefin comonomers. Examples of such multicyclic olefin comonomers include norbornene.

[0038] The cyclic olefin comonomers may for example comprise a single vinylic unsaturation in the cyclic structure. Alternatively, the cyclic olefin comonomers may for example comprise multiple vinylic unsaturations in the cyclic structure, such as two vinylic unsaturations. For example the cyclic olefin comonomers comprising multiple vinylic unsaturations may be a cyclic diene. For example, such cyclic diene may be cyclooctadiene.

[0039] For example, the cyclic olefin comonomer may be cyclohexene, cyclooctene or cyclooctadiene.

[0040] Ethylene polymers according to the present invention may for example be produced in a high-pressure free radical polymerisation process. Such polymerisation process may for example be conducted in an autoclave reactor. Such autoclave reactor may for example be a reactor such as described in Nexant PERP Report 2013-2, 'Low Density Polyethylene', pages 48-63.

[0041] Alternatively, such polymerisation process may for example be conducted in a tubular reactor. Such tubular reactor may for example be a reactor such as described in Nexant PERP Report 2013-2, 'Low Density Polyethylene', pages 31-48. Such tubular reactor may for example be operated at pressures ranging from 150 to 300 MPa. The tubular reactor may have a tube length of for example between 1500 and 3000 m. The tubular reactor may for example have a ratio of length to inner diameter of $\geq 500:1$, alternatively $\geq 1000:1$, alternatively $\geq 5000:1$. Such tubular reactors may for example have an inner tubular diameter of ≥ 0.01 m and ≤ 0.20 m, alternatively ≥ 0.05 m and ≤ 0.15 m.

[0042] For example, such high-pressure free radical polymerisation process comprise more than one of said autoclave reactors and/or said tubular reactors, for example positioned in series. For example, such high-pressure free radical polymerisation process comprise two reactors in series. For example, the process may comprise a first polymerisation in an autoclave reactor and a further polymerisation in a tubular reactor. Alternatively, the process may comprise a first polymerisation in a tubular reactor and a further polymerisation in an autoclave reactor. Alternatively, the process may comprise a first polymerisation in a tubular reactor and a further polymerisation in a further tubular reactor. Alternatively, the process may comprise a first polymerisation in an autoclave reactor and a further polymerisation in an autoclave reactor.

[0043] The autoclave process and the tubular process result in different chain architecture (Tacx et al., Polymer, Vol. 39, 1998, p. 3109-3113) and different molecular weight distribution of the polymer (Kaltenbacher, TAPPI, Vol. 50, 1967, p. 20).

[0044] Polymerisation in a tubular reactor may for example have an advantage in that the consumption of utilities such as electricity and cooling water per quantity of ethylene polymer that is produce, is lower compared to polymerisation in autoclave reactors. Tubular reactors also have an advantage in that they may be built to produce larger quantities of ethylene polymer on annual basis, compared to autoclave reactors.

[0045] For example, the ethylene polymer may be produced in a polymerisation process at a pressure of ≥ 180 MPa and ≤ 400 MPa.

[0046] For example, the ethylene polymer is produced in a polymerisation process at a pressure of ≥ 180 MPa, alternatively ≥ 200 MPa, alternatively ≥ 220 MPa, alternatively ≥ 240 MPa, alternatively ≥ 260 MPa.

[0047] In an embodiment, the ethylene polymer may for example be produced in a tubular reactor. The tubular reactor may for example comprise an inlet and an outlet. The inlet may for example comprise a position for entering a first feed stream into the tubular reactor.

[0048] The first feed stream that is fed to the tubular reactor at the inlet of the tubular reactor may for example comprise ethylene and comonomers. The first feed stream that is fed to the tubular reactor at the inlet of the tubular reactor may for example comprise $\geq 80.00\%$, alternatively $\geq 85.00\%$, alternatively $\geq 90.00\%$, alternatively $\geq 95.00\%$ by weight of ethylene, compared to the total weight of said first feed stream that is fed to the tubular reactor at the inlet of the tubular reactor. The first stream that is fed to the inlet of the tubular reactor may for example comprise $\leq 99.99\%$, alternatively $\leq 99.95\%$, alternatively $\leq 99.90\%$, alternatively $\leq 99.50\%$ by weight of ethylene, compared to the total weight of said first feed stream that is fed to the tubular reactor at the inlet of the tubular reactor. For example, the first feed stream that is fed to the tubular reactor at the inlet if the tubular reactor may comprise $\geq 80.00\%$ and $\leq 99.99\%$, alternatively $\geq 85.00\%$ and $\leq 99.90\%$, alternatively $\geq 90.00\%$ and $\leq 99.50\%$ by weight of ethylene, compared to the total weight of said first feed stream that is fed to the tubular reactor at the inlet of the tubular reactor.

[0049] The first feed stream that is fed to the tubular reactor at the inlet of the tubular reactor may for example comprise $\leq 5.00\%$, alternatively $\leq 3.00\%$, alternatively $\leq 1.00\%$, alternatively $\leq 0.50\%$, alternatively $\leq 0.30\%$ by weight of comonomers, compared to the total weight of said first feed stream that is fed to the tubular reactor at the inlet of the tubular reactor. The first feed stream that is fed to the inlet of the tubular reactor may for example comprise $\geq 0.01\%$, alternatively $\geq 0.02\%$, alternatively $\geq 0.05\%$, alternatively $\geq 0.10\%$ by weight of comonomers, compared to the total weight of said

first feed stream that is fed to the tubular reactor at the inlet of the tubular reactor. For example, the first feed stream that is fed to the tubular reactor at the inlet of the tubular reactor may comprise $\geq 0.01\%$ and $\leq 5.00\%$, alternatively $\geq 0.05\%$ and $\leq 1.00\%$, alternatively $\geq 0.10\%$ and $\leq 0.50\%$ by weight of comonomers, compared to the total weight of said first feed stream that is fed to the inlet of the tubular reactor.

[0050] The inlet for entering a first feed stream at the inlet of the tubular reactor may for example also be used to feed first additional compound streams to the tubular reactor. Such first additional compound streams may for example comprise initiators. Such initiators may for example be used to control the polymerisation. Such initiator may for example be an initiator composition comprising one or more selected from organic peroxides or azo compounds. Suitable organic peroxides may for example include diacyl peroxides, dialkyl peroxides, peroxy monocarbonates, peroxydicarbonates, peroxyketals, peroxyesters, cyclic peroxides, hydroperoxides. Suitable azo compounds may for example include 2,2'-azodi(isobutyronitrile), 2,2'-azodi(2-methylbutyronitrile), 1,1'-azodi(hexahydrobenzonitrile).

[0051] Examples of suitable diacyl peroxides are diisobutyryl peroxide, di(3,5,5-trimethylhexanoyl) peroxide, dilauroyl peroxide, didecanoyl peroxide, dibenzoyl peroxide.

[0052] Examples of suitable dialkyl peroxides are dicumyl peroxide, di(tert-butylperoxyisopropyl)benzene, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, tert-butyl cumyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne, di-tert-butyl peroxide, di-isononanoyl peroxide, di-tert-amyl peroxide, didecanoyl peroxide.

[0053] In an embodiment, the free radical initiator composition may for example comprise 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane.

[0054] Examples of suitable peroxy monocarbonates are tert-amylperoxy 2-ethylhexyl carbonate, tert-butylperoxy isopropyl carbonate, tert-butylperoxy 2-ethylhexyl carbonate.

[0055] Examples of suitable peroxydicarbonates are di(3-methoxybutyl)peroxydicarbonate, di-sec-butyl peroxydicarbonate, diisopropyl peroxydicarbonate, di(4-tert-butylcyclohexyl) peroxydicarbonate, di(2-ethylhexyl) peroxydicarbonate, dibutyl peroxydicarbonate, diacetyl peroxy dicarbonate, dimyristyl peroxydicarbonate, dicyclohexyl peroxydicarbonate.

[0056] Examples of suitable peroxyketals are 1,1-di(*tert*-butyl peroxy)-3,5,5-trimethylcyclohexane, 1,1-di(*tert*-amyl peroxy)cyclohexane, 1,1-di(*tert*-butyl peroxy)cyclohexane, 2,2-di(*tert*-butyl peroxy)butane, butyl 4,4-di(*tert*-butyl peroxy)valerate, *n*-ethyl-4,4-di-(*tert*-butylperoxy)valerate, ethyl-3,3-di(*tert*-butylperoxy)butyrate, ethyl-3,3-di(*tert*-amylperoxy)butyrate.

[0057] Examples of suitable peroxyesters are cumyl peroxyneodecanoate, 1,1,3,3,-tetramethylbutylperoxyneodecanoate, cumyl peroxyneohexanoate, tert-amyl peroxyneodecanoate, tert-butyl peroxyneodecanoate, tert-butyl peroxyisooctanoate, tert-butyl permaleate, tert-butyl peroxydiethylisobutyrate, 1,1,3,3-tetramethylbutyl peroxyisobutyrate, tert-butyl peroxyneohexanoate, tert-amyl peroxyisobutyrate, tert-butyl peroxyisobutyrate, 2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy)hexane, 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate, tert-amyl peroxy-2-ethylhexanoate, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxydiethylacetate, tert-butyl peroxyisobutyrate, tert-amyl peroxyacetate, tert-butyl peroxy-3,5,5-trimethylhexanoate, tert-amyl peroxybenzoate, tert-butyl peroxybenzoate, tert-butyl peroxybenzoate.

[0058] Examples of suitable cyclic peroxides are 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxononane, 3,3,5,7,7-pentamethyl-1,2,4-trioxepane, 3,3,6,6,9,9-hexamethyl-1,2,4,5-tetraoxacyclononane.

[0059] Examples of suitable hydroperoxides are isopropylcumyl hydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, cumyl hydroperoxide, tert-butyl hydroperoxide, tert-amyl hydroperoxide, methyl isobutyl ketone hydroperoxide, diisopropyl hydroxyperoxide.

[0060] Such initiators may for example be fed to the tubular reactor in a pure form or as a solution in a solvent. As solvent, for example a C₂-C₂₀ normal paraffin or C₂-C₂₀ isoparaffin may be used. For example, such solution may comprise ≥ 2.0% and ≤ 65.0 % by weight of initiator, alternatively ≥ 5.0% and ≤ 40.0% by weight, alternatively ≥ 10.0% and ≤ 30.0% by weight, compared to the total weight of the solution.

[0061] Such initiators may for example be introduced into the polymerisation reactor in quantities of ≤ 200 ppm, compared to the total weight of the materials fed to the polymerisation reactor.

[0062] Such first additional compound streams may for example comprise modifiers. Examples of such modifiers may include inhibitors, scavengers and/or chain regulators, such as aldehydes, ketones and aliphatic hydrocarbons. Examples of chain regulators are propene, propylene and propione aldehyde. Such modifiers may for example be fed to the tubular reactor in a pure form or as a solution in a solvent.

[0063] The tubular reactor may along the length of the reactor have multiple further feed inlets. Such further feed inlets may for example be used to feed further feed streams to the tubular reactor. Such further feed streams may for example have the same or different composition than the first feed stream. Such further feed streams may each have the same or different composition.

[0064] The further feed streams may for example comprise ethylene and comonomers. The further feed streams may for example comprise $\geq 80.00\%$, alternatively $\geq 85.00\%$, alternatively $\geq 90.00\%$, alternatively $\geq 95.00\%$ by weight of ethylene, compared to the total weight of said further feed streams. The further feed streams may for example comprise $\leq 99.99\%$, alternatively $\leq 99.95\%$, alternatively $\leq 99.90\%$, alternatively $\leq 99.50\%$ by weight of ethylene, compared to the

total weight of said further feed streams. For example, the further feed streams may comprise $\geq 80.00\%$ and $\leq 99.99\%$, alternatively $\geq 85.00\%$ and $\leq 99.90\%$, alternatively $\geq 90.00\%$ and $\leq 99.50\%$ by weight of ethylene, compared to the total weight of said further feed streams.

[0065] The further feed streams may for example comprise $\leq 5.00\%$, alternatively $\leq 3.00\%$, alternatively $\leq 1.00\%$, alternatively $\leq 0.50\%$, alternatively $\leq 0.30\%$ by weight of comonomers, compared to the total weight of said further feed streams. The further feed streams may for example comprise $\geq 0.01\%$, alternatively $\geq 0.02\%$, alternatively $\geq 0.05\%$, alternatively $\geq 0.10\%$ by weight of comonomers, compared to the total weight of said further feed streams. For example, the further feed streams may comprise $\geq 0.01\%$ and $\leq 5.00\%$, alternatively $\geq 0.05\%$ and $\leq 1.00\%$, alternatively $\geq 0.10\%$ and $\leq 0.50\%$ by weight of comonomers, compared to the total weight of said further feed streams.

[0066] Such additional feed inlets may for example be used to feed further additional compound streams to the tubular reactor. Such further additional compound streams may for example be the same or different than the first additional compound streams. Such further additional compound streams may each have the same or different composition.

[0067] The free-radical addition polymerisation process of ethylene and cyclic olefin comonomers may be conducted using an initiator to support the formation of free radicals based on ethylene and/or the cyclic olefin comonomers. Such free-radical addition polymerisation process is an exothermic process. In the case that the polymerisation process for the production of ethylene polymers according to the present invention is performed in a tubular reactor, said tubular reactor may be provided with external cooling. Such external cooling may for example be performed via cooling jackets. Such cooling jackets may for example be operated using water as medium that removes heat from the tubular reactor.

[0068] The ethylene polymers comprising recurring units according to the present invention may for example have a density as measured according to ISO 1183-1 (2012), method A of ≥ 935 and ≤ 960 kg/m³. For example, the ethylene polymers according to the present invention may have a density of ≥ 930 kg/m³, alternatively ≥ 934 kg/m³, alternatively ≥ 935 kg/m³, alternatively ≥ 939 kg/m³, alternatively ≥ 940 kg/m³, alternatively ≥ 944 kg/m³, alternatively ≥ 945 kg/m³. For example, the ethylene polymers according to the present invention may have a density of ≤ 971 kg/m³, alternatively ≤ 970 kg/m³, alternatively ≤ 965 kg/m³, alternatively ≤ 960 kg/m³, alternatively ≤ 959 kg/m³, alternatively ≤ 955 kg/m³, alternatively ≤ 954 kg/m³. For example, the ethylene polymers according to the present invention may have a density of ≥ 930 kg/m³ and ≤ 970 kg/m³, alternatively ≥ 934 kg/m³ and ≤ 965 kg/m³, alternatively ≥ 939 kg/m³ and ≤ 959 kg/m³, alternatively ≥ 944 kg/m³ and ≤ 954 kg/m³.

[0069] The ethylene polymer may for example have a molecular weight distribution, also referred to as MWD, as determined according to ASTM D-6474 (2012) of ≥ 3.0 , alternatively ≥ 4.0 , alternatively ≥ 6.0 . The ethylene polymer may for example have an MWD of ≤ 13.0 , alternatively ≤ 12.0 , alternatively ≤ 11.0 . The ethylene polymer may for example have an MWD ≥ 3.0 and ≤ 13.0 , alternatively ≥ 6.0 and ≤ 12.0 . Said MWD is defined as the ratio between the weight average molecular weight M_w and the number average molecular weight M_n , (M_w/M_n) as determined according to ASTM D-6474 (2012).

[0070] In an embodiment, the present invention relates to a polymer composition that may for example comprise an ethylene polymer according to the present invention. Such polymer composition may for example comprise ≥ 50.0 wt%, alternatively ≥ 75 wt%, alternatively ≥ 90 wt%, alternatively ≥ 95 wt% of the ethylene polymer, compared to the total weight of the polymer composition.

[0071] Furthermore, the present invention relates to a film that may for example comprise an ethylene polymer according to the present invention.

[0072] The invention further relates to a package for fresh food products that may for example comprise a layer comprising an ethylene polymer according to the present invention.

[0073] Packages for example include packages for fresh food products, such as for example fruit juices, dairy products, meat, cheese, fish, fruits, vegetables and/or baked goods.

[0074] In an embodiment, said layer may for example comprise $\geq 80.0\%$ by weight of an ethylene polymer according to any one of claims 1-9 compared to the total weight of said layer. In an embodiment, said layer may for example be present in the form of one or more of a single-layer film, one or more layer(s) of a multi-layer film, and/or an extrusion-coated film.

[0075] Single-layer or multi-layer films may for example be produced by blown film production or cast film production. Both processes are known in the art and described in e.g. the Handbook of Plastic Films, E.M Abdel-Bary (ed.), Rapra Technology Ltd., 2003, in sections 2.3 and 2.4. The film according to the present invention may be produced via either blown film production or cast film production. Such films may for example be flexible films. Such films may for example have a thickness of ≤ 200.0 μm , alternatively ≤ 100.0 μm , alternatively ≤ 50.0 μm , alternatively ≤ 25.0 μm .

[0076] Extrusion-coated films may for example be produced by deposition of a layer of molten material onto a substrate, followed by cooling of the molten material for form a layer adhering to the substrate. For example, the molten material may comprise the ethylene polymer according to the present invention. For example, the substrate may be paper, paperboard, cardboard, foils such as aluminium foils, and/or polymer films such as polyamide films and/or EVOH films. For example, the substrate may have a top planar surface onto which the layer of ethylene polymer is deposited and a bottom planar surface. For example, such layer may have a thickness of 3.0 to 50.0 μm , for example 5.0 to 25.0 μm .

For example, said layer of molten material may be deposited by extruding the molten material onto a substrate onto the top planar surface wherein the substrate is guided by a pressure roll contacting the bottom planar surface, and wherein the substrate, following deposition of the molten material, is on the side of the top planar surface contacted by a cooling cylinder that reduces the temperature of the deposited material to a temperature below the softening temperature of the deposited material.

[0077] The ethylene polymers according to the present invention have for example a low permeability to oxygen and water vapour. In the context of the present invention, permeability is to be understood to be the degree to which a film comprising at least one layer of the ethylene polymer, for example a single-layer film or a multilayer film, enables molecules of certain defined compounds to pass through said film, for example by means of diffusion. For example, such compound may be oxygen. Alternatively, such compound may be water, for example in the form of water vapour. Certain applications of films may require a certain oxygen permeability. Certain applications of films may require a certain water vapour permeability. Oxygen permeability is expressed as oxygen transmission rate determined in accordance with ISO 15105-2 (2003), method A. Water vapour permeability is expressed as water vapour transmission rate determined in accordance with ISO 15106-3 (2003).

[0078] The invention will now be illustrated by the following non-limiting examples.

Experiment I: Preparation of ethylene polymer

[0079] In a high-pressure polymerisation reactor, an ethylene polymer was prepared by reacting a reaction mixture comprising ethylene an amount of comonomer. The comonomer was fed as a 1.45 mol% solution in isopropyl alcohol. The reaction was performed at a pressure of 200 MPa. The reaction temperature was kept between 200 and 230°C. The reaction was initiated by addition of a solution of t-butyl peroxy pivalate in heptane. The obtained ethylene polymer was collected. The examples were prepared using different comonomers and quantities as presented in table I:

Table I

	Ethylene polymer A	Ethylene polymer B	Ethylene polymer C
Comonomer	cyclohexene	cyclooctene	cyclooctene
Comonomer feed concentration	0.2 mol%	0.7 mol%	0.2 mol%
Initiator feed concentration	0.00153 mol%	0.00179 mol%	0.00250 mol%

[0080] Wherein the mol% is to be understood to be the fraction in mol% compared to the total quantity of reactive ingredients fed to the reaction. The reactive ingredients in the above examples are ethylene, comonomer and initiator.

Experiment II: Determination of intrinsic viscosity and molecular weight

[0081] Ethylene polymer A, B and C according to the invention as obtained in experiment I and for comparative purposes ethylene polymer D, a commercial polyethylene material grade 0863F, obtainable from SABIC, ethylene polymer E, a commercial polyethylene material grade LDPE 1922, and ethylene polymer F, a commercial polyethylene material grade ICP4907S, all obtainable from SABIC, were subjected to Size Exclusion Chromatography (SEC) using a Polymer Laboratories PL-GPC220 high-temperature GPC/SEC system, to obtain fractions of the ethylene polymer having a certain molecular weight. The column set used are three Polymer Laboratories 13 μ m PLgel Olexis, 300 x 7.5 mm. The calibration for the molar mass was performed with a linear polyethylene as standard. The molecular weight was determined according to ISO 16014-1 (2012).

[0082] The intrinsic viscosity of these fractions was subsequently determined using a Polymer Laboratories BV-400 viscometer. Refractive index detector: Polymer Char IR5 infrared detector. The intrinsic viscosity was determined in accordance with ASTM D5225 (2014).

[0083] Results are presented in table II.

Table II

Molecular weight (kg/mol)	Intrinsic viscosity (dl/g)					
	Ethylene polymer					
	A	B	C	D	E	F
10	0.292	0.292	0.288	0.348	0.341	0.371

(continued)

Molecular weight (kg/mol)	Intrinsic viscosity (dl/g)					
	Ethylene polymer					
	A	B	C	D	E	F
50	0.809	0.800	0.742	1.055	0.803	1.085
100	1.174	1.138	1.033	1.820	1.127	1.846
200	1.585	1.482	1.298	3.020	1.471	3.007
300	1.904	1.731	1.489	4.064	1.686	4.014
400	2.133	1.914	1.589	5.023	1.845	4.908
500	2.540	2.136	1.692	5.840	1.982	5.741
600	2.833	2.405	1.777	6.194	2.090	6.472

Experiment III: Determination of material properties

[0084] Material properties of the sample ethylene polymers A-F were determined. The results are presented in table III.

Table III

Property (Unit)	Method	Ethylene polymer					
		A	B	C	D	E	F
Melting temperature (°C)	ISO 11357-3 (2011) heating rate 10 K.	115	116	118	134	112	131
Density (kg/m ³)	ISO 1183-1 (2012), method A	936	938	940	964	926	949
Transparency (%)	ASTM D1746 (2015)		92	90		86	
Water vapour transmission rate (g/ (m ² *24h))	ISO 15106-3 (2003)	0.9	1.1	1.1	4.0	1.8	2.3
Oxygen transmission rate (cm ³ / (m ² *bar*24h))	ISO 15105-2 (2003), method A	1335	1474	2135	1000	6389	1339
Molecular Weight Distribution (-)	ASTM D6474 (2012)	3.7	4.4	9.9	5.3	21.7	

[0085] ISO 16014-1 (2012) relates to determination of average molecular mass and molecular mass distribution using size-exclusion chromatography.

[0086] ISO 11357-3 (2011) relates to determination of temperature and enthalpy of melting and crystallisation via differential scanning calorimetry.

[0087] ISO 1183-1 (2012) relates to determination of density of non-cellular plastics.

[0088] ISO 15106-3 (2003) relates to determination of water vapour transmission rate of film and sheeting.

[0089] ISO 15105-2 (2003) relates to determination of gas transmission rate of film and sheeting.

[0090] ASTM D-5225 (2014) relates to a standard test method for measuring solution viscosity of polymers with a differential viscometer.

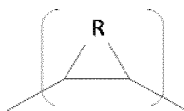
[0091] ASTM D6474 (2012) relates to a standard test method for determining molecular weight distribution and molecular weight averages of polyolefins by high temperature gel permeation chromatography.

[0092] ASTM D1746 (2015) relates to a standard test method for transparency of plastic sheeting.

[0093] From the results obtained in experiments II and III, it becomes apparent that ethylene polymers according to the present invention having a high density, high purity and good processability, whilst maintaining barrier properties for oxygen and water vapour at a level similar to high-density polyethylenes produced via catalytic processes.

Claims

1. Ethylene polymer comprising moieties according to formula I:



Formula I

wherein R is a moiety comprising ≥ 1 and ≤ 10 carbon atoms;
wherein

- the ethylene polymer has a molecular weight distribution defined as the ratio between the weight average molecular weight M_w and the number average molecular weight M_n , (M_w/M_n) as determined according to ASTM D-6474 (2012) of ≥ 3.0 and ≤ 13.0 ;
- the ethylene polymer has a melting temperature as determined according to ISO 11357-3 (2011) at a heating rate of 10 K of ≥ 115 °C;
- the ethylene polymer has a density as measured according to ISO 1183-1 (2012), method A of ≥ 935 and ≤ 960 kg/m³;
- the ethylene polymer is essentially free from chromium, hafnium, zirconium and tetrahydrofuran;
- for the fraction of the ethylene polymer having a molecular weight > 100 kg/mol, the intrinsic viscosity of the ethylene polymer is related to the molecular weight according to the inequality:

$$\log I.V. < 0.65 * \log M - 3.10$$

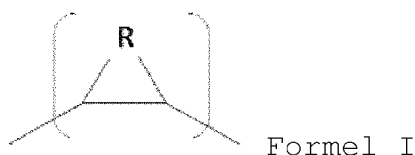
wherein I.V. is the intrinsic viscosity, expressed in dl/g, of a fraction of the ethylene polymer having a molecular weight M, the molecular weight M expressed in kg/mol;
wherein the molecular weight is determined via Size Exclusion Chromatography (SEC) according to ISO 16014-1 (2012);
and wherein the intrinsic viscosity is determined via differential viscometry of the fractions obtained from SEC, in accordance with ASTM D5225 (2014).

2. Ethylene polymer according to claim 1 wherein R is a moiety selected from linear alkanes, branched alkanes, cyclic alkanes, linear alkenes, branched alkenes or cyclic alkenes.
3. Ethylene polymer according to one or more of claims 1-2 wherein R is a moiety selected from $-C_2H_4-$, $-C_3H_6-$, $-C_4H_8-$, $-C_5H_{10}-$, $-C_6H_{12}-$.
4. Ethylene polymer according to one or more of claims 1-3 wherein the ethylene polymer is produced in a polymerisation process at a pressure of ≥ 180 MPa and ≤ 400 MPa.
5. Ethylene polymer according to one or more of claims 1-4 wherein the ethylene polymer is produced in a tubular reactor.
6. Ethylene polymer according to one or more of claims 1-5 wherein the ethylene polymer is produced by reacting a reaction mixture comprising ethylene and one or more cyclic olefin comonomers.
7. Ethylene polymer according to one or more of claims 1-6 wherein the cyclic olefin comonomer is one or more selected from cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclooctadiene, cyclononene, cyclodecene, 1-methyl cyclohexene, 3-methyl cyclohexene, α -pinene, and/or norbornene.
8. Ethylene polymer according to one or more of claims 6-7 wherein reaction mixture comprises ≥ 0.10 and ≤ 2.00 mol% of the cyclic olefin comonomer compared to the total molar composition of the reaction mixture.
9. Ethylene polymer according to one or more of claims 1-8 wherein the ethylene polymer comprises ≥ 0.05 and ≤ 6.00 % of moieties according to formula I compared to the total number of recurring moieties in the ethylene copolymer.

10. Polymer composition comprising an ethylene polymer according to one or more of claims 1-9.
11. Film comprising an ethylene polymer according to one or more of claims 1-9.
12. Package for fresh food products comprising a layer comprising an ethylene polymer according to any one of claims 1-9.
13. Package according to claim 12 wherein said layer comprises ≥ 80.0 % by weight of an ethylene polymer according to any one of claims 1-9 compared to the total weight of said layer.
14. Package according to claims 12-13 wherein said layer is present in the form of one or more of a single-layer film, one or more layer(s) of a multi-layer film, and/or an extrusion-coated film.

Patentansprüche

1. Ethylenpolymer, umfassend Gruppierungen der Formel I:



wobei R für eine Gruppierung mit ≥ 1 und ≤ 10 Kohlenstoffatomen steht;
wobei

- das Ethylenpolymer eine als das Verhältnis zwischen dem gewichtsmittleren Molekulargewicht M_w und dem zahlenmittleren Molekulargewicht M_n (M_w/M_n) definierte Molekulargewichtsverteilung gemäß Bestimmung nach ASTM D-6474 (2012) von $\geq 3,0$ und $\leq 13,0$ aufweist;
- das Ethylenpolymer eine Schmelztemperatur gemäß Bestimmung nach ISO 11357-3 (2011) bei einer Aufheizrate von 10 K von ≥ 115 °C aufweist;
- das Ethylenpolymer eine Dichte gemäß Messung nach ISO 1183-1 (2012), Methode A von ≥ 935 und ≤ 960 kg/m³ aufweist;
- das Ethylenpolymer weitgehend frei von Chrom, Hafnium, Zirkonium und Tetrahydrofuran ist;
- für die Fraktion des Ethylenpolymers mit einem Molekulargewicht > 100 kg/mol die intrinsische Viskosität des Ethylenpolymers gemäß der folgenden Ungleichung mit dem Molekulargewicht zusammenhängt:

$$\log I.V. < 0,65 * \log M - 3,10$$

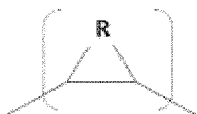
wobei I.V. für die in dl/g ausgedrückte intrinsische Viskosität einer Fraktion des Ethylenpolymers mit einem Molekulargewicht M steht, wobei das Molekulargewicht M in kg/mol ausgedrückt ist;
wobei das Molekulargewicht durch Größenausschlusschromatographie (Size Exclusion Chromatography, SEC) nach ISO 16014-1 (2012) bestimmt wird;
und wobei die intrinsische Viskosität durch Differentialviskosimetrie der aus der SEC erhaltenen Fraktionen nach ASTM D5225 (2014) bestimmt wird.

2. Ethylenpolymer nach Anspruch 1, wobei R für eine Gruppierung steht, die aus linearen Alkanen, verzweigten Alkanen, cyclischen Alkanen, linearen Alkenen, verzweigten Alkenen oder cyclischen Alkenen ausgewählt ist.
3. Ethylenpolymer nach einem oder mehreren der Ansprüche 1-2, wobei R für eine Gruppierung steht, die aus $-C_2H_4-$, $-C_3H_6-$, $-C_4H_8-$, $-C_5H_{10}-$, $-C_6H_{12}-$ ausgewählt ist.
4. Ethylenpolymer nach einem oder mehreren der Ansprüche 1-3, wobei das Ethylenpolymer in einem Polymerisationsverfahren bei einem Druck ≥ 180 MPa und ≤ 400 MPa hergestellt wird.

5. Ethylenpolymer nach einem oder mehreren der Ansprüche 1-4, wobei das Ethylenpolymer in einem Rohrreaktor hergestellt wird.
6. Ethylenpolymer nach einem oder mehreren der Ansprüche 1-5, wobei das Ethylenpolymer durch das Umsetzen einer Reaktionsmischung, die Ethylen und ein oder mehrere Cycloolefin-Comonomere umfasst, hergestellt wird.
7. Ethylenpolymer nach einem oder mehreren der Ansprüche 1-6, wobei es sich bei dem Cycloolefin-Comonomer um eines oder mehrere handelt, die aus Cyclobuten, Cyclopenten, Cyclohexen, Cyclohepten, Cycloocten, Cyclooctadien, Cyclononen, Cyclodecen, 1-Methylcyclohexen, 3-Methylcyclohexen, α -Pinen und/oder Norbornen ausgewählt ist.
8. Ethylenpolymer nach einem oder mehreren der Ansprüche 6-7, wobei die Reaktionsmischung $\geq 0,10$ und $\leq 2,00$ Mol-% des Cycloolefin-Comonomers, bezogen auf die gesamte molare Zusammensetzung der Reaktionsmischung, umfasst.
9. Ethylenpolymer nach einem oder mehreren der Ansprüche 1-8, wobei das Ethylenpolymer $\geq 0,05$ und $\leq 6,00$ % Gruppierungen gemäß Formel I, bezogen auf die Gesamtzahl wiederkehrender Gruppierungen in dem Ethylenpolymer, umfasst.
10. Polymerzusammensetzung, umfassend ein Ethylenpolymer nach einem oder mehreren der Ansprüche 1-9.
11. Folie, umfassend ein Ethylenpolymer nach einem oder mehreren der Ansprüche 1-9.
12. Verpackung für frische Lebensmittelprodukte, die eine Schicht umfasst, die ein Ethylenpolymer nach einem der Ansprüche 1-9 umfasst.
13. Verpackung nach Anspruch 12, wobei die Schicht $\geq 80,0$ Gew.-% eines Ethylenpolymers nach einem der Ansprüche 1-9, bezogen auf das Gesamtgewicht der Schicht, umfasst.
14. Verpackung nach den Ansprüchen 12-13, wobei die Schicht in Form einer einschichtigen Folie, einer oder mehreren Schichten einer mehrschichtigen Folie und/oder einer extrusionsbeschichteten Folie vorliegt.

Revendications

1. Polymère d'éthylène comprenant des fragments selon la formule I :



Formule I

dans laquelle R est un fragment comprenant ≥ 1 et ≤ 10 atomes de carbone ; dans lequel

- le polymère d'éthylène a une distribution de poids moléculaire définie comme étant le rapport entre le poids moléculaire moyen en poids M_w et le poids moléculaire moyen en nombre M_n , (M_w/M_n) tel que déterminé selon l'ASTM D-6474 (2012) de $\geq 3,0$ et $\leq 13,0$;
- le polymère d'éthylène a une température de fusion telle que déterminée selon l'ISO 11357-3 (2011) à une vitesse de chauffage de 10 K de ≥ 115 °C ;
- le polymère d'éthylène a une masse volumique telle que mesurée selon l'ISO 1183-1 (2012), procédé A de ≥ 935 et ≤ 960 kg/m³ ;
- le polymère d'éthylène est essentiellement exempt de chrome, d'hafnium, de zirconium et de tétrahydrofurane ;
- pour la fraction du polymère d'éthylène ayant un poids moléculaire > 100 kg/mol, la viscosité intrinsèque du polymère d'éthylène est liée au poids moléculaire selon l'inégalité :

$$\log I.V. < 0,65 * \log M - 3,10$$

dans laquelle I.V. est la viscosité intrinsèque, exprimée en dl/g, d'une fraction du polymère d'éthylène ayant un poids moléculaire M, le poids moléculaire M étant exprimé en kg/mol ;
 dans lequel le poids moléculaire est déterminé par chromatographie d'exclusion (SEC) selon l'ISO 16014-1 (2012) ;
 et dans lequel la viscosité intrinsèque est déterminée par viscosimétrie différentielle des fractions obtenues par SEC, selon l'ASTM D5225 (2014).

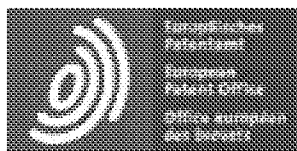
2. Polymère d'éthylène selon la revendication 1 dans lequel R est un fragment choisi parmi des alcanes linéaires, des alcanes ramifiés, des alcanes cycliques, des alcènes linéaires, des alcènes ramifiés ou des alcènes cycliques.
3. Polymère d'éthylène selon une ou plusieurs des revendications 1 à 2 dans lequel R est un fragment choisi parmi $-C_2H_4-$, $-C_3H_6-$, $-C_4H_8-$, $-C_5H_{10}-$, $-C_6H_{12}-$.
4. Polymère d'éthylène selon une ou plusieurs des revendications 1 à 3, le polymère d'éthylène étant produit dans un procédé de polymérisation à une pression de ≥ 180 MPa et ≤ 400 MPa.
5. Polymère d'éthylène selon une ou plusieurs des revendications 1 à 4, le polymère d'éthylène étant produit dans un réacteur tubulaire.
6. Polymère d'éthylène selon une ou plusieurs des revendications 1 à 5, le polymère d'éthylène étant produit par réaction d'un mélange de réaction comprenant de l'éthylène et un ou plusieurs comonomères d'oléfine cyclique.
7. Polymère d'éthylène selon une ou plusieurs des revendications 1 à 6 dans lequel le comonomère d'oléfine cyclique est l'un ou plusieurs choisis parmi cyclobutène, cyclopentène, cyclohexène, cycloheptène, cyclooctène, cyclooctadiène, cyclononène, cyclodécène, 1-méthylcyclohexène, 3-méthylcyclohexène, α -pinène et/ou norbornène.
8. Polymère d'éthylène selon une ou plusieurs des revendications 6 à 7, le mélange de réaction comprenant $\geq 0,10$ et $\leq 2,00$ % en moles du comonomère d'oléfine cyclique par rapport à la composition molaire totale du mélange de réaction.
9. Polymère d'éthylène selon une ou plusieurs des revendications 1 à 8, le polymère d'éthylène comprenant $\geq 0,05$ et $\leq 6,00$ % de fragments selon la formule I par rapport au nombre total de fragments récurrents dans le copolymère d'éthylène.
10. Composition de polymère comprenant un polymère d'éthylène selon une ou plusieurs des revendications 1 à 9.
11. Film comprenant un polymère d'éthylène selon une ou plusieurs des revendications 1 à 9.
12. Emballage pour produits alimentaires frais comprenant une couche comprenant un polymère d'éthylène selon l'une quelconque des revendications 1 à 9.
13. Emballage selon la revendication 12 dans lequel ladite couche comprend $\geq 80,0$ % en poids d'un polymère d'éthylène selon l'une quelconque des revendications 1 à 9 par rapport au poids total de ladite couche.
14. Emballage selon les revendications 12 à 13 dans lequel ladite couche est présente sous la forme de l'un ou plusieurs d'un film monocouche, une ou plusieurs couche(s) d'un film multicouche, et/ou un film revêtu par extrusion.

REFERENCES CITED IN THE DESCRIPTION

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ABSTRACT EP3144127

The invention relates to a medical packaging, in particular pharmaceutical packaging, comprising - a first thermoplastic plastic part body (310) of a first material, - a second thermoplastic plastic part body (320) of a second material, characterized in that - between the first plastic part body (310) and the second plastic part body (320), at least one internal boundary surface with scattering effect, which preferably lead to an extended path length of irradiated light, is arranged.

(19)



(11)

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(12)

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(54) **MEDIZINISCHES PACKMITTEL, INSBESONDERE PHARMAVERPACKUNG SOWIE VERFAHREN ZUM VERBINDEN VON KUNSTSTOFFTEILEN VON MEDIZINISCHEN PACKMITTELN**

MEDICAL PACKAGING, IN PARTICULAR PHARMACEUTICAL PACKAGING AS WELL AS A METHOD FOR CONNECTING PLASTIC PARTS OF MEDICAL PACKAGING

MATERIAU D'EMBALLAGE MEDICAL, EN PARTICULIER PHARMACEUTIQUE ET PROCEDE DE LIAISON DE PARTIES EN PLASTIQUES DE MATERIAUX D'EMBALLAGE MEDICAL

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• **"Simultan in einem Schuss", KUNSTSTOFFE, 1. Juni 2015 (2015-06-01), Seiten 34-37, XP055199503, DE ISSN: 0023-5563**

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Beschreibung

[0001] Die Erfindung betrifft ein medizinisches Packmittel, insbesondere eine Pharmaverpackung, umfassend einen ersten thermoplastischen Kunststoffteilkörper aus einem ersten Material und einen zweiten thermoplastischen Kunststoffteilkörper aus einem zweiten Material. Erstes und zweites Material können verschieden oder auch identisch sein. Des Weiteren betrifft die Erfindung ein Verfahren zum Verbinden von Kunststoffteilen von medizinischen Packmitteln mit Hilfe von Laserschweißen.

[0002] Aus dem Stand der Technik ist für thermoplastische Kunststoffe bekannt, dass zwei Bauteile mit Hilfe von Laserschweißen miteinander verbunden werden können. Dies ist darauf zurückzuführen, dass thermoplastische Kunststoffe eine Schmelzphase besitzen. Thermoplastische Kunststoffe werden durch Laserstrahlung aufgeschmolzen. Beim Abkühlen verbinden sich die Kunststoffe, sie werden verschweißt. Allerdings ist es notwendig wegen der geringen Absorption von Laserstrahlung in den meisten thermoplastischen Kunststoffen, dass die thermoplastischen Kunststoffe durch Addition von Zusatzstoffen wie z.B. Farbpigmenten oder Ruß in ihrer Absorptionsfähigkeit verbessert werden. Bekannt ist Kunststoffschweißen mit Laser mittels Durchstrahlschweißen bei der ein oder zwei Arten von thermoplastischen Kunststoffen miteinander verbunden werden. Ein Fügepartner ist dabei ein lasertransparenter ein anderer Fügepartner ein absorbierender Kunststoff. Bei einer derartigen Schweißmethode durchdringt der Laserstrahl den oberen lasertransparenten Grundstoff und trifft auf den darunterliegenden absorbierenden Kunststoff. Der Laser schmilzt die Oberfläche des absorbierenden Kunststoffes auf. Durch den Wärmeeintrag aufgrund der Absorption schmilzt auch der transparente Fügepartner. Es kommt zu einem Überlappungsschweißen. Der Vorteil des Überlappungsschweißens besteht darin, dass die Schweißnaht im Inneren des Bauteils ohne Freisetzung von jeglichen Partikeln entsteht. Ein großer Vorteil des Laserschweißens besteht in der lokalen Wärmeeinbringung.

[0003] Aus der WO 2005/100 000 A1 ist ein Laserschweißverfahren für Kunststoffmaterialien, die ein Absorberpigment und/oder ein Streupigment umfassen, bekannt geworden. Als Absorber- und/oder Streupigment ist in der WO 2005/100 000 A1 ein Infrarot-Absorber und/oder TiO_2 in einer Konzentration bis 10 Gew.-% beschrieben. Als Kunststoff wird Polyethylen, bevorzugt LDPE eingesetzt. Die TiO_2 -Partikel in der WO 2005/100 000 A1 sind Streupigmente, die zu einer Vergrößerung der optischen Weglänge führen und über die größere Weglänge zu einer höheren Absorptionswirkung. Die WO 2005/100 000 A1 zeigt ein Laserschweißverfahren und ein Produkt hergestellt mit einem Laserschweißverfahren, jedoch kein medizinisches Packmittel, insbesondere keine Pharmaverpackung, für die hohe Anforderungen in Bezug auf eine Zulassung bestehen. Das Verfah-

ren gemäß der WO 2005/100000 A1 ist auch nicht wegen der Absorber- und/oder Streupigmente für medizinische Packmittel anwendbar.

[0004] Die US 2005/0224472 A1 zeigt ebenfalls ein Laserschweißverfahren, bei dem Absorber- und Streupigmente eingesetzt werden. Hierbei handelt es sich um TiO_2 -Partikel mit einer mittleren Partikelgröße von 300 nm. Auch aus der US 2005/0224472 A1 sind keine medizinischen Packmittel bekannt geworden.

[0005] Die DE 100 03 423 A1 beschreibt ein Laserschweißverfahren, bei dem Laserpigmente zum Einsatz kommen, die die Laserstrahlung absorbieren, was zu einem Erwärmen und Aufschmelzen der zu verbindenden Komponenten führt. Auch aus der DE 100 03 423 A1 geht kein medizinisches Packmittel hervor.

[0006] Die WO 02/00144 A1 beschreibt ein Verfahren zum Verbinden von zwei Schichten eines Kunststoffes mit Hilfe von Laserlicht. Dabei weist wenigstens eine Schicht eine absorbierende Komponente auf, die Laserlicht einer bestimmten Wellenlänge absorbiert. Die absorbierende Komponente ist entweder in wenigstens einen Kunststoff oder eine Zwischenschicht eingebracht.

[0007] Die EP 2 189 270 A1 zeigt ein Verfahren zum Aufbringen eines Kunststofffilmes auf einen Anschluss eines medizinischen Packmittels, wobei zwischen dem Kunststofffilm und dem medizinischen Packmittel eine Schicht mit einem Absorbermaterial für IR-Licht eingebracht ist.

[0008] Die US 2004/0030384 A1 beschreibt die Verbindung von zwei Kunststoffteilen mit Hilfe von Laserlicht.

[0009] Aus der WO 2005/100000 A1 ist ein Verfahren zum Laserverschweißen von zwei Schichten bekannt geworden, wobei die Schichten eine hohe Absorption bei der eingestrahlten Laserwellenlänge aufweisen. Auch eine Streuschicht zwischen den beiden Schichten ist in der WO 2005/100000 A1 beschrieben.

[0010] Die US 2005/0224472 A1 beschreibt ein Verfahren, um den Absorptionskoeffizienten μ_a und den Streukoeffizienten μ_s zu beeinflussen.

[0011] Aus der JP 2009/039872 A1 ist das Verbinden von Kunststoffschichten bekannt geworden, wobei ein das Laserlicht absorbierendes Material eingesetzt wird.

[0012] Der Artikel "Simultan in einem Schuss" in Kunststoffen 6/2015, S. 34-37, beschreibt allgemein das Fügen von Thermoplasten mittels prozessgeregeltem Laserschweißen.

[0013] Nachteilig an den Verfahren nach dem Stand der Technik war, dass zumindest einem der Kunststoffteile, die mit dem Laser verschweißt werden, ein Additiv hinzugefügt werden muss, das den Laserstrahl absorbiert und partiell Wärme erzeugt.

[0014] Für die Verwendung in pharmazeutischen Verpackungen sind nur bestimmte Kunststoffe zugelassen, die im Allgemeinen keine derartigen Additive enthalten. Durch die Zugabe derartiger Additiven erlischt aber die Zulassung für den Kunststoff für die Verwendung in pharmazeutischen Verpackungen, da die Ursprungsrezeptur

verändert wird, so dass ein derartiges Schweißverfahren im Bereich pharmazeutischer Produkte in der Regel nicht in Frage kommt. Bei medizinischen Packmitteln ist der Einsatz von Absorber- und/oder Streupigmenten nicht möglich.

[0015] Andere Schweißverfahren wie Ultraschweißen, Vibrationsschweißen, Hochfrequenzschweißen, Heizelementschweißen als das Laserschweißen sind für Kunststoffe im Bereich der Medizintechnik nicht anwendbar, da sie mit aufwändigen Reinigungsverfahren verbunden sind. So müssen Verunreinigungen anschließend an das Schweißen beseitigt werden.

[0016] Aufgabe der Erfindung ist es somit, ein medizinisches Packmittel, insbesondere eine Pharmaverpackung, anzugeben, die die Nachteile des Standes der Technik vermeidet. Insbesondere soll ein medizinisches Packmittel angegeben werden, bei dem Teilkörper durch Laserschweißen ohne Absorber- und Streupigmenten verbunden sind.

[0017] Diese Aufgabe wird durch ein medizinisches Packmittel gemäß Anspruch 1 und ein Verfahren gemäß Anspruch 9 gelöst. Erfindungsgemäß ist bei einem medizinischen Packmittel, insbesondere einer Pharmaverpackung, zwischen einem ersten thermoplastischen Kunststoffteilkörper und einem zweiten thermoplastischen Kunststoffteilkörper, wenigstens eine interne Grenzfläche mit Streuwirkung, angeordnet. Erfindungsgemäß sind die interne Grenzfläche und der erste und der zweite Kunststoffteilkörper frei von Absorberpigmenten und Streupigmenten. In einer besonders bevorzugten Ausführungsform ist vorgesehen, dass das medizinische Packmittel mehrere interne Grenzflächen umfasst. Besonders bevorzugt ist es, wenn die interne Grenzfläche mit Streuwirkung aus dem ersten Material des ersten thermoplastischen Kunststoffteils und/oder dem zweiten Material des zweiten thermoplastischen Kunststoffteils gebildet wird. Bevorzugt ist es, wenn die interne Grenzfläche mit Streuwirkung einen Verbindungskörper umfasst. Besonders bevorzugt ist es, wenn das Material für den ersten Kunststoffteilkörper gleich dem Material für den zweiten Kunststoffteilkörper ist, d.h. erster Kunststoffteilkörper und zweiter Kunststoffteilkörper aus demselben Material bestehen. Der Verbindungskörper ist bevorzugt als gepresster Verbindungskörper ausgeführt, der bevorzugt gemahlene Kunststoffpartikel mit Korngrenzen umfasst. Der Verbindungskörper ist frei von zusätzlichen Absorberteilchen und Absorberpigmenten und Streuteilchen und Streupigmenten, wie beispielsweise TiO_2 -Teilchen. Bevorzugt ist das Material des Verbindungskörpers dasselbe Material wie das Material des ersten und/oder des zweiten thermoplastischen Kunststoffteiles. Bei Verwendung im Bereich von Arzneimitteln ist dann eine Neuzulassung nicht erforderlich, da nur zertifizierte Materialien eingesetzt werden. Das Material des Verbindungskörpers führt auf Grund seines Aufbaus mit Korngrenzen, die unter anderem durch Verpressung von Polymerpulver entstehen, zu Reflektion und Streuung des eingestrahnten Laserlichts, so

dass eine für die Verschweißung erforderliche Laserabsorption analog zur Laserabsorption bei Additiven alleine durch die Reflektion und Streuung, d.h. der Verlängerung der Weglänge des eingestrahnten Lichtes erfolgen kann.

5 Durch die Reflektion und Streuung des Laserlichtes in bzw. an der Grenzfläche wird das Kunststoffteil aufgeschmolzen und verbindet sich dann mit den beiden anderen Fügepartnern nämlich dem ersten Kunststoffteilkörper und dem zweiten Kunststoffteilkörper. Ein Absorptionspigment und/oder ein Streupigment sind bei einem derartigen Aufbau nicht notwendig.

[0018] Bei Verwendung im pharmazeutischen Bereich ist es vorteilhaft, wenn der Verbindungskörper aus demselben Material wie dem Material für den ersten und/oder zweiten Kunststoffteilkörper besteht. Die erfindungsgemäßen medizinischen Packmittel bestehen aus wenigstens zwei Kunststoffteilkörpern, die mit Hilfe wenigstens einer internen Grenzfläche mit Hilfe von Streuwirkung miteinander verbunden werden. Insbesondere handelt es sich bei den medizinischen Packmitteln um solche, die Inhaltsstoffe aufnehmen, beispielsweise Hyaluronsäure, ein Anästhetika oder Neuroleptika.

[0019] Neben dem medizinischen Packmittel, insbesondere der Pharmaverpackung, stellt die Erfindung auch ein Verfahren zum Verbinden von einem ersten Kunststoffteilkörper und einem zweiten Kunststoffteilkörper zu einem Kunststoffteil mit einer zwischen ersten Kunststoffteilkörper und zweiten Kunststoffteilkörper angeordneten, wenigstens einer Grenzfläche, zur Verfügung. Erfindungsgemäß sind die interne Grenzfläche und der erste und der zweite Kunststoffteilkörper frei von Absorberpigmenten und Streupigmenten. Besonders bevorzugt wird die interne Grenzfläche mit Streuwirkung durch einen Verbindungskörper zur Verfügung gestellt. Der Verbindungskörper ist frei von Absorberpigmenten und Streupigmenten. Bei dem Verfahren wird ein Laserstrahl mit mindestens einer Wellenlänge auf die Grenzfläche gelenkt und zwar derart, dass durch Reflektion und Streuung an der Grenzfläche oder in der Grenzfläche, die für eine Verschweißung von erstem Kunststoffteilkörper und zweitem Kunststoffteilkörper erforderliche Erwärmung auftritt.

[0020] Bedingt durch die Lichtbrechung an bzw. in der Grenzfläche bzw. durch Reflektion und Streuung an der Grenzfläche erwärmt sich diese und wird aufgeschmolzen, so dass sie sich der erste mit dem zweiten Kunststoffteilkörper verbindet, d. h. fügt. Auf diese Art und Weise werden erster und zweiter Kunststoffteilkörper miteinander verbunden. Besonders bevorzugt wird die Wellenlänge des Lasers zwischen 800 und 1500 nm, bevorzugt 800 und 1200 nm gewählt. Für das Verbinden von erstem und zweitem Kunststoffteilkörper ist bei der erfindungsgemäßen Ausgestaltung weder ein Absorber- noch ein Streupigment notwendig.

55 **[0021]** Eine ausreichende Erwärmung der Grenzfläche, insbesondere des Verbindungskörpers, wird erreicht, wenn der Laser für eine gewisse Zeit auf die Grenzfläche, insbesondere den Verbindungskörper, mit

beispielsweise einer Leistung von 100 bis 600 W, bevorzugt 100 bis 300 W oder auch 600 W und mehr einwirkt. Die Einwirkzeiten sind abhängig vom Kunststoffmaterial, dem Absorptionsgrad, der Wandstärke und der Größe des Bauteils. Um die beiden Kunststoffteile miteinander zu verbinden, werden erste und zweite Kunststoffteilkörper aneinandergelegt. Die Zeitdauer, für die der Laser auf die Grenzfläche, insbesondere den Verbindungskörper einwirkt, ist abhängig vom Schmelzpunkt des Kunststoffmaterials, der Wandstärke, der Größe des Bauteils, der Geometrie und dem Absorptionsgrad des Kunststoffmaterials. Die Einwirkzeit

[0022] beträgt wenige Sekunden, bevorzugt 0,1 bis 100 Sekunden, insbesondere 5 bis 60 Sekunden. Der Laserstrahl arbeitet punktuell. Das Material wird punktuell erwärmt, sobald das Aufschmelzen erfolgt ist. Wenn ein Aufschmelzen punktuell erfolgt ist, wird der Laser und/oder das Bauteil weiter bewegt, d.h. zur nächsten Schweißstelle. Der komplette Schweißvorgang ist abhängig von der Größe des Bauteils.

[0023] Bei dem erfindungsgemäßen Verfahren müssen die miteinander zu verbindenden Bauteile nicht verspannt oder verpresst werden. Ein Verspannen/Verpressen wäre sogar kontraproduktiv, da bei einem Verspannen/Verpressen Spannungen in das Bauteil eingetragen werden bzw. der aufgeschmolzene Verbindungskörper bzw. das aufgeschmolzene Verbindungsteil einen Wulst ausbilden würde, was vermieden werden soll. Die Bauteile werden entweder in einer Vorrichtung gegen Verschieben gestützt oder nur aneinandergelegt.

[0024] Mehrere Möglichkeiten für die Herstellung eines Verbindungskörpers, der die interne Grenzfläche zur Verfügung stellt, sind denkbar.

[0025] Die erste Möglichkeit der Herstellung des Verbindungskörpers ist das Verpressen von Mikrogranulat. Bei diesem Verfahren wird Mikrogranulat mit einer Größe $\geq 400 \mu\text{m}$ unter Druck verpresst. Die Drücke liegen dabei materialabhängig zwischen 15 und 100 kN/cm^3 . Je nach Material kann der Pressling zusätzlich wärmebehandelt werden, um die Verbundfestigkeit zu erhöhen. Die Temperaturen sind materialabhängig und liegen bei teilkristallinen Werkstoffen, z. B. PE, PP, PA oder PET oberhalb der Kristallitschmelztemperatur, bei amorphen Materialien, z. B. PC, COC, COP oder PMMA oberhalb der Glasübergangstemperatur.

[0026] Alternativ zu einem Mikrogranulat kann auch ein Kunststoffpulver verpresst werden. Hierzu wird ein Kunststoffpulver mit einer Größe $\geq 10 \mu\text{m}$ unter Druck verpresst. Die Drücke liegen materialabhängig bei $15 - 100 \text{ kN/cm}^3$. Je nach Material kann der Pressling zusätzlich wärmebehandelt werden, um die Verbundfestigkeit zu erhöhen. Die Temperaturen sind materialabhängig und liegen bei teilkristallinen Werkstoffen, z. B. PE, PP, PA, PET, oberhalb der Kristallitschmelztemperatur, bei amorphen Materialien, z. B. PC, COC, COP, PMMA oberhalb der Glasübergangstemperatur. Die Zeitdauer ist abhängig von der Bauteilgröße und Wandstärke des Körpers und liegt im Sekundenbereich.

[0027] Eine weitere Möglichkeit der Herstellung eines Verbindungskörpers ist das Spritzgießen mit physikalischem Schäumen. Hierzu wird während des Spritzgießens des Verbindungskörpers ein inertes Gas, üblicherweise CO_2 oder N_2 , der Schmelze zugeführt, so dass eine Schaumstruktur entsteht. Durch die Schaumstruktur des Schweißkörpers kann der Laserstrahl an den Grenzflächen absorbiert werden, was zu einem Aufschmelzen des Schweißkörpers bzw. Schweißteils führt.

[0028] Ein weiteres alternatives Herstellungsverfahren ist die Bauteilherstellung des Verbindungskörpers aus Mikrotröpfchen:

Wird dieses Verfahren eingesetzt, so wird das Bauteil aus Mikrotröpfchen des thermoplastischen Kunststoffs zusammengesetzt. Dadurch ist gewährleistet, dass auch transparente Kunststoffe ihre Transparenz durch die Grenzflächen der Tröpfchen verlieren und somit der Laserstrahl absorbiert wird, was zu einem Aufschmelzen des Verbindungskörpers bzw. Verbindungsteiles führt.

Ein letztes Verfahren zur Herstellung des Verbindungskörpers ist das Spritzgießen mit reduzierter Massetemperatur. Durch Spritzgießen des Verbindungskörpers mit reduzierter Massetemperatur werden Granulatkörner teilweise nicht vollständig aufgeschmolzen, so dass dadurch die Transparenz beeinträchtigt wird und an den Grenzflächen der Laserstrahl absorbiert wird, was zu einem Aufschmelzen des Verbindungskörpers führt.

[0029] Die Erfindung soll nunmehr anhand der nachfolgenden Zeichnungen beispielhaft ohne Beschränkung hierauf beschrieben werden. Es zeigen:

Fig. 1 Der Aufbau eines traditionellen Verfahrens zum Laserschweißen von Kunststoff;

Fig. 2a - 2c Draufsicht auf unterschiedliche Arten von gepressten Verbindungskörpern;

Fig. 3 medizinisches Packmittel, insbesondere Pharmaverpackung gemäß der Erfindung.

[0030] In Figur 1 ist ein Kunststofflaserschweißprozess wie er aus dem Stand der Technik bekannt ist dargestellt. Ein erster Kunststoffteilkörper 10 besteht aus einem lasertransparenten Material, d. h. einem Kunststoffmaterial, das das Laserlicht im eingestrahnten Wellenlängenbereich zu weitgehend 100% transmittiert. Das durch den ersten Kunststoffteilkörper 10 transmittierte Laserlicht 100 trifft auf den zweiten absorbierenden Kunststoffteilkörper 20. Der zweite absorbierende Kunststoffteilkörper 20 umfasst ein Additiv 22, das die eingestrahlte Laserstrahlung 100 absorbiert, und/oder streut, bspw. TiO_2 Teilchen, wodurch der zweite Kunststoffteil-

körper erwärmt wird, so dass er an seiner Oberfläche 24 schmilzt. Hierdurch werden der erste Kunststoffteilkörper 10 und der zweite Kunststoffteilkörper 20 miteinander verbunden. Die Wellenlänge des Laserstrahls 100 beträgt bevorzugt zwischen 800 nm und 1100 nm.

[0031] In den Figuren 2a bis 2c werden Ausführungsformen der Erfindung gezeigt, bei denen die internen Grenzflächen mit Streuwirkung durch einen separaten Verbindungskörper (100) zur Verfügung gestellt werden. Der Verbindungskörper wird dann zwischen die zu ver- 5 bindenen Kunststoffteilkörper eingebracht. Selbstverständlich wäre es auch möglich, das die Grenzfläche an jedem Kunststoffteilkörper selbst zur Verfügung gestellt wird.

[0032] Figur 2a zeigt die prinzipielle Ansicht eines Ver- 10 bindungskörpers 100, der eine Grenzfläche 120 zur Verfügung stellt, wie er bzw. es gemäß der Erfindung Verwendung findet. Bei dem Verbindungskörper handelt es sich vorliegend um einen gepressten Sinterkörper aus gemahlenen Kunststoffpartikeln 200 mit einer Größe von 20 ungefähr 400 Mikrometer. Figur 2a ist eine Draufsicht auf einen derartigen Verbindungskörper 100. Wie zuvor beschrieben, kann der Verbindungskörper, der eine Grenzfläche zur Verfügung stellt, auch auf andere Art und Weise hergestellt werden.

[0033] Möglich ist das Verpressen von Kunststoffpul- 25 ver mit einer Größe $\geq 10 \mu\text{m}$. Eine weitere Möglichkeit ist das Spritzgießen mit gleichzeitigem Verschäumen oder die Bauteilherstellung aus Mikrotröpfchen. Eine weitere Möglichkeit ist das Spritzgießen mit reduzierter Massetemperatur. Diesbezüglich wird auf die Beschreibung im einleitenden Teil verwiesen. In jedem Fall stellt der Verbindungskörper wenigstens eine Grenzfläche zur 30 Verfügung, bei der ein Wärmeeintrag aufgrund einer verlängerten Weglänge durch Reflektion und Streuung des eingestrahnten Lichtes zur Verfügung gestellt wird und nicht durch Absorption an Fremdpartikeln wie im Stand der Technik. Der Verbindungskörper ist somit frei von Absorber- und Streupigmenten.

[0034] Figur 2b zeigt das Verhalten des Verbindungs- 35 körpers 100 bei Einstrahlung von Laserlicht 110. Das Laserlicht 110 wird an den Grenzflächen 120 der gemahlenen Kunststoffpartikel 200 reflektiert und gestreut. Die Reflektion und Streuung des Lichtes 110 führt zu einer Laserabsorption an den Grenzflächen 120.

[0035] Figur 2c zeigt eine Draufsicht auf einen erfindungsgemäßen Verbindungskörper 100 in zylindrischer Bauform. Gleiche Bauteile wie in Fig. 2a - 2b sind mit denselben Bezugsziffern belegt.

[0036] Figur 3 zeigt die Verbindung eines ersten Kunst- 40 stoffteilkörpers 310 mit einem zweiten Kunststoffteilkörper 320 zu einem erfindungsgemäßen medizinischen Packmittel. Die Verbindung von erstem Kunststoffteilkörper 310 und zweitem Kunststoffteilkörper 320 erfolgt in der dargestellten Ausführungsform mittels eines Verbin- 45 dungskörpers, wie es beispielsweise in Fig. 2a bis 2c dargestellt ist. Bei dem ersten Kunststoffteilkörper handelt es sich um einen für die Wellenlänge des Laser-

strahls 400 transparentes Material. Durch den ersten transparenten Kunststoffteilkörper 310 hindurchtreten- 5 des Licht trifft auf den Verbindungskörper 100. Im Material 330 des Verbindungskörpers 100 wird der Laserstrahl 400 gebrochen und durch die Lichtbrechung und Streuung der Laserstrahlen 410 innerhalb des Sintermaterials mit seinen Grenzflächen der Verbindungskörper 100 oder das Kunststoffsin- 10 terteil aufgeschmolzen. Hierdurch verbindet der Verbindungskörper 100 die beiden Fügepartner, nämlich den ersten Kunststoffteilkörper 310 und den zweiten Kunststoffteilkörper 320. Ein Absorberpigment und ein Streupigment sind im zweiten Kunststoffteilkörper 320 ebensowenig wie im ersten Kunststoffteil- 15 körper 310 und im Verbindungskörper 100 vorhanden. Die Verbindung von erstem Kunststoffteilkörper und zweitem Kunststoffteilkörper wird ohne Absorber- und Streupigmente zur Verfügung gestellt. Der zweite Kunststoffteilkörper kann transparent sein wie der erste Kunst- 20 stoffteilkörper. Bevorzugt ist das Material vom ersten Kunststoffteilkörper und zweiten Kunststoffteilkörper sowie gegebenenfalls dem Verbindungskörper identisch. Die Wellenlänge des eingestrahnten Laserlichts liegt bevorzugt im Bereich 800 bis 1500 nm, bevorzugt 800 bis 1200 nm.

[0037] Mit der Erfindung wird erstmals ein medizini- 25 sches Packmittel, insbesondere eine Pharmaverpackung, angegeben, das frei von Absorberpigmenten und/oder Streupigmenten in einem zu fügenden Kunststoffteil ist. Das auf diese Art und Weise hergestellte 30 Kunststoffteil eignet sich exzellent für eine Verwendung bei der Herstellung pharmazeutischer Produkte, bei denen eine Veränderung der Zusammensetzung des verwendeten Kunststoffmaterials nicht zulässig ist.

Patentansprüche

1. Medizinisches Packmittel, insbesondere Pharma- 35 verpackung, umfassend
 - einen ersten thermoplastischen Kunststoffteil- 40 körper (310) aus einem ersten Material,
 - einen zweiten thermoplastischen Kunststoffteilkörper (320) aus einem zweiten Material, wo- 45 bei
 - zwischen dem ersten Kunststoffteilkörper (310) und dem zweiten Kunststoffteilkörper (320), wenigstens eine interne Grenzfläche mit Streuwirkung, die bevorzugt zu einer verlängerten Weglänge von eingestrahlt 50 em Licht führt, angeordnet ist, wobei
 - die interne Grenzfläche und
 - der erste und zweite Kunststoffteilkörper frei von Absorberpigmenten und Streupigmenten 55 sind.
2. Medizinisches Packmittel, insbesondere Pharma- verpackung, nach Anspruch 1,

dadurch gekennzeichnet, dass

mehrere interne Grenzflächen vorgesehen sind, die eine hohe Streuwirkung des eingestrahltten Lichtes aufweisen.

3. Medizinisches Packmittel nach einem der Ansprüche 1 bis 2,

dadurch gekennzeichnet, dass

das Material des ersten Kunststoffteilkörpers und das Material des zweiten Kunststoffteilkörpers identisch sind.

4. Medizinisches Packmittel nach einem der Ansprüche 1 bis 3,

dadurch gekennzeichnet, dass

die interne Grenzfläche mit Streuwirkung aus dem ersten Material und/oder dem zweiten Material gebildet wird.

5. Medizinisches Packmittel nach einem der Ansprüche 1 bis 4,

dadurch gekennzeichnet, dass

die interne Grenzfläche mit Streuwirkung durch einen Verbindungskörper (100) ausgebildet wird, der frei von Absorberpigmenten und Streupigmenten ist.

6. Medizinisches Packmittel gemäß einem der Ansprüche 1 bis 5,

dadurch gekennzeichnet, dass

die interne Grenzfläche mit Streuwirkung und/oder der Verbindungskörper (100) eines der nachfolgenden Teile sind:

- ein gepresster Verbindungskörper aus einem Mikrogranulat mit einer Partikelgröße $\geq 400 \mu\text{m}$, insbesondere aus PE, PP, PA, PET, PC, COC, COP oder PMMA;
- ein gepresstes Kunststoffschweißteil aus einem Kunststoffpulver mit einer Partikelgröße $\geq 10 \mu\text{m}$, insbesondere aus PE, PP, PA, PET, PC, COC, COP oder PMMA;
- ein während des Spritzgießens mit einem inerten Gas versetzter Verbindungskörper;
- ein aus Mikrotröpfchen eines thermoplastischen Kunststoffs zusammengesetzter Verbindungskörper;
- ein durch Spritzgießen mit reduzierter Masstemperatur hergestellter Verbindungskörper.

7. Medizinisches Packmittel nach einem der Ansprüche 1 bis 6,

dadurch gekennzeichnet, dass

der Verbindungskörper (100) aus dem ersten und/oder dem zweiten Material besteht.

8. Medizinisches Packmittel nach einem der Ansprüche 1 bis 7,

dadurch gekennzeichnet, dass

das Packmittel einen Inhaltsstoff insbesondere Hyaluronsäure, ein Anästhetika oder ein Neuroleptika umfasst.

9. Verfahren zum Verbinden von Kunststoffteilen von medizinischen Packmitteln, insbesondere Pharmaverpackungen, umfassend einen ersten Kunststoffteilkörper (310) und einen zweiten Kunststoffteilkörper (320) sowie wenigstens eine zwischen erstem und zweitem Kunststoffteilkörper vorhandene bzw. eingebrachte interne Grenzfläche mit Streuwirkung, wobei ein Laserstrahl mit mindestens einer Wellenlänge auf die interne Grenzfläche einwirkt, derart, dass durch Reflektion und/oder Streuung eine für eine Verschweißung von erstem Kunststoffteilkörper (310) und zweitem Kunststoffteilkörper (320) erforderliche Laserabsorption auftritt, wobei die interne Grenzfläche und der erste und zweite Kunststoffteilkörper frei von Absorberpigmenten und Streupigmenten sind.

10. Verfahren nach Anspruch 9,

dadurch gekennzeichnet, dass

die interne Grenzfläche mit Streuwirkung einen Verbindungskörper (100) umfasst, der frei von Absorberpigmenten und Streupigmenten ist.

11. Verfahren nach einem der Ansprüche 9 oder 10,

dadurch gekennzeichnet, dass

durch die Absorption des Laserstrahls bedingt durch Lichtbrechung an der wenigstens ersten Grenzfläche, insbesondere dem Verbindungskörper der erste Kunststoffteilkörper und/oder der zweite Kunststoffteilkörper und/oder der Verbindungskörper aufgeschmolzen wird und erste und zweite Kunststoffteilkörper (310, 320) sich verbinden.

12. Verfahren nach einem der Ansprüche 9 bis 11,

dadurch gekennzeichnet, dass

die Wellenlänge zwischen 800 und 1500 nm, bevorzugt 800 bis 1200 nm liegt.

Claims

1. Medical packaging, in particular pharmaceutical, comprising

- a first thermoplastic plastic partial body (310) made of a first material,
- a second thermoplastic plastic partial body (320) made of a second material, wherein
- between the first plastic partial body (310) and the second plastic partial body (320), at least one internal boundary surface with a scattering effect is arranged, which preferably causes an increase in the wavelength of incident light,

wherein

- the internal boundary surface and
- the first and second plastic partial body are free of absorber pigments and scattering pigments.

2. Medical packaging, in particular pharmaceutical, according to Claim 1,
characterized in that
a plurality of internal boundary surfaces are provided, which have a high scattering effect of the incident light.

3. Medical packaging according to either of Claims 1 to 2,
characterized in that
the material of the first plastic partial body and the material of the second plastic partial body are identical.

4. Medical packaging according to any one of Claims 1 to 3,
characterized in that
the internal boundary surface with scattering effect is formed from the first material and/or the second material.

5. Medical packaging according to any one of Claims 1 to 4,
characterized in that
the internal boundary surface with scattering effect is realized by a connecting body (100), which is free of absorber pigments and scattering pigments.

6. Medical packaging according to any one of Claims 1 to 5,
characterized in that
the internal boundary surface with scattering effect and/or the connection body (100) are one of the following parts:

- a pressed connection body made from a microgranulate with a particle size greater than or equal to 400 μm , in particular made of PE, PP, PA, PET, PC, COC, COP or PMMA;
- a pressed plastic welding part made from a plastic powder with a particle size greater than or equal to 10 μm , in particular made of PE, PP, PA, PET, PC, COC, COP or PMMA;
- a connection body infused with an inert gas during the injection moulding process;
- a connection body composed of micro-droplets of a thermoplastic plastic;
- a connection body produced by injection moulding with reduced melt temperature.

7. Medical packaging according to any one of Claims 1 to 6,

characterized in that

the connection body (100) is composed of the first and/or second material.

8. Medical packaging according to any one of Claims 1 to 7,
characterized in that
the packaging comprises an ingredient, in particular hyaluronic acid, an anaesthetic or a neuroleptic.

9. Method for joining plastic parts of medical packaging, in particular pharmaceutical packaging, comprising a first plastic partial body (310) and a second plastic partial body (320), as well as at least one internal boundary surface with scattering effect which is either present or introduced between the first and second plastic partial body,
wherein
a laser beam with at least one wavelength acts on the internal boundary surface in such a way that, due to reflection and/or scattering, a laser absorption occurs that is necessary for welding the first plastic partial body (310) and second plastic partial body (320), wherein the internal boundary surface and the first and second plastic partial bodies are free of absorber pigments and scattering pigments.

10. Method according to Claim 9,
characterized in that
the internal boundary surface with scattering effect comprises a connecting body (100), which is free of absorber pigments and scattering pigments.

11. Method according to either of Claims 9 or 10,
characterized in that
due to the absorption of the laser beam caused by refraction of light at the at least first boundary surface, in particular the connection body, the first plastic partial body and/or the second plastic partial body and/or the connection body is/are melted and the first and second plastic partial body (310, 320) are connected together.

12. Method according to any of Claims 9 to 11,
characterized in that
the wavelength is between 800 and 1500 nm, preferably 800 to 1200 nm.

Revendications

1. Matériau d'emballage médical, en particulier pharmaceutique, comprenant
- un premier corps de partie en plastique thermoplastique (310) constitué d'un premier matériau,
 - un second corps de partie en plastique ther-

- moplastique (320) constitué d'un second matériau,
dans lequel
- au moins une interface interne ayant un effet de diffusion est agencée entre le premier corps de partie en plastique thermoplastique (310) et le second corps de partie en plastique thermoplastique (320), menant de préférence à un trajet rallongé de la lumière irradiée,
 - l'interface interne et
 - les premier et second corps de partie en plastique sont dépourvus de pigments absorbants et de pigments de diffusion.
2. Matériau d'emballage médical, en particulier pharmaceutique, selon la revendication 1,
caractérisé en ce que
plusieurs interfaces internes sont prévues, lesquelles présentent un effet de diffusion important de la lumière irradiée.
3. Matériau d'emballage médical selon l'une des revendications 1 à 2,
caractérisé en ce que
le matériau du premier corps de partie en plastique et le matériau du second corps de partie en plastique sont identiques.
4. Matériau d'emballage médical selon l'une des revendications 1 à 3,
caractérisé en ce que
l'interface interne ayant un effet de diffusion est formée par le premier matériau et/ou le second matériau.
5. Matériau d'emballage médical selon l'une des revendications 1 à 4,
caractérisé en ce que
l'interface interne ayant un effet de diffusion est conçue avec un corps de liaison (100) qui est dépourvu de pigments absorbants et de pigments de diffusion.
6. Matériau d'emballage médical selon l'une des revendications 1 à 5,
caractérisé en ce que
l'interface interne ayant un effet de diffusion et/ou le corps de liaison (100) sont l'une des parties suivantes, à savoir :
- un corps de liaison pressé constitué de microgranulés ayant une granulométrie $\geq 400 \mu\text{m}$, en particulier de PE, PP, PA, PET, PC, COC, COP ou PMMA ;
 - une partie soudée en plastique pressée constituée d'une poudre plastique ayant une granulométrie $\geq 10 \mu\text{m}$, en particulier de PE, PP, PA, PET, PC, COC, COP ou PMMA ;
- un corps de liaison dans lequel un gaz inerte est ajouté durant le moulage par injection ;
 - un corps de liaison qui est constitué de microgouttelettes de plastique thermoplastique ;
 - un corps de liaison qui est produit par moulage par injection à une température de masse réduite.
7. Matériau d'emballage médical selon l'une des revendications 1 à 6,
caractérisé en ce que
le corps de liaison (100) est constitué du premier et/ou du second matériau.
8. Matériau d'emballage médical selon l'une des revendications 1 à 7,
caractérisé en ce que
le matériau d'emballage comprend en outre un ingrédient, en particulier de l'acide hyaluronique, un anesthésique ou un neuroleptique.
9. Procédé pour lier des parties en plastique de matériaux d'emballage médicaux, en particulier pharmaceutiques, comprenant un premier corps de partie en plastique (310) et un second corps de partie en plastique (320) ainsi qu'au moins une interface interne ayant un effet de diffusion déposée ou présente entre le premier et le second corps de partie en plastique.
dans lequel
un faisceau laser ayant au moins une longueur d'onde agit sur l'interface interne de telle sorte que, par réflexion et/ou diffusion, il se produise une absorption laser nécessaire au soudage du premier corps de partie en plastique (310) et du second corps de partie en plastique (320), l'interface interne et les premier et second corps de partie en plastique étant dépourvus de pigments absorbants et de pigments de diffusion.
10. Procédé selon la revendication 9,
caractérisé en ce que
l'interface interne ayant un effet de diffusion comprend un corps de liaison (100) qui est dépourvu de pigments absorbants et de pigments de diffusion.
11. Procédé selon l'une des revendications 9 ou 10,
caractérisé en ce que
grâce à l'absorption du faisceau laser causée par réfraction au niveau d'au moins la première interface, en particulier du corps de liaison, le premier corps de partie en plastique et/ou le second corps de partie en plastique et/ou le corps de liaison sont fondus et le premier et le second corps de partie en plastique (310, 320) sont liés.
12. Procédé selon l'une des revendications 9 à 11,
caractérisé en ce que

la longueur d'onde est comprise entre 800 et 1500 nm, de préférence 800 et 1200 nm.

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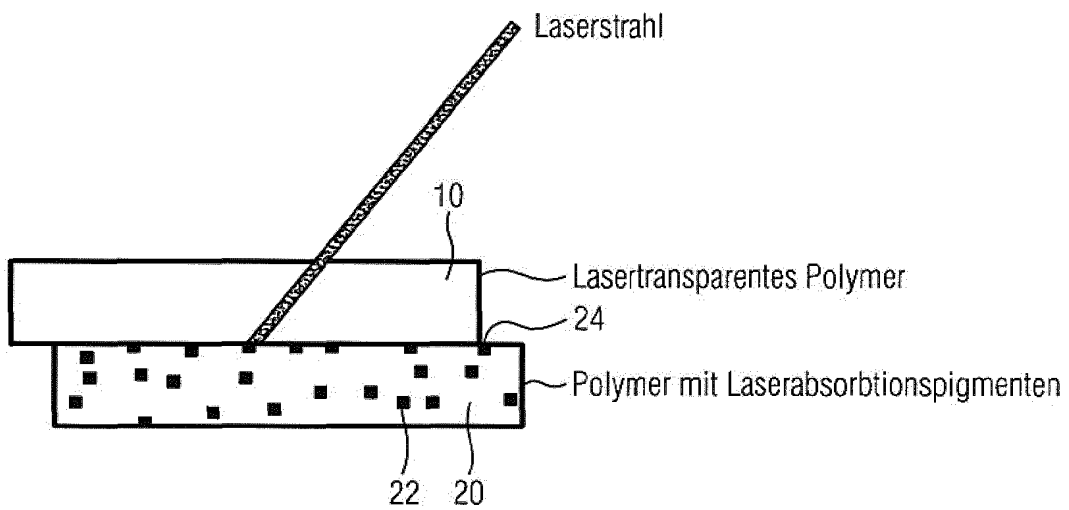
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FIG. 1

Herkömmlicher Laserschweisprozess



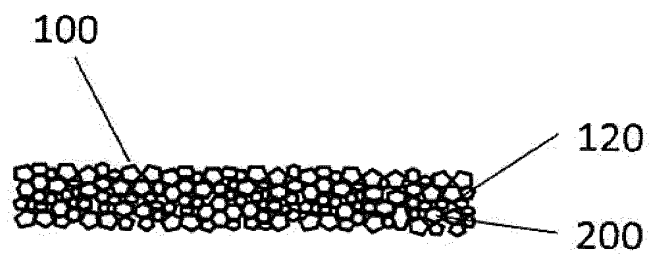


Fig. 2a

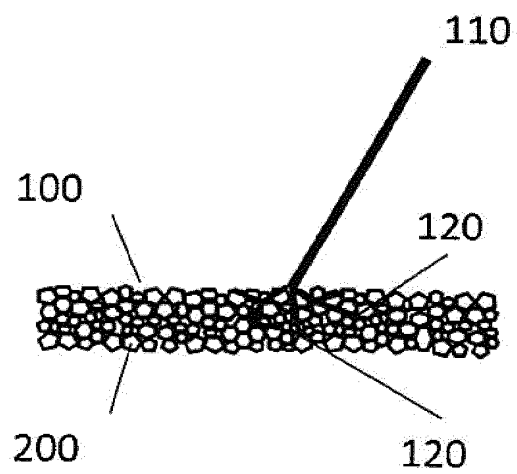


Fig. 2b

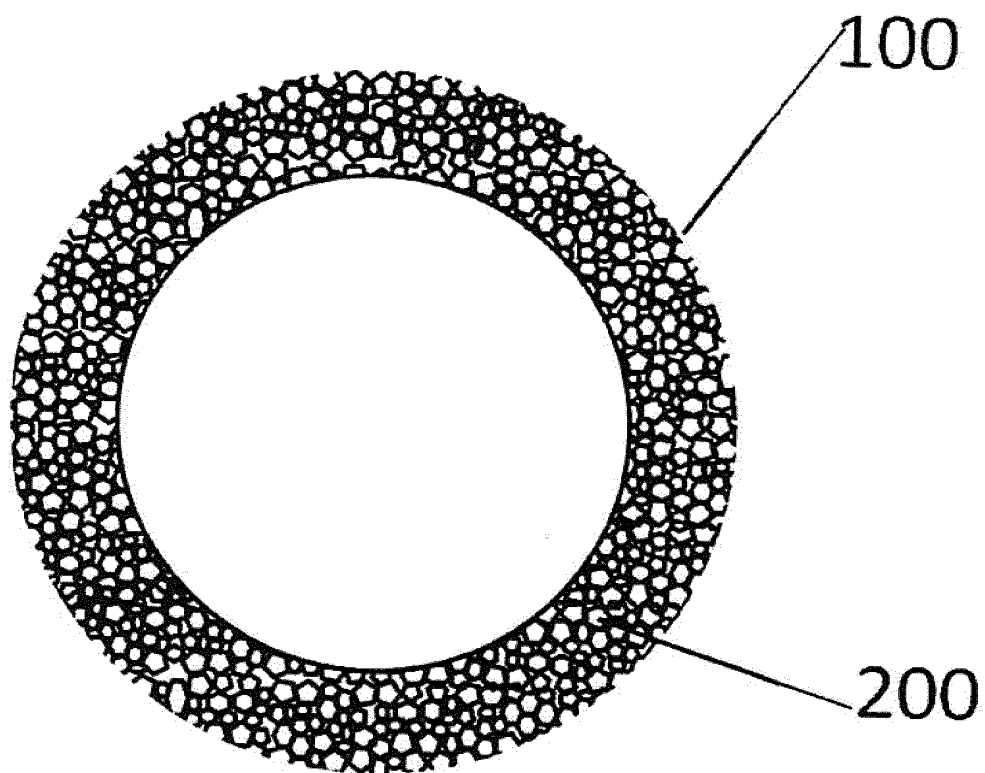
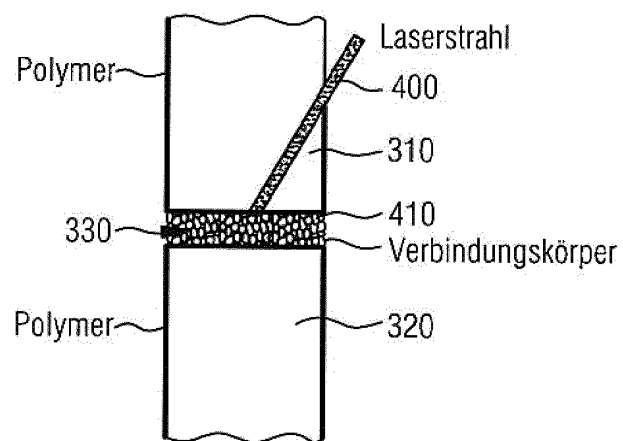


Fig. 2c

FIG. 3

Schweissvorgang



IN DER BESCHREIBUNG AUFGEFÜHRTE DOKUMENTE

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- US 20050224472 A1 [0004] [0010]
- DE 10003423 A1 [0005]
- WO 0200144 A1 [0006]
- EP 2189270 A1 [0007]
- US 20040030384 A1 [0008]
- JP 2009039872 A [0011]

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- Simultan in einem Schuss. *Kunststoffe*, Juni 2015, 34-37 [0012]

(19)



(11)

EP 3 210 907 B1

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(54) **LAMINATE FOR BLISTER PACK, BLISTER PACK USING SAME, BLISTER PACK PACKAGE, AND METHOD FOR MANUFACTURING SAME**

LAMINAT FÜR BLISTERPACKUNG, BLISTERPACKUNG DAMIT, BLISTERPACKVERPACKUNG
UND VERFAHREN ZUR HERSTELLUNG DAVON

STRATIFIÉ POUR EMBALLAGE-COQUE, EMBALLAGE-COQUE L'UTILISANT, ET ENSEMBLE
EMBALLAGE-COQUE, ET PROCÉDÉ POUR LEUR FABRICATION

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WO-A1-2013/140821 JP-A- 2013 079 086
JP-A- 2013 169 666

EP 3 210 907 B1

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a laminate for a blister package (blister pack), a blister package that uses said laminate, and a blister packaging product (blister pack package). More particularly, the present invention relates to a laminate for a blister package that is free of the occurrence of molding defects even if a pocket is formed at a certain depth in order to package a large pharmaceutical drug, to a blister package that uses said laminate, to a blister packaging product and to a production process of said laminate.

BACKGROUND ART

10 **[0002]** While powdered pharmaceutical drugs are enclosed in thin-walled paper pouches or pouches made of plastic film, drugs such as tablets or capsules are enclosed in blister packages referred to as press-through packages (PTP). The drug can be removed by breaking a sheet-like cover by pressing on the drug enclosed in the blister package with a finger.

15 **[0003]** Pharmaceutical drugs are subject to deterioration of the pharmacologically active ingredient following absorption of moisture. Consequently, a desiccant such as silica gel has conventionally been enclosed within the outer pouch that encloses the blister package. However, the work of placing a desiccant in the outer pouch is labor-intensive, and there is also the risk of the desiccant being accidentally swallowed or consumed. In addition, there was also the problem of a low level of humidity being unable to be maintained within the blister package after opening the outer pouch, thereby resulting in progression of deterioration of the pharmaceutical drug. Moreover, since certain drugs are susceptible to oxidative degradation or emit a peculiar odor, there is also the need to be able to absorb oxygen and odors present within the blister package.

20 **[0004]** Patent Document 1 discloses a technology whereby long-term stability of a pharmaceutical drug is improved by laminating an adsorbing layer having an adsorbent within a blister package. In this technology, a dome-shaped pocket is first formed in a laminate formed by dry-laminating a substrate film and an absorbing layer having an adsorbing layer. A pharmaceutical drug in the form of a tablet is then placed in the pocket and sealed therein by a cover. According to this technology, the maintaining of a dry state, prevention of oxidation and efficient removal of odors are thought to be possible even if a desiccant and the like is not included in the outer pouch.

25 **[0005]** In addition, since some pharmaceutical drugs are susceptible to ultraviolet light, if a transparent packaging container is used, there is the risk of degradation of the pharmacologically active ingredient. Patent Document 1 discloses a so-called aluminum blister package that employs a technology whereby an aluminum layer is also formed in the laminate for a blister package on the top side instead of only in a cover on the back side of the blister package. According to this technology, since an aluminum layer is provided in the blister package, although it is no longer possible to visualize the pharmaceutical contained therein, ultraviolet light can be blocked and barrier properties can be further enhanced.

30 **[0006]** In an aspect that simply combines the aforementioned two technologies, problems such as rupturing of the roof of the dome or the formation of cracks in the skirt or shoulder of the dome occur when a dome-shaped pocket is formed in a laminate for a blister package. In order to overcome these problems, Patent Document 2 dry-laminates an absorbing film with a substrate obtained by laminating a stiff reinforcing layer made of a specific polymer on the absorbing film side of an aluminum layer. In Patent Document 2, overall laminate strength is improved and molding defects are reduced by providing a stiff reinforcing layer.

35 **[0007]** Patent Document 3 discloses a blister pack obtained by sandwich laminating an absorbing layer and a substrate layer with an adhesive resin layer having a thickness of 20 μm .

40 **[0008]** The EP 2 612 824 A1 discloses a container including an absorbing layer absorbing at least one of liquid and gas; a reinforcing layer laminated on the absorbing layer with an adhesive layer interposed there between; an aluminum layer laminated on the reinforcing layer with an adhesive layer interposed there between; and a barrier layer laminated on the aluminum layer with an adhesive layer interposed there between and suppressing entry of at least one of liquid and gas. The WO 2013/140821 A1 discloses a layered body for a PTP or blister pack in which an absorption layer is layered on a substrate layer via an adhesive layer. The absorption layer has a configuration in which an outer skin layer, an intermediate layer, and an inner skin layer are layered in the stated sequence, and the outer skin layer is bonded to the substrate layer via the adhesive layer. The outer skin layer is composed of a polyethylene resin, the intermediate layer is composed of a mixture of a polyethylene resin and an absorbent, and the inner skin layer is composed of a blended resin having 25 to 50 mass% of a linear low-density polyethylene, and 75 to 50 mass% of a high-density polyethylene having a higher melting point as a material than the preheating temperature in the molding process. The blended resin of the inner skin layer has 10 to 50 mass% of a linear low-density polyethylene, and 90 to 50 mass% of a high-density polyethylene having a higher melting point as a material than the preheating temperature in the molding process. The JP 2013/169666 A discloses a multilayer film for deep-drawing packaging formed by laminating five or

more layers of at least an outer layer, an adhesive layer, a gas barrier layer, an adhesive layer and a heat seal layer in this order. In the multilayer film for deep-drawing packaging, the outer layer is composed of polyethylene blended with 5 to 40 wt. % of thermoplastic elastomer. The JP 2013/079086 A discloses a sealant having at least an oxygen-absorbing resin layer and a food contact layer. When the food contact layers of the sealant are heat-bonded to each other, the sealing strength at 23 °C is 23 to 100 N/15 mm and the sealing strength at 90 °C is 5 to 25 N/15 mm. The WO 2012/029899 A1 discloses a package being provided with a container sheet having formed therein a concave receptacle that accommodates a solid preparation containing a succinic acid solifenacin or a 1-[(a-iso-butanoyloxy-ethoxy) carbonyl] aminomethyl)-1-cyclohexane acetic acid; and an airtight cover material sheet for encapsulating the solid preparation. The container sheet comprises a package film obtained by layering an adsorption layer, at least one layer of a substrate layer configured from resin, aluminum foil, and a barrier layer. The adsorption layer is layered with the substrate layer, is positioned on the side that accommodates the solid preparation, and contains at least zeolite.

[Prior Art Documents]

[Patent Documents]

[0009]

[Patent Document 1] International Publication No. WO 2006/115264

[Patent Document 2] International Publication No. WO 2012/029323

[Patent Document 3] International Publication No. WO 2013/140821

DISCLOSURE OF THE INVENTION

[Problems to be Solved by the Invention]

[0010] In the case of attempting to form a relatively deep pocket exceeding 10 mm in diameter and 3.3 mm in depth, there are still many cases in which molding defects occur even when using the laminate described in Patent Document 2 that reduces molding defects, thereby making this inadequate. When the inventors of the present invention conducted a study on the laminates described in Patent Documents 1 and 2 with the aim of reducing molding defects occurring in the case of forming such a deep pocket, it was found that molding defects cause so-called delamination in which the substrate film and absorbing film undergo partial separation.

[0011] Namely, in the case of the laminate described in Patent Document 2, it was found that there are cases in which delamination occurs between the absorbing film and the reinforcing layer, and as a result thereof, force is not uniformly transmitted to the molded article when molding a pocket and stress concentrates in a portion thereof resulting in the occurrence of molding defects. When the cause of this delamination was investigated further, it was determined that, even if the absorbing film has a skin layer, fine irregularities are formed on the surface of the absorbing film caused by the presence of inorganic absorbent. Then, it was determined that surface roughness increases, thereby causing a portion of the adhesion between the dry-laminated absorbing film and reinforcing layer to become defective.

[0012] In addition, although Patent Document 3 demonstrates some improvement in comparison with the laminates described in Patent Documents 1 and 2, in the case of attempting to mold a deep pocket, a large number of molding defects continue to occur, thereby making this inadequate.

[0013] An object of the present invention is to provide a laminate for a blister package that is resistant to the occurrence of molding defects even if a pocket is molded to a certain depth in order to package large contents such as a drug, to a blister package and a blister packaging product that use that laminate, and to a method for producing that laminate.

[Means for Solving the Problems]

[0014] With this in mind, the inventors of the present invention completed the laminate of the present invention, which is capable of preventing delamination between an absorbing film and substrate film and reducing the occurrence of molding defects, by having a comparatively thick resin layer present adjacent to the absorbing film that alleviates surface roughness of the absorbing film.

[0015] Namely, the inventors of the present invention found that the aforementioned problems can be solved by the present invention having the aspects indicated below.

[Aspect 1]

[0016] A laminate for a blister package, comprising a substrate film, an adhesive resin layer, and an absorbing film in

that order; wherein,
the adhesive resin layer has a thickness of 25 μm to 100 μm , and
the absorbing film comprises an absorbing layer containing a thermoplastic resin and an inorganic absorbent.

5 [Aspect 2]

[0017] The laminate described in Aspect 1, wherein the adhesive resin layer comprises a polyolefin-based resin.

10 [Aspect 3]

[0018] The laminate described in Aspect 1 or Aspect 2, wherein the adhesive resin layer is formed through sandwich lamination.

15 [Aspect 4]

[0019] The laminate described in any of Aspects 1 to 3, wherein the adhesive resin layer has a thickness of 25 μm to 50 μm .

20 [Aspect 5]

[0020] The laminate described in any of Aspects 1 to 4, wherein the absorbing film comprises an outer skin layer on the side of the adhesive resin layer, the absorbing layer, and an inner skin layer.

25 [Aspect 6]

[0021] The laminate described in Aspect 5, wherein the outer skin layer, the absorbing film and the inner skin layer of the absorbing film are formed through co-extrusion.

30 [Aspect 7]

[0022] A laminate for a blister package composed of the following layers:

35 a substrate layer having a thickness of 12 μm to 25 μm and comprising a resin selected from the group consisting of a polyolefin-based resin, polyvinyl chloride, polyvinylidene chloride, polychlorotrifluoroethylene, polytetrafluoroethylene, saturated or unsaturated polyester, polyamide and polyacrylonitrile;
an aluminum layer having a thickness of 7 μm to 45 μm ;
a reinforcing layer having a thickness of 8 μm to 60 μm and comprising a resin selected from the group consisting of polyvinyl chloride, saturated or unsaturated polyester and polyamide;
40 an adhesive resin layer having a thickness of 25 μm to 50 μm , comprising a polyolefin-based resin, and formed by sandwich lamination;
an outer skin layer having a thickness of 10 μm to 30 μm and comprising a polyolefin-based resin;
an absorbing layer having a thickness of 10 μm to 200 μm and comprising a polyolefin-based resin and 5% by volume to 70% by volume of zeolite; and
45 an inner skin layer having a thickness of 10 μm to 30 μm and comprising a polyolefin-based resin.

<Aspect 8>

50 [0023] A blister package comprising the laminate described in any of Aspects 1 to 7 and a cover having a heat seal layer and an aluminum layer, wherein the laminate and the cover are at least partially adhered, and the laminate has a pocket so that contents are able to be contained between the laminate and the cover.

<Aspect 9>

55 [0024] A blister packaging product having the blister package described in Aspect 8 and having contents contained in the pocket.

<Aspect 10>

[0025] A method for producing a laminate for a blister package, comprising the following:

5 providing a substrate film;
providing an absorbing film comprising an absorbing layer containing a thermoplastic resin and an inorganic absorbent; and,
forming an adhesive resin layer having a thickness of 25 μm to 100 μm between the absorbing film and the substrate film, on the absorbing film or on the substrate film, to adhere the absorbing film and the substrate film.

<Aspect 11>

[0026] The method for producing a laminate for a blister package described in Aspect 10, wherein

15 the substrate film comprises a substrate layer, aluminum layer and reinforcing layer in that order, the absorbing film comprises an outer skin layer and an inner skin layer that sandwich the absorbing layer, and the adhesive resin layer is formed between the outer skin layer of the absorbing film and the reinforcing layer of the substrate film, or on the outer skin layer of the absorbing film or on the reinforcing layer of the substrate film.

[Effects of the Invention]

[0027] According to the present invention, a blister package provided with an absorbing layer having a pocket of a certain depth can be produced with minimal occurrence of molding defects. The use of such a blister package makes it possible to store comparatively large contents in a stable state over a long period of time.

25 **[0028]** The present invention can provide the effect of reducing the occurrence of molding defects by having a comparatively thick adhesive resin layer present between a substrate film and an absorbing film. The effect is unexpected in consideration of the fact that molding defects occurred in the aforementioned Patent Document 2 when a reinforcing layer composed of a soft resin was used between an absorbing film and an aluminum layer (such as in Comparative Example 4 of Patent Document 2), and that moldability typically tends to decrease when the overall thickness of a laminate for a blister package increases.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029]

35 FIG. 1 is a schematic diagram of a blister package provided with an absorbing layer.
FIG. 2 is a schematic diagram of the layer structure of the blister package of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

<<Laminate for Blister Pack and Production Method Thereof>>

45 **[0030]** The laminate for a blister pack of the present invention has a substrate film, an absorbing film, and an adhesive resin layer that adheres the two. The substrate film at least has a substrate layer and preferably further has an aluminum layer and a reinforcing layer on the side of the absorbing film in that order. In addition, the absorbing film has an absorbing layer comprising a thermoplastic resin and an inorganic absorbent, and further has an inner skin layer and an outer skin layer. The laminate for a blister pack of the present invention preferably comprises or is composed of an outermost substrate layer, an aluminum layer, a reinforcing layer, an adhesive resin layer, an outer skin layer, an absorbing layer and an inner skin layer that contacts a cover, in that order.

50 **[0031]** The thickness of the laminate of the present invention can be, for example, 500 μm or less, 400 μm or less, 300 μm or less, 250 μm or less, 200 μm or less, 150 μm or less, 100 μm or less, 90 μm or less, 85 μm or less or 80 μm or less, and 50 μm or more, 60 μm or more or 70 μm or more in consideration of strength and stiffness of the laminate, and ease of pushing through the blisters and barrier properties when molded into a blister packaging product.

55 **[0032]** Furthermore, in the present description, although a "laminate composed of a layer A and a layer B" refers to a laminate substantially only comprising the layer A and the layer B, it also means that it may also comprise other layers in addition to the layer A and the layer B within a range that allows the advantageous effects of the present invention to be obtained or a range over which the advantageous effects are not lost. For example, the laminate may be expressed as a "laminate composed of a layer A and a layer B" even if an anchor coat layer and the like is formed between the

layer A and the layer B.

<Substrate Film>

[0033] The substrate film isolates the absorbing film from the external environment and imparts suitable stiffness, strength and the like to the entire laminate. The substrate film comprises a substrate layer and may further comprise an aluminum layer and a reinforcing layer in that order. In this case, the substrate layer may be the outermost layer of the laminate for a blister pack.

[0034] The thickness of the substrate film can be, for example, 150 μm or less or 100 μm or less and 20 μm or more, 30 μm or more or 50 μm or more in consideration of maintaining barrier properties and imparting strength and the like to the entire laminate of the present invention.

[0035] The substrate layer comprises a thermoplastic resin, and examples of that thermoplastic resin include a polyolefin-based resin, polyvinyl chloride, polyvinylidene chloride (PVDC), polychlorotrifluoroethylene, polytetrafluoroethylene, saturated or unsaturated polyester (such as polyethylene terephthalate (PET) or polybutylene terephthalate), polyamide (such as Nylon, Nylon 6 or Nylon MXD6) and polyacrylonitrile (PAN), and these films can be used for the substrate layer as a single layer or a combination of a plurality of layers.

[0036] Examples of polyolefin-based resins include low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), medium-density polyethylene (MDPE), high-density polyethylene (HDPE), polyethylene polymerized using a metallocene catalyst, propylene homopolymer, propylene-ethylene block copolymer, propylene-ethylene random copolymer, polypropylene polymerized using a metallocene catalyst, chlorinated polypropylene, polymethylpentene, ethylene-acrylic acid copolymer (EAA), ethylene-methacrylic acid copolymer (EMAA), ethylene-ethyl acrylate copolymer (EEA), ethylene-methyl acrylate copolymer (EMA), ethylene-ethyl acrylate copolymer, ethylene-vinyl acetate copolymer (EVA), ionomer, carboxylic acid-modified polyethylene, carboxylic acid-modified polypropylene, and carboxylic acid-modified polyethylene-vinyl acetate copolymer.

[0037] The thickness of the substrate layer can be, for example, 8 μm or more, 10 μm or more or 12 μm or more, and 50 μm or less or 25 μm or less.

[0038] The aluminum layer may be a layer comprising pure aluminum (Al) foil or an aluminum alloy foil. Other examples of the aluminum layer include resin layers having an aluminum vapor-deposited film, and examples of resin films in which these vapor-deposited layers are deposited include polyolefin-based resins (and particularly, oriented or cast polypropylene), polyvinyl chloride, saturated polyester (such as polyethylene terephthalate (PET) or polybutylene terephthalate) and polyamide (such as Nylon, Nylon 6 or Nylon MXD6).

[0039] The thickness of the aluminum layer can be, for example, 7 μm or more, 10 μm or more or 12 μm or more, and 50 μm or less, 45 μm or less or 30 μm or less.

[0040] A resin layer capable of being used as a substrate layer can also be used for the reinforcing layer. The reinforcing layer preferably comprises polyamide, saturated or unsaturated polyester (such as polyethylene terephthalate (PET) or polybutylene terephthalate) and polyvinyl chloride in order to impart suitable stiffness. The reinforcing layer is particularly preferably the reinforcing layer disclosed in Patent Document 2.

[0041] The thickness of the reinforcing layer can be, for example, 8 μm or more, 10 μm or more or 12 μm or more, and 80 μm or less, 60 μm or less, 50 μm or less or 25 μm or less.

[0042] A known lamination method such as dry lamination or extrusion lamination can be used for the method used to laminate each layer of the substrate film.

<Adhesive Resin Layer>

[0043] The adhesive resin layer has a thickness of 25 μm to 100 μm and adheres the substrate film and the absorbing film.

[0044] Although there are no particular limitations on the adhesive resin layer provided it is a layer that is capable of alleviating surface irregularities of the absorbing film, the thickness thereof can be 25 μm or more, 26 μm or more, 30 μm or more, 35 μm or more or 40 μm or more, and 100 μm or less, 80 μm or less, 60 μm or less or 50 μm or less in order to demonstrate the advantageous effects thereof. In the case of a thickness of 50 μm or less, it becomes easy to form the adhesive resin layer between the substrate film and the absorbing film by sandwich lamination, thereby making this preferable. Since the thickness of an adhesive resin layer formed by sandwich lamination is normally about 10 μm to 15 μm , the adhesive resin layer used in the present invention can be said to be comparatively thick.

[0045] The adhesive resin layer can contain, for example, a polyolefin-based resin, and the polyolefin-based resin is particularly preferably low-density polyethylene (LDPE).

[0046] The adhesive resin layer may be formed by extruding a molten resin to serve as the adhesive resin layer between the absorbing film and the substrate film followed by subjecting to sandwich lamination to adhere the molten resin there between.

<Absorbing film>

[0047] The absorbing film comprises an absorbing layer containing an inorganic absorbent and a thermoplastic resin. The absorbing film preferably comprises a skin layer containing a thermoplastic resin on at least one side of the absorbing layer for the purpose of adjusting absorption rate and surface roughness of the absorbing layer. More preferably, the absorbing film has an outer skin layer located on the side of the substrate film, an absorbing layer and an inner skin layer in that order. In this case, the inner skin layer preferably has heat sealability with the cover. Namely, the inner skin layer may compose the outermost layer of the laminate for a blister pack on the opposite side from the substrate film or substrate layer.

[0048] The absorbing layer, outer skin layer and inner skin layer comprise thermoplastic resins, and examples of these resins include polyolefin-based resins, saturated or unsaturated polyester, polyvinyl chloride (PVC), polystyrene, polycarbonate, polyamide and mixtures thereof, with polyolefin-based resins being preferable.

[0049] Since the organic layer contains an inorganic absorbent, it is able to absorb at least one of a liquid and gas. Examples of absorption targets particularly include water and organic and inorganic gases such as carbon dioxide, ammonia, hydrogen sulfide, oxygen, chlorine and hydrogen chloride. The inorganic absorbent may be contained in the outer skin layer and/or inner skin layer.

[0050] Examples of inorganic absorbents include chemical absorbents such as calcium oxide, calcium chloride, calcium sulfate, magnesium sulfate, sodium sulfate, calcium carbonate, magnesium oxide, barium oxide, diphosphorus pentoxide, magnesium perchlorate, potassium permanganate, sodium permanganate or sodium thiosulfate, and physical absorbents such as alumina, aluminum oxide, magnesium silicate, quicklime, silica gel or inorganic molecular sieves. There are no particular limitations on the inorganic molecular sieves, and examples thereof include aluminosilicate minerals, clay, porous glass, microporous activated carbon, zeolite, activated carbon and compounds having an opening structure that allows diffusion of water and other small molecules, and these compounds can be used alone or by combining a plurality thereof.

[0051] In addition, other examples of inorganic absorbents may be oxygen scavengers including iron-based oxygen absorbents such as iron powder (such as reduced iron powder, atomized iron powder or activated iron powder), ferrous oxide and ferrous salt; metal halides (such as sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium bromide, potassium iodide, calcium chloride, magnesium chloride and barium chloride); oxygen-deficient cerium oxide; sulfites; bisulfites; and dithionite salts.

[0052] Among these, zeolite is preferable for the inorganic absorbent. Examples of zeolite that can be used include natural zeolite, artificial zeolite and synthetic zeolite. Zeolite is a porous, granular substance used to separate substances according to differences in molecular size, has a structure consisting of uniform pores, and since it has the action of a type of sieve by absorbing small molecules that enter the cavities of those pores, is capable of absorbing water (including steam and water vapor) and organic gases. An example of synthetic zeolite is a molecular sieve (UNION SHOWA K.K.), and among these, molecular sieves having a pore diameter (absorption opening) of 0.3 nm to 1 nm in particular can be used. For examples, molecular sieves having a pore diameter of 0.3 nm, 0.4 nm, 0.5 nm or 1 nm can be respectively used as molecular sieve 3A, molecular sieve 4A, molecular sieve 5A and molecular sieve 13X.

[0053] Although there are no particular limitations on the average particle diameter (particle diameter having an integrated value of 50% in a particle size distribution determined by laser diffraction scattering) of the inorganic absorbent, the volume-based median diameter (d_{50}), for example, may be 100 nm or more, 500 nm or more, 1 μm or more or 5 μm or more, and 100 μm or less, 50 μm or less, 30 μm or less or 15 μm or less. In the present invention, different types of the aforementioned inorganic absorbent can be used as is appropriate according to such factors as the properties of the absorbed substance and contents, surface roughness of the absorbing film or target absorption rate.

[0054] From the viewpoint of absorption capacity, the inorganic absorbent can be contained in the absorbing layer within the range of 5% by weight or more, 10% by weight or more, 20% by weight or more, 30% by weight or more, 40% by weight or more or 50% by weight or more based on the weight of the absorbing layer, and from the viewpoint of dispersibility in the thermoplastic resin and moldability, can be contained in the absorbing layer within the range of 90% by weight or less, 80% by weight or less, 70% by weight or less or 60% by weight or less.

[0055] In addition, the inorganic absorbent can be contained at 5% by volume or more, 10% by volume or more, 20% by volume or more or 30% by volume or more and 70% by volume or less, 65% by volume or less, 60% by volume or less, 55% by volume or less or 50% by volume or less.

[0056] Furthermore, in the case of calculating the volume percentage of inorganic absorbent contained in a layer and the specific gravity of the inorganic absorbent is uncertain, after having first determined the specific gravity of that layer by measuring, the volume percentage of the inorganic absorbent may then be determined from the weights at which the inorganic absorbent and thermoplastic resin have been added and the specific gravity of the thermoplastic resin. For example, in the case of a layer having specific gravity of 1.1 g/cm³ that has been formed using 50 g of inorganic absorbent and 50 g of thermoplastic resin having specific gravity of 0.9 g/cm³, the inorganic absorbent contained in that layer can be calculated to have a specific gravity of 1.41 g/cm³ and can be said to be present in that layer at 38.9% by volume.

[0057] Although the inorganic absorbent may be contained in the inner skin layer and/or outer skin layer, the content of inorganic absorbent in the outer skin layer in consideration of such factors as the formability of these layers or ease of lamination with other layers is preferably 10% by volume or less, 7% by volume or less or 5% by volume or less, while the content of inorganic absorbent in the inner skin layer is preferably 40% by weight or less, 30% by volume or less, 28.8% by volume or less, 20% by volume or less, 10% by volume or less, 7% by volume or less or 5% by volume or less.

[0058] The thickness of the absorbing film is, for example, 300 μm or less, 200 μm or less, 150 μm or less or 130 μm or less, and 30 μm or more, 40 μm or more or 50 μm or more. A thickness of 150 μm or less is particularly preferable since ease of pushing through the blisters is favorable.

[0059] The thickness of the absorbing layer is, for example, 200 μm or less, 150 μm or less or 100 μm or less, and 20 μm or more, 30 μm or more or 40 μm or more.

[0060] The thickness of the inner skin layer and outer skin layer is, for example, 30 μm or less, 20 μm or less or 15 μm or less, and 5 μm or more, 8 μm or more or 10 μm or more.

[0061] An absorbing film having a single absorbing layer can be formed by forming with the inorganic absorbent and thermoplastic resin by inflation molding, T-die molding, calendering, casting, press molding, extrusion molding or injection molding.

[0062] An absorbing film comprising an outer skin layer, absorbing layer and inner skin layer can be produced by multilayer inflation process. This method consists of simultaneously extruding a plurality of resins into the shape of a tube with a plurality of extruding machines and inflating the tubes by blowing air inside to produce a multilayer film. An absorbing film can be obtained by co-extruding and molding the absorbing layer and skin layers in this manner.

[0063] Prior to producing the absorbing film by inflation process, a resin composition (pellets) for the absorption layer is preferably prepared by processing the thermoplastic resin and inorganic absorbent into pellets after heating and kneading with a twin screw kneader. Moreover, the content of the inorganic absorbent may be adjusted by diluting by dry blending the aforementioned pellets with pellets of the thermoplastic resin. The absorbing film is then produced by carrying out multilayer film deposition by multilayer inflation process using pellets for the absorbing layer and pellets of the thermoplastic resin for the skin layers. After having produced the absorbing layer by inflation process, the separately produced skin layers may be laminated, for example by thermocompression bonding and the like, to obtain the absorbing film.

[0064] In the case of producing an absorbing film having a single absorbing layer by T-die process, a film can be formed by first preparing pellets containing the inorganic absorbent and thermoplastic resin in advance. At this time, an absorbing film containing an absorbing layer and skin layers may be obtained by co-extruding the skin layers on one or both sides of the absorbing layer.

[0065] The absorbing layer and skin layers are respectively formed into the shape of a film or sheet by inflation process, T-die process, calendering, casting, pressing, extrusion processor injection process followed by laminating the layers using a known method to obtain an absorbing film.

[0066] In the case of forming the absorbing layer and skin layers by co-extruding by multilayer T-die process or multilayer inflation process, surface roughness attributable to the absorbing layer in particular is easily reflected in the surface of the absorbing film since the skin layers are adhered to the absorbing layer in a molten state. Thus, the present invention is particularly advantageous in the case of using an absorbing film formed by co-extrusion since the present invention alleviates surface roughness of the absorbing film by providing an adhesive resin layer.

<Other>

[0067] In addition to the aforementioned layers, the laminate for a blister package of the present invention may also further have a printing layer, an anchor coat layer for enhancing adhesion between two layers or a primer layer and the like between any two arbitrary layers.

<<Blister package and Blister packaging product>>

[0068] The blister package of the present invention has the aforementioned laminate for a blister package and a cover. The laminate for a blister package and the cover are at least partially adhered. After having molded a pocket for containing contents such as tablets in the laminate for a blister package, the contents can be contained in the pocket followed by adhering the cover to produce a blister packaging product in which the contents are contained in the pocket of the blister package.

<Contents>

[0069] There are no particular limitations on the contents of the blister package of the present invention provided it is a substance that can be deteriorated by contact with the outside air, and examples thereof include drugs, foods, cosmetics,

medical devices and electronic components. In addition, examples of contents include detergents and agricultural chemicals in addition to prescription drugs.

<Cover>

[0070] The cover comprises a heat seal layer and an aluminum layer. A thermoplastic resin able to be used for the aforementioned skin layers can also be used for the heat seal layer, and polypropylene can be used preferably. Corresponding resins can be suitably selected for the heat seal layer of the cover and layer of the laminate for a blister package that contacts the cover from the viewpoint of enhancing adhesion.

[0071] An aluminum layer similar to the aluminum layer previously described with respect to the substrate film can be used for the aluminum layer of the cover. The cover is preferably of a form in which a heat seal layer in the form of polypropylene is coated onto aluminum foil.

[0072] The cover can also be of a form in which an easy peeling resin such as a polyolefin-based polymer alloy is coated onto aluminum foil, or a form in which an easy peeling film is laminated thereon. In this case, contents can be removed easily since the blister package and cover are made to separate at the adhesive interface.

[0073] FIG. 1 is a schematic view of a blister packaging product A. Here, a cover 40 is adhered to a laminate for a blister package B obtained by laminating an adhesive resin layer 20 and an absorbing film 30 onto a substrate film 10 in that order, and contents 100 are enclosed in a dome-shaped pocket of the laminate B.

[0074] FIG. 2 is a schematic view of the layer structure of the blister packaging product A of the present invention. This drawing shows an end of the blister packaging product A where the pocket is not formed, and the cover 40 is adhered to the laminate for a blister package B obtained by laminating the substrate film 10, comprising a substrate layer 11, an aluminum layer 12 and a reinforcing layer 13, the adhesive resin layer 20 and the absorbing film 30 in that order. The absorbing film 30 is composed of an outer skin layer 31, a second absorbing layer 32 and an inner skin layer 33, and the cover 40 is composed of a heat seal layer 41 and an aluminum layer 42.

[Examples]

<<Production of Laminate for Blister package>>

<Production of Substrate Film>

[0075] A reinforcing layer in the form of polyethylene terephthalate having a thickness of 12 μm (Lumirror 12S10, TORAY INDUSTRIES INC.) was laminated onto a laminate composed of a substrate layer in the form of a Nylon (Ny) film having a thickness of 25 μm and an aluminum layer in the form of aluminum (Al) foil having a thickness of 40 μm (AL/AL Substrate, UACJ FOIL CORP.) using a dry laminator (INVEX Pilot Coater, TECHNO SMART CORP.) to obtain a substrate film. Here, a polyurethane-based adhesive comprising a main agent (Takelac® XA1151, MITSUI CHEMICALS, INC.) and a curing agent (Takenate® A12, MITSUI CHEMICALS, INC.) was used for the adhesive for dry lamination, and an adhesive layer having a thickness of 5 μm was formed at a feeding speed of 10 m/min.

<Production of Absorbing film>

[0076] Inorganic absorbent in the form of zeolite (Molecular Sieve 4A, UNION SHOWA K.K.) and pellets of a thermoplastic resin in the form of LDPE (Petrocene 202, TORAY INDUSTRIES INC.) were kneaded and pelletized using a twin screw extruder (PCM70, IKEGAI CORP.) to obtain pellets containing 47% by weight of zeolite content for the absorbing layer.

[0077] Pellets of LLDPE (Evolue SP2520, PRIME POLYMER CO., LTD.) were prepared for use as the resin for the inner skin layer and outer skin layer, and these pellets were subjected to co-extrusion process with the aforementioned pellets for the absorbing layer by air-cooled inflation process at a temperature of 170°C and feeding speed of 10 m/min to obtain an absorbing film. Here, a three-layer inflation machine (TUL-600R, PLACO CO., LTD.) was used. In addition, the thickness of the absorption layer was made to be 90 μm and the thicknesses of the inner skin layer and outer skin layer were made to be 20 μm .

<Adhesion of Substrate Film and Absorbing film by Adhesive Resin Layer>

* Laminate of Comparative Example 1

[0078] The reinforcing layer of the substrate film and the outer skin layer of the absorbing film were adhered by dry lamination. Here, an adhesive layer having a thickness of 5 μm was formed using a dry laminator (INVEX Pilot Coater,

TECHNO SMART CORP.) and a polyurethane-based adhesive comprising a main agent (Takelac® XA1151, MITSUI CHEMICALS, INC.) and a curing agent (Takenate® A12, MITSUI CHEMICALS, INC.) were used at a feeding speed of 10 m/min to obtain the laminate of Comparative Example 1.

* Laminates of Comparative Examples 2 and 3 and Examples 1 to 3

[0079] Laminates of Comparative Examples 2 and 3 and Examples 1 to 3 were obtained by bonding the reinforcing layer of the substrate film and the outer skin layer of the absorbing film by sandwich lamination while changing the thickness of the adhesive resin layer. Here, LDPE for adhesive resin (Suntec-LD L1850K, ASAHI KASEI CHEMICALS CORP.) was melted at 300°C and extruded using a sandwich laminator (TP45.45 P46010, PLACO CO., LTD.) to obtain laminates at a feeding speed of 30 m/min to 45 m/min. Furthermore, prior to adhering the respective layers, an anchor coating agent (main agent: Takelac® XA1151, MITSUI CHEMICALS, INC., curing agent: Takenate® A12, MITSUI CHEMICALS, INC.) was coated onto the reinforcing layer of the substrate film at a thickness of 1 μm.

<<Evaluation>>

[0080] A pocket for containing contents was formed in the laminates obtained in this manner with a blister molding machine to evaluate the incidence of molding defects.

[0081] More specifically, pockets having a depth of 5.75 mm were molded in the aforementioned laminates at room temperature. A high-speed hydraulic press (HYP505H) manufactured by JAPAN AUTOMATIC MACHINE CO., LTD. was used for the molding machine. The plug material consisted of ultra-high molecular weight polyethylene resin having a viscosity average molecular weight of 5.5 million (New Light®, SAXIN CORP.), the plug diameter was made to be 13 mm, and the molding speed was made to be 200 mm/s. This test was repeated ten times, and those laminates in which cracks, scratches or other visual defects did not occur in the molded pocket to a degree that could be determined with the naked eye were evaluated as acceptable and the number of acceptable laminates was investigated.

[0082] The results are shown in the table below.

[Table 1]

	Thickness of Adhesive Resin Layer	No. of Acceptable Laminates	Percentage of Acceptable Laminates
Comp. Example 1	5 μm	2/10	20%
Comp. Example 2	15 μm	4/10	40%
Comp. Example 3	20 μm	5/10	50%
Example 1	25 μm	8/10	80%
Example 2	30 μm	8/10	80%
Example 3	40 μm	10/10	100%

[0083] As is clear from these results, it was determined that the incidence of molding defects decreases as the thickness of the adhesive resin layer increases, and if an adhesive resin layer is formed at a thickness of 40 μm, molding defects no longer occur even if the pocket is molded at a depth of 5.75 mm.

INDUSTRIAL APPLICABILITY

[0084] A laminate for a blister package that uses the absorbing layer of the present invention allows the molding of a deep pocket therein, and a blister package using that laminate makes it possible to store comparatively large contents in a stable state (by inhibiting deterioration) over a long period of time.

BRIEF DESCRIPTION OF THE REFERENCE SYMBOLS

[0085]

- 10 Substrate film
- 11 Substrate layer

- 12 Aluminum layer
- 13 Reinforcing layer
- 20 Adhesive resin layer
- 30 Absorbing film
- 5 31 Outer skin layer
- 32 Absorbing layer
- 33 Inner skin layer
- 40 Cover
- 41 Heat seal layer
- 10 42 Aluminum layer
- 100 Contents
- A Blister packaging product
- B Laminate for blister package

Claims

1. A laminate (B) for a blister package, comprising a substrate film (10), an adhesive resin layer (20), and an absorbing film (30) in that order; wherein,
 - the adhesive resin layer (20) has a thickness of 25 μm to 100 μm , and
 - the absorbing film (30) comprises an absorbing layer (32) containing a thermoplastic resin and an inorganic absorbent.
2. The laminate (B) according to claim 1, wherein the adhesive resin layer (20) comprises a polyolefin-based resin.
3. The laminate (B) according to claim 1 or 2, wherein the adhesive resin layer (20) is formed through sandwich lamination.
4. The laminate (B) according to any one of claims 1 to 3, wherein the adhesive resin layer (20) has a thickness of 25 μm to 50 μm .
5. The laminate (B) according to any one of claims 1 to 4, wherein the absorbing film (30) comprises an outer skin layer (31) on the side of the adhesive resin layer (20), the absorbing layer (32), and an inner skin layer (33).
6. The laminate (B) according to claim 5, wherein the outer skin layer (31), the absorbing film (30) and the inner skin layer (33) of the absorbing film (30) are formed through co-extrusion.
7. The laminate (B) for a blister package according to claim 1, composed of the following layers:
 - a substrate layer (11) having a thickness of 12 μm to 25 μm and comprising a resin selected from the group consisting of a polyolefin-based resin, polyvinyl chloride, polyvinylidene chloride, polychlorotrifluoroethylene, polytetrafluoroethylene, saturated or unsaturated polyester, polyamide and polyacrylonitrile;
 - an aluminum layer (42) having a thickness of 7 μm to 45 μm ;
 - a reinforcing layer (13) having a thickness of 8 μm to 60 μm and comprising a resin selected from the group consisting of polyvinyl chloride, saturated or unsaturated polyester and polyamide;
 - an adhesive resin layer (20) having a thickness of 25 μm to 50 μm , comprising a polyolefin-based resin, and formed by sandwich lamination;
 - an outer skin layer (31) having a thickness of 10 μm to 30 μm and comprising a polyolefin-based resin;
 - an absorbing layer (32) having a thickness of 10 μm to 200 μm and comprising a polyolefin-based resin and 5 % by volume to 70 % by volume of zeolite; and
 - an inner skin layer (33) having a thickness of 10 μm to 30 μm and comprising a polyolefin-based resin.
8. A blister package comprising the laminate (B) according to any one of claims 1 to 7 and a cover (40) having a heat seal layer (41) and an aluminum layer (42), wherein the laminate (B) and the cover (40) are at least partially adhered, and the laminate (B) has a pocket so that contents (100) are able to be contained between the laminate (B) and the cover (40).

9. A blister packaging product (A) having the blister package according to claim 8 and having contents (100) contained in the pocket.

10. A method for producing a laminate (B) for a blister package, comprising the following:

providing a substrate film (10);
providing an absorbing film (30) comprising an absorbing layer (32) containing a thermoplastic resin and an inorganic absorbent; and,
forming an adhesive resin layer (20) having a thickness of 25 μm to 100 μm between the absorbing film (30) and the substrate film (10), on the absorbing film (30) or on the substrate film (10), to adhere the absorbing film and the substrate film (10).

11. The method for producing a laminate (B) for a blister package according to claim 10, wherein

the substrate film (10) comprises a substrate layer (11), aluminum layer (42) and reinforcing layer (13) in that order, the absorbing film (30) comprises an outer skin layer (31) and an inner skin layer (33) that sandwich the absorbing layer (32), and the adhesive resin layer (20) is formed between the outer skin layer (31) of the absorbing film (30) and the reinforcing layer (13) of the substrate film (10), or on the outer skin layer (31) of the absorbing film (30) or on the reinforcing layer (13) of the substrate film (10).

Patentansprüche

1. Laminat (B) für eine Blisterpackung, die einen Substratfilm (10), eine klebende Harzschicht (20) und einen absorbierenden Film (30) in dieser Reihenfolge aufweist, wobei,

die klebende Harzschicht (20) eine Dicke von 25 μm bis 100 μm aufweist und der absorbierende Film (30) eine absorbierende Schicht (32) aufweist, die ein thermoplastisches Harz und ein anorganisches Absorptionsmittel enthält.

2. Laminat (B) nach Anspruch 1, wobei die klebende Harzschicht (20) ein auf Polyvinylchlorid basierendes Harz aufweist.

3. Laminat (B) nach Anspruch 1 oder 2, wobei die klebende Harzschicht (20) durch eine Sandwichlaminierung gebildet worden ist.

4. Laminat (B) nach einem der Ansprüche 1 bis 3, wobei die klebende Harzschicht (20) eine Dicke von 25 μm bis 50 μm aufweist.

5. Laminat (B) nach einem der Ansprüche 1 bis 4, wobei der absorbierende Film (30) eine äußere Hautschicht (31) auf der Seite der klebenden Harzschicht (20), die absorbierende Schicht (32) und eine innere Hautschicht (33) aufweist.

6. Laminat (B) nach Anspruch 5, wobei die äußere Hautschicht (31), die absorbierende Schicht (30) und die innere Hautschicht (33) der absorbierenden Schicht (30) durch eine Coextrusion gebildet worden sind.

7. Laminat (B) für eine Blisterverpackung nach einem der vorhergehenden Ansprüche, die aus folgenden Schichten gebildet worden ist:

eine Substratschicht (11), die eine Dicke von 12 μm bis 25 μm und die ein Harz aufweist, das aus der Gruppe ausgewählt worden ist, die ein auf Polyvinylchlorid basierendes Harz, ein Polyvinylchlorid, ein Polyvinylidenchlorid, ein Polychlortrifluorethylen, ein Polytetrafluorethylen, ein gesättigtes oder ungesättigtes Polyester, ein Polyamid und ein Polyacrylnitril umfasst,

eine Aluminiumschicht (42), die eine Dicke von 7 μm bis 45 μm aufweist,

eine verstärkende Schicht (13), die eine Dicke von 8 μm bis 60 μm und die ein Harz aufweist, das aus der Gruppe ausgewählt worden ist, die ein Polyvinylchlorid, ein gesättigtes oder ungesättigtes Polyester und ein Polyamid umfasst,

eine klebende Harzschicht (20), die eine Dicke von 25 µm bis 50 µm und ein auf Polyolefin basierendes Harz aufweist und die durch eine Sandwichlaminierung gebildet worden ist,
 eine äußere Hautschicht (31), die eine Dicke von 10 µm bis 30 µm und ein auf Polyolefin basierendes Harz aufweist,
 5 eine absorbierende Schicht (32), die eine Dicke von 10 µm bis 200 µm und die ein auf Polyolefin basierendes Harz und 5 Volumenprozent bis 70 Volumenprozent Zeolith aufweist, und
 eine innere Hautschicht (33), die eine Dicke von 10 µm bis 30 µm und ein auf Polyolefin basierendes Harz aufweist.

8. Blisterpackung, die das Laminat (B) nach einem der Ansprüche 1 bis 7 und eine Abdeckung (40) mit einer Heißsiegelschicht (41) und einer Aluminiumschicht (42) aufweist, wobei das Laminat (B) und die Abdeckung (40) zumindest teilweise verklebt sind, und das Laminat (B) eine Tasche so aufweist, dass ein Inhalt (100) zwischen dem Laminat (B) und der Abdeckung (40) enthalten sein kann.

9. Blisterverpackungsprodukt (A), das die Blisterverpackung nach Anspruch 8 und einen Inhalt (100) aufweist, der in der Tasche enthalten ist.

10. Verfahren zur Herstellung eines Laminats (B) für eine Blisterpackung, welches das Folgende umfasst:

ein Bereitstellen eines Substratfilms (10),
 ein Bereitstellen eines absorbierenden Films (30), das eine absorbierende Schicht (32) aufweist, die ein thermoplastisches Harz und ein anorganisches Absorptionsmittel enthält, und,
 ein Ausbilden einer klebenden Harzschicht (20), die eine Dicke von 25 µm bis 100 µm zwischen dem absorbierenden Film (30) und dem Substratfilm (10) aufweist, auf dem absorbierenden Film (30) oder auf dem Substratfilm (10), um den absorbierenden Film und den Substratfilm (10) anzuhaften.

11. Verfahren zur Herstellung eines Laminats (B) für eine Blisterpackung nach Anspruch 10, wobei

der Substratfilm (10) eine Substratschicht (11), eine Aluminiumschicht (42) und eine verstärkende Schicht (13) in dieser Reihenfolge aufweist,
 der absorbierende Film (30) eine äußere Hautschicht (31) und eine innere Hautschicht (33) aufweist, die die absorbierende Schicht (32) zwischen sich aufnehmen, und
 die klebende Harzschicht (20) zwischen der äußeren Hautschicht (31) des absorbierenden Films (30) und der verstärkenden Schicht (13) des Substratfilms (10) oder auf der äußeren Hautschicht (31) des absorbierenden Films (30) oder auf der verstärkenden Schicht (13) des Substratfilms (10) gebildet worden ist.

Revendications

1. Stratifié (B) pour une plaquette thermoformée, comprenant un film de substrat (10), une couche de résine adhésive (20), et un film absorbant (30) dans cet ordre ; dans lequel,

la couche de résine adhésive (20) a une épaisseur de 25 µm à 100 µm, et
 le film absorbant (30) comprend une couche absorbante (32) contenant une résine thermoplastique et un absorbant inorganique.

2. Stratifié (B) selon la revendication 1, dans lequel la couche de résine adhésive (20) comprend une résine à base de polyoléfine.

3. Stratifié (B) selon la revendication 1 ou 2, dans lequel la couche de résine adhésive (20) est formée par stratification sandwich.

4. Stratifié (B) selon l'une quelconque des revendications 1 à 3, dans lequel la couche de résine adhésive (20) a une épaisseur de 25 µm à 50 µm.

5. Stratifié (B) selon l'une quelconque des revendications 1 à 4, dans lequel le film absorbant (30) comprend une couche d'enveloppe externe (31) du côté de la couche de résine adhésive (20), la couche absorbante (32), et une couche d'enveloppe interne (33).

6. Stratifié (B) selon la revendication 5, dans lequel la couche d'enveloppe externe (31), le film absorbant (30) et la couche d'enveloppe interne (33) du film absorbant (30) sont formés par co-extrusion.

7. Stratifié (B) pour une plaquette thermoformée selon la revendication 1, composé des couches suivantes :

une couche de substrat (11) ayant une épaisseur de 12 μm à 25 μm et comprenant une résine choisie dans le groupe constitué d'une résine à base de polyoléfine, de chlorure de polyvinyle, de chlorure de polyvinylidène, de polychlorotrifluoroéthylène, de polytétrafluoroéthylène, de polyester saturé ou insaturé, de polyamide et de polyacrylonitrile ;

une couche d'aluminium (42) ayant une épaisseur de 7 μm à 45 μm ;

une couche de renforcement (13) ayant une épaisseur de 8 μm à 60 μm et comprenant une résine choisie dans le groupe constitué de chlorure de polyvinyle, de polyester saturé ou insaturé et de polyamide ;

une couche de résine adhésive (20) ayant une épaisseur de 25 μm à 50 μm , comprenant une résine à base de polyoléfine, et formée par stratification sandwich ;

une couche d'enveloppe externe (31) ayant une épaisseur de 10 μm à 30 μm et comprenant une résine à base de polyoléfine ;

une couche absorbante (32) ayant une épaisseur de 10 μm à 200 μm et comprenant une résine à base de polyoléfine et 5 % en volume à 70 % en volume de zéolite ; et

une couche d'enveloppe interne (33) ayant une épaisseur de 10 μm à 30 μm et comprenant une résine à base de polyoléfine.

8. Plaquette thermoformée comprenant le stratifié (B) selon l'une quelconque des revendications 1 à 7 et un revêtement (40) ayant une couche thermoscellable (41) et une couche d'aluminium (42), dans laquelle le stratifié (B) et le revêtement (40) sont au moins partiellement collés, et le stratifié (B) comporte une poche de telle sorte que le contenu (100) peut être contenu entre le stratifié (B) et le revêtement (40).

9. Produit de plaquette thermoformée (A) ayant la plaquette thermoformée selon la revendication 8 et ayant le contenu (100) contenu dans la poche.

10. Procédé de production d'un stratifié (B) pour une plaquette thermoformée, comprenant les étapes suivantes :

fourniture d'un film de substrat (10) ;

fourniture d'un film absorbant (30) comprenant une couche absorbante (32) contenant une résine thermoplastique et un absorbant inorganique ; et,

formation d'une couche de résine adhésive (20) ayant une épaisseur de 25 μm à 100 μm entre le film absorbant (30) et le film de substrat (10), sur le film absorbant (30) ou sur le film de substrat (10), pour coller le film absorbant et le film de substrat (10).

11. Procédé de production d'un stratifié (B) pour une plaquette thermoformée selon la revendication 10,

dans lequel

le film de substrat (10) comprend une couche de substrat (11), une couche d'aluminium (42) et une couche de renforcement (13) dans cet ordre,

le film absorbant (30) comprend une couche d'enveloppe externe (31) et une couche d'enveloppe interne (33) qui prennent en sandwich la couche absorbante (32), et

la couche de résine adhésive (20) est formée entre la couche d'enveloppe externe (31) du film absorbant (30) et la couche de renforcement (13) du film de substrat (10), ou sur la couche d'enveloppe externe (31) du film absorbant (30) ou sur la couche de renforcement (13) du film de substrat (10).

FIG. 1

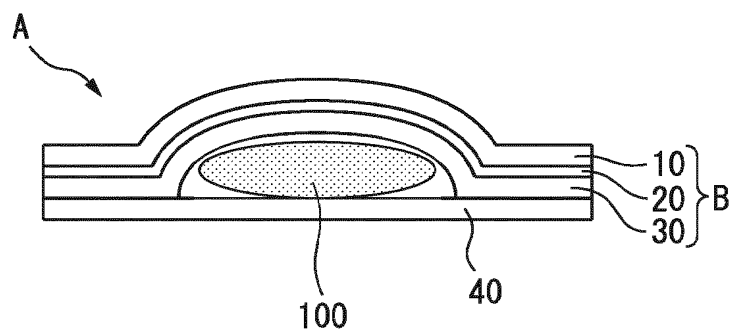
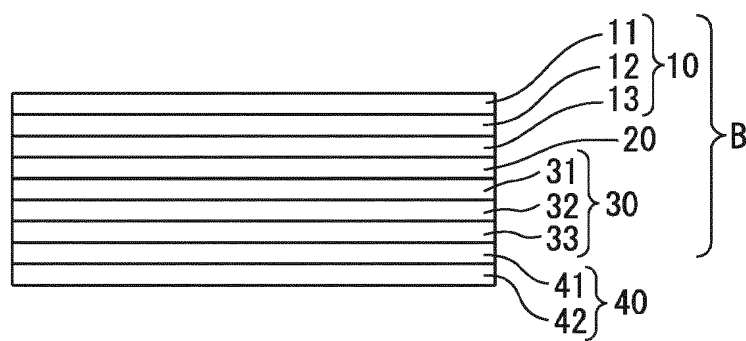


FIG. 2



REFERENCES CITED IN THE DESCRIPTION

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(54) **MULTILAYER CONTAINER FOR MEDICAL USE AND METHOD FOR PRODUCING
MULTILAYER CONTAINER FOR MEDICAL USE**

(57) Provided is a medical multilayer vessel with gas barrier performance and transparency suitable enough for medical packaging materials which are subject to heat sterilization. The medical multilayer vessel containing layer (X) contains a water vapor barrier polymer that contains polyolefin resin(s), and a gas barrier layer (Y) composed of a polyamide resin composition (P), the polyamide resin composition (P) contains 10 to 45% by mass

of polyamide resin (A) that contains a diamine unit with a content of a structural unit derived from xylylenediamine of 70 mol% or more, and a dicarboxylic acid unit with a content of a structural unit derived from a straight-chain aliphatic dicarboxylic acid having 6 to 18 carbon atoms of 70 mol% or more; and, 90 to 55% by mass of a poly(hexamethylene isophthalamide)/poly(hexamethylene terephthalamide) copolymer (B).

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Description

TECHNICAL FIELD

5 **[0001]** This invention relates to a multilayer vessel, and in particular to a multilayer vessel for medical packaging (medical multilayer vessel), and a method for manufacturing the medical multilayer vessel.

BACKGROUND ART

10 **[0002]** Glass vessels in the forms of ampule, vial and prefilled syringe have been used for storing chemicals filled therein in a sealed manner. These glass vessels, however, suffer from that they generate a fine vitreous substance called "flakes", and that they easily fractures upon impact caused by dropping or the like. Another disadvantage of the glass vessels is that the vessels *per se* are heavy due to a relatively large specific gravity of glass.

15 **[0003]** In contrast, plastic is lighter than glass, and some of them even excels in impact resistance, heat resistance and transparency, depending on their materials. Plastic vessels have therefore been investigated as a substitute for the glass vessels. For example, Patent Literature 1 discloses a medical vessel made of a polyester resin. Also cycloolefin polymer (occasionally be referred to as "COP", hereinafter) has widely been used as a substitute for glass materials in the field of medical vessel, by virtue of its high impact resistance, heat resistance and transparency.

20 **[0004]** Many of the plastic vessels are, however, inferior to the glass vessels in terms of gas barrier performance, which is desired to be improved. With the aim of improving the gas barrier performance of plastic vessels, there has been investigated a multilayer vessel having a gas barrier layer as an intermediate layer. For example, Patent Literature 2 discloses a prefilled syringe whose innermost layer and outermost layer are made of a polyolefin resin, and whose intermediate layer is made of a resin with a high barrier performance.

25 **[0005]** Polymetaxylylene adipamide (occasionally be referred to as "N-MXD6", hereinafter) has been known as a thermoplastic resin with a high oxygen barrier performance (Patent Literatures 3 to 6). N-MXD6, however, very quickly crystallizes at 250 to 320°C, which is a temperature range for heat forming of the polyolefin resin such as COP. Hence, in some case when forming a multilayer vessel that uses N-MXD6 for the gas barrier layer and uses COP for the innermost layer and the outermost layer, the N-MXD6 layer would cause breakage, non-uniform thickness or blushing, resulting in degraded performances such as gas barrier performance and transparency, or deformation. It would also cause blushing after heat sterilization, damaging the transparency.

30 **[0006]** Known methods for suppressing N-MXD6 from causing blushing includes a method of adding a specific metal salt of aliphatic acid as a blushing inhibitor, and a method of adding a specific diamide compound or a diester compound. These methods for suppressing blushing with the aid of additives are known to be effective for a single-layered film which is brought into direct contact with water, or for an application associated with stretching, such as a multilayer stretched bottle with a layer structure of PET/N-MXD6/PET using polyethylene terephthalate (occasionally be referred to as "PET", hereinafter) . However, as for a multilayer vessel with a layer structure of COP/N-MXD6/COP, an effect of suppressing blushing after heat sterilization is not satisfactory. Other known methods include a method of adding a nucleation agent for crystallization to N-MXD6; and a method of blending a crystalline polyamide resin such as nylon 6, which acts as a nucleation agent for crystallization, with N-MXD6 in the process of heat sterilization. Again with these methods, obtainable is only an unsatisfactory effect of suppressing blushing after heat sterilization, for the multilayer vessel with a layer structure of COP/N-MXD6/COP.

CITATION LIST

45 PATENT LITERATURE

[0007]

50 [Patent Literature 1] JP-A-08-127641
 [Patent Literature 2] JP-A-2004-229750
 [Patent Literature 3] JP-A-2012-201412
 [Patent Literature 4] JP-A-2012-30556
 [Patent Literature 5] JP-A-2014-69829
 [Patent Literature 6] JP-A-2014-68767

55

SUMMARY OF THE INVENTION

TECHNICAL PROBLEM

5 **[0008]** This invention is aimed at solving the above-described problems, and is to provide a medical multilayer vessel with gas barrier performance and transparency suitable enough for medical packaging materials which are subject to heat sterilization.

SOLUTION TO PROBLEM

10

[0009] The present inventors have extensively studied the medical multilayer vessel which excels both in gas barrier performance and transparency after heat sterilization, and found that excellent gas barrier performance and transparency could be achieved even after heat sterilization, by using a specific polyamide resin composition for the gas barrier layer. The finding led us to complete this invention.

15

[0010] That is, the present invention relates to a medical multilayer vessel. Specifically, the present invention relates to the following <1>, preferably <2>~<12>.

20

<1> A medical multilayer vessel comprising a layer (X) containing, as a major ingredient, a water vapor barrier polymer that contains at least one species or more of polyolefin resin(s), and a gas barrier layer (Y) composed of a polyamide resin composition (P),
the polyamide resin composition (P) comprising:

25

10 to 45% by mass of polyamide resin (A) that contains a diamine unit with a content of a structural unit derived from xylylenediamine of 70 mol% or more, and a dicarboxylic acid unit with a content of a structural unit derived from a straight-chain aliphatic dicarboxylic acid having 6 to 18 carbon atoms of 70 mol% or more; and, 90 to 55% by mass of a poly(hexamethylene isophthalamide)/poly(hexamethylene terephthalamide) copolymer (B).

30

<2> The medical multilayer vessel of <1>, wherein the polyolefin resin is at least one or more species selected from the group consisting of cycloolefin polymer, cycloolefin copolymer and polypropylenes.

<3> The medical multilayer vessel of <1>, wherein the polyolefin resin is at least one or more species selected from the group consisting of cycloolefin polymer and cycloolefin copolymer.

35

<4> The medical multilayer vessel of any one of <1> to <3>, wherein the xylylenediamine is metaxylylenediamine, paraxylylenediamine or a mixture of them, and the straight-chain aliphatic dicarboxylic acid is adipic acid, sebacic acid or a mixture of them.

40

<5> The medical multilayer vessel of any one of <1> to <4>, wherein the dicarboxylic acid unit of the polyamide resin (A) contains a structural unit derived from aromatic dicarboxylic acid, and, the molar ratio of the structural unit derived from straight-chain aliphatic dicarboxylic acid and the structural unit derived from aromatic dicarboxylic acid (straight-chain aliphatic dicarboxylic acid/aromatic dicarboxylic acid) is 80/20 to 99/1.

<6> The medical multilayer vessel of <5>, wherein the aromatic dicarboxylic acid contains isophthalic acid.

<7> The medical multilayer vessel of any one of <1> to <3>, wherein the polyamide resin (A) contains: a diamine unit with a content of a structural unit derived from metaxylylenediamine of 90 mol% or more; and a dicarboxylic acid unit with a content of an adipic acid-derived structural unit of 90 to 100 mol% and with a content of an isophthalic acid-derived structural unit of 10 to 0 mol%.

45

<8> The medical multilayer vessel of any one of <1> to <7>, having the layer (X) as each of an inner layer and an outer layer, and having at least one gas barrier layer (Y) as an intermediate layer.

<9> The medical multilayer vessel of any one of <1> to <8>, wherein the gas barrier layer (Y) has a thickness that accounts for 2 to 40% of the total thickness of the multilayer vessel.

50

<10> The medical multilayer vessel of any one of <1> to <9>, being an ampule, vial, vacuum blood collecting tube or prefilled syringe.

<11> The medical multilayer vessel of any one of <1> to <10>, being an injection blow molded article.

<12> A method for manufacturing a medical multilayer vessel, comprising forming the medical multilayer vessel described in any one of <1> to <10> by injection blow molding.

55

ADVANTAGEOUS EFFECTS OF INVENTION

[0011] The medical multilayer vessel of this invention has gas barrier performance and transparency suitable enough for medical packaging materials which are subject to heat sterilization. The medical multilayer vessel can therefore store

the content for a long period, allows the content to be seen through even after heat sterilization, and can be a substitute for glass vessels, with an improved convenience for customers.

DESCRIPTION OF EMBODIMENTS

[0012] This invention will be detailed below. Note that all numerical ranges given in this specification, using "to" preceded and succeeded by numerals, are used to represent the ranges including these numerals respectively as the lower and upper limit values.

[0013] The medical multilayer vessel of this invention (occasionally be referred to as "the multilayer vessel of this invention", hereinafter) has at least: a layer containing, as a major ingredient, a water vapor barrier polymer that contains at least one species or more of polyolefin resin(s), which is more preferably a layer (occasionally be referred to as "water vapor barrier layer", hereinafter) (X) containing, as a major ingredient, a water vapor barrier polymer that contains at least one or more species selected from the group consisting of cycloolefin polymer, cycloolefin copolymer (occasionally be abbreviated as "COC", hereinafter), and polypropylenes (occasionally be abbreviated as "PP", hereinafter); and a gas barrier layer (Y).

[0014] The layer structure of the multilayer vessel of this invention is not specifically limited. There are no special limitations on the number and types of the water vapor barrier layer (X) (may simply be referred to as "layer (X)", hereinafter) and the gas barrier layer (Y) (may simply be referred to as "layer (Y)", hereinafter).

[0015] The medical multilayer vessel of this invention may be composed of at least 3 layers, more preferably 3 to 10 layers, and more preferably 3 to 5 layers.

[0016] The number of layers (X) in the medical multilayer vessel of this invention is preferably 1 to 5, and more preferably 2 to 4. The number of layers (Y) in the multilayer vessel is preferably 1 to 3, and more preferably 1 or 2.

[0017] An exemplary structure may be an X/Y structure of or an Y/X structure, composed of a single layer (X) and a single layer (Y); or a three-layered structure X/Y/X composed of two layers (X) and a single layer (Y). The multilayer vessel of this invention may have therein the layer (X) and the layer (Y) brought into direct contact, or may have an optional layer such as an adhesive layer (AD) composed of an adhesive thermoplastic resin. The multilayer vessel of this invention preferably has a three-layered structure of water vapor barrier layer (X) /gas barrier layer (Y)/water vapor barrier layer (X) arranged in this order from the inner layer towards the outer layer; or a five-layered structure of water vapor barrier layer (X)/adhesive layer (AD)/gas barrier layer (Y)/adhesive layer (AD)/water vapor barrier layer (X) arranged in this order from the inner layer towards the outer layer. Besides them, a variety of thermoplastic resin layers may further be stacked depending on needs.

[0018] The multilayer vessel of this invention preferably has the layers (X) for the inner layer and the outer layer, and has the layer (Y) for at least one of the intermediate layer (s) (X/Y/X structure).

[0019] The inner layer in this context means a layer which resides on the inner side of the layer (Y) which is one intermediate layer out of layers composing the multilayer vessel, and, the outer layer means a layer which resides on the outer side of the layer (Y) which is one intermediate layer out of layers composing the multilayer vessel. The inner layer and the outer layer may be the innermost layer and the outermost layer, respectively, or there may be additional innermost layer and outermost layer. In this invention, at least the innermost layer is the layer (X).

1. Water Vapor Barrier Layer (X)

[0020] The water vapor barrier layer (X) that composes the multilayer vessel of this invention is a layer containing, as a major ingredient, a water vapor barrier polymer that contains at least one species or more of polyolefin resin(s), and is more preferably a layer containing, as a major ingredient, a water vapor barrier polymer that contains at least one or more species selected from the group consisting of COP, COC and PP.

[0021] Now, the phrase stating "containing, as a major ingredient," means that the content of the polyolefin resin (water vapor barrier polymer) in the layer (X) is 70% by mass or more, preferably 80% by mass or more, more preferably 90 to 100% by mass, and even more preferably 95 to 100% by mass. The layer (X) may contain only one species of polyolefin resin, or may contain two or more species. When two or more species of polyolefin resins are contained, the total content falls within the above described ranges.

[0022] Besides the water vapor barrier polymer, the layer (X) may contain additive(s) such as antioxidant, matting agent, weathering stabilizer, UV absorber, crystal nucleating agent, plasticizer, flame retardant and antistatic agent, depending on desired performances without damaging the effects of this invention. The multilayer vessel of this invention may have two or more layers (X), and such two or more layers may have the same composition or different composition.

[0023] The water vapor barrier layer (X) preferably has a thickness of, but not limited to, 20 to 2000 μm from the viewpoint of strength and cost, which is more preferably 50 to 1500 μm . If there are two or more layers (X), the thickness in this context is given by the total thickness.

[0024] It is particularly preferable in this invention that the layer (X) that resides at the innermost of the medical multilayer

vessel, out of all water vapor barrier layers (X), has a minimum thickness of 50 μm or above, more preferably 80 μm or above, even more preferably 100 μm or above, and yet more preferably 150 μm or above. The layer (X) which resides at the innermost preferably has a maximum thickness of 400 μm or below, more preferably 350 μm or below, even more preferably 300 μm or below, and yet more preferably 250 μm or below.

[0025] Meanwhile, the layer (X) that resides at the outermost of the medical multilayer vessel, out of all water vapor barrier layers (X), has a maximum thickness of 100 μm or above, more preferably 400 μm or above, and even more preferably 500 μm or above. The layer (X) which resides at the outermost preferably has a maximum thickness of 1000 μm or below, more preferably 800 μm or below, and even more preferably 700 μm or below.

[0026] The ratio of the thickness of the layers (X) which reside at the outermost and the innermost of the medical multilayer vessel (innermost layer (X) : outermost layer (X)) is preferably 1.0:2.0 to 1.0:4.0, and more preferably 1.0:2.5 to 1.0:3.5.

[0027] The water vapor barrier polymer is the best material since the chemical properties such as heat resistance and light stability, and chemical resistance are features derived from polyolefin resin; meanwhile the physical properties such as mechanical characteristics, melting, fluidity, and dimensional accuracy are features derived from amorphous resin.

Polyolefin Resin

[0028] The polyolefin resin used in this invention is not specifically limited, for which any of known polyolefin resins are employable. The polyolefin resin is specifically exemplified by those described in paragraphs [0101] to [0103] of JP-A-2014-068767, the contents of which are incorporated into this specification.

[0029] The polyolefin resin is preferably COP, COC or polypropylenes (PP). COP and COC are preferable since they have chemical properties such as heat resistance and light stability, are chemical resistance expectable from polyolefin resin; and has physical properties such as mechanical characteristics, melting, fluidity, and dimensional accuracy expectable from amorphous resin. Meanwhile, PP is preferable from the viewpoint of oil resistance.

1-1. Cycloolefin Polymer (COP)

[0030] COP is a polymer obtained typically by ring-opening polymerization of norbornene, followed by hydrogenation. COP is described for example in JP-A-H05-317411, and commercially available as ZEONEX (registered trademark) or ZEONOR (registered trademark) from ZEON Corporation, and as Daikyo Resin CZ (registered trademark) from Daikyo Seiko Ltd.

1-2. Cycloolefin Copolymer (COC)

[0031] COC is typically a copolymer originated from olefins such as norbornene and ethylene; or a copolymer originated from olefins such as tetracyclododecene and ethylene. COC is commercially available as APEL (registered trademark) from Mitsui Chemicals, Inc.

1-3. Polypropylenes

[0032] For PP, any of known polymers such as propylene homopolymer, propylene-ethylene block copolymer, and propylene-ethylene random copolymer are employable. PP is commercially available, for example, as Bormed RB845MO from Borealis AG.

2. Gas Barrier Layer (Y)

[0033] The gas barrier layer (Y) that composes the multilayer vessel of this invention acts to block oxygen from entering the vessel from the outside, and to prevent the content of vessel from degrading through oxidation. From the viewpoint of good gas barrier performance, the gas barrier layer (Y) preferably has an oxygen transmission coefficient in an environment at 23°C with 60% relative humidity (RH) of 1.0 mL $\cdot$ mm/(m²·day·atm) or smaller, and more preferably 0.05 to 0.8 mL $\cdot$ mm/(m²·day·atm). The oxygen transmission coefficient may be measured in accordance with ASTM D3985, typically by using "OX-TRAN (registered trademark) 2/61" (from Mocon Inc.).

[0034] The multilayer vessel of this invention may have two or more gas barrier layers (Y), and such two or more gas barrier layers (Y) may have the same structure or different structures. The thickness of the gas barrier layer (Y) is preferably, but not specifically limited to, 1 to 800 μm from the viewpoint of gas barrier performance and transparency, and is more preferably 100 to 700 μm . If there are two or more layers (Y), the thickness of the layer (Y) in this context is given by the total thickness.

[0035] The thickness of the gas barrier layer (Y) in the multilayer vessel of this invention preferably falls within the

range from 2 to 40% relative to the total thickness of the multilayer vessel, from the viewpoint of gas barrier performance and transparency, which is more preferably 5 to 38%, and even more preferably 10 to 35%. The thickness of the gas barrier layer (Y) in the multilayer vessel may be measured after cutting the vessel, and separating it from the water vapor barrier layer (X).

[0036] The ratio of the thickness of the gas barrier layer (Y), and the layer (X) which resides at the innermost of the multilayer vessel of this invention (layer (Y) : innermost layer (X)) is preferably 0.5:1.5 to 1.5:0.5, and more preferably 0.8:1.2 to 1.2:0.8. The ratio of the thickness of the gas barrier layer (Y), and the layer (X) which resides at the outermost of the multilayer vessel of this invention (layer (Y) : outermost layer (X)) is preferably 1.0:2.0 to 1.0:4.0, and more preferably 1.0:2.5 to 1.0:3.5.

3. Polyamide Resin Composition (P)

[0037] The gas barrier layer (Y) composing the multilayer vessel of this invention is made of a polyamide resin composition (P). The polyamide resin composition (P) contains 10 to 45% by mass of polyamide resin (A) that contains a diamine unit with a content of a structural unit derived from xylylenediamine of 70 mol% or more, and a dicarboxylic acid unit with a content of a structural unit derived from a straight-chain aliphatic dicarboxylic acid having 6 to 18 carbon atoms of 70 mol% or more; and, 90 to 55% by mass of a poly(hexamethylene isophthalamide)/poly(hexamethylene terephthalamide) copolymer (B) (occasionally be abbreviated as "N-6I/6T", and also occasionally be referred to as polyamide resin (B)).

3-1. Polyamide Resin (A)

[0038] The polyamide resin (A) is a xylylene group-containing polyamide, containing a diamine unit with a content of a structural unit derived from xylylenediamine of 70 mol% or more, and a dicarboxylic acid unit with a content of a structural unit derived from a straight-chain aliphatic dicarboxylic acid having 6 to 18 carbon atoms of 70 mol% or more.

<Diamine Unit>

[0039] The diamine unit of the polyamide resin (A) contains 70 mol% or more of the structural unit derived from xylylenediamine. The content of the structural unit derived from xylylenediamine in the diamine unit of the polyamide resin (A) is preferably 80 to 100 mol%, more preferably 90 to 100 mol%, and even more preferably 95 to 100 mol%.

[0040] Xylylenediamine is preferably metaxylylenediamine, paraxylylenediamine, or mixture of them, and more preferably metaxylylenediamine, or mixture of metaxylylenediamine and paraxylylenediamine. From the viewpoint of achieving an excellent gas barrier performance, the content of the structural unit derived from metaxylylenediamine in the diamine unit of the polyamide resin (A) is preferably 70 mol% or more, more preferably 80 to 100 mol%, even more preferably 90 to 100 mol%, and yet more preferably 95 to 100 mol%.

[0041] Diamine compounds capable of composing the diamine unit besides xylylenediamine are exemplified by, but not limited to, aliphatic diamines such as tetramethylenediamine, pentamethylenediamine, 2-methylpentanediamine, hexamethylenediamine, heptamethylenediamine, octamethylenediamine, nonamethylenediamine, decamethylenediamine, dodecamethylenediamine, 2,2,4-trimethyl-hexamethylenediamine, and 2,4,4-trimethyl-hexamethylenediamine; alicyclic diamines such as 1,3-bis(aminomethyl)cyclohexane, 1,4-bis(aminomethyl)cyclohexane, 1,3-diaminocyclohexane, 1,4-diaminocyclohexane, bis(4-aminocyclohexyl)methane, 2,2-bis(4-aminocyclohexyl)propane, bis(aminomethyl)decalin, and bis(aminomethyl)tricyclodecane; and aromatic ring-containing diamines such as bis(4-aminophenyl) ether, paraphenylenediamine, and bis(aminomethyl)naphthalene.

<Dicarboxylic Acid Unit>

[0042] The dicarboxylic acid unit of the polyamide resin (A) contains 70 mol% or more of the structural unit derived from straight-chain aliphatic dicarboxylic acid having 6 to 18 carbon atoms. The content of the structural unit derived from straight-chain aliphatic dicarboxylic acid having 6 to 18 carbon atoms, in the dicarboxylic acid unit of the polyamide resin (A), is preferably 80 mol% to 100 mol%, more preferably 90 mol% to 100 mol%, and even more preferably 90 mol% to 97 mol%.

[0043] The straight-chain aliphatic dicarboxylic acid having 6 to 18 carbon atoms is preferably α,ω -straight-chain aliphatic dicarboxylic acid having 6 to 18 carbon atoms, and is exemplified by adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, 1,10-decanedicarboxylic acid, 1,11-undecanedicarboxylic acid, and 1,12-dodecanedicarboxylic acid. Among them, at least one species selected from adipic acid and sebacic acid is preferable from the viewpoint of achieving an excellent oxygen barrier performance, where adipic acid is more preferable. They may be used independently, or two or more species may be used in combination.

[0044] Dicarboxylic acid components other than the straight-chain aliphatic dicarboxylic acid having 6 to 18 carbon atoms are exemplified by, but not limited to, aliphatic dicarboxylic acids such as oxalic acid, malonic acid, succinic acid and glutaric acid; and aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid and 2,6-naphthalenedicarboxylic acid. They may be used independently, or two or more species may be used in combination.

[0045] From the viewpoint of transparency of the medical multilayer vessel particularly after heat sterilization, the dicarboxylic acid unit of the polyamide resin (A) preferably contains the structural unit derived from straight-chain aliphatic dicarboxylic acid having 6 to 18 carbon atoms and the structural unit derived from aromatic dicarboxylic acid. The aromatic dicarboxylic acid is preferably one species selected from isophthalic acid and 2,6-naphthalenedicarboxylic acid, wherein isophthalic acid is more preferable.

[0046] When assuming the dicarboxylic acid unit of the polyamide resin (A) as 100 mol% in total, the molar ratio of the structural unit derived from straight-chain aliphatic dicarboxylic acid having 6 to 18 carbon atoms and the aromatic dicarboxylic acid-derived structural unit (straight-chain aliphatic dicarboxylic acid/aromatic dicarboxylic acid) is preferably 80/20 to 99/1, more preferably 85/15 to 98/2, and even more preferably 90/10 to 97/3.

[0047] In particular, the polyamide resin (A) in this invention preferably contains the diamine unit with a content of a structural unit derived from metaxylylenediamine of 90 mol% or more; and the dicarboxylic acid unit with a content of an adipic acid-derived structural unit of 90 to 100 mol%, and with a content of an isophthalic acid-derived structural unit of 10 to 0 mol%; and more preferably contains the diamine unit with a content of a structural unit derived from metaxylylenediamine of 95 mol% or more; and the dicarboxylic acid unit with a content of an adipic acid-derived structural unit of 90 to 97 mol%, and with a content of an isophthalic acid-derived structural unit of 10 to 3 mol%.

[0048] The polyamide resin (A) used in this invention, which is composed of the diamine unit and the dicarboxylic acid unit, can also contain some other moiety, such as a structural unit other than the diamine unit and dicarboxylic acid unit, or a terminal group. Such other structural unit is exemplified by, but not limited to, lactams such as ϵ -caprolactam, valerolactam, laurolactam and undecalactam; and aminocarboxylic acid-derived structural unit such as 11-aminoundecanoic acid and 12-aminododecanoic acid. The polyamide resin (A) can also contain trace components such as additives used for the synthesis. In the polyamide resin (A) used in this invention, the diamine unit or the dicarboxylic acid unit typically account for 95% by mass or more, and preferably 98% by mass or more.

<Preparation of Polyamide Resin (A) >

[0049] The polyamide resin (A) may be prepared by a method and under polymerization conditions which are freely selected without special limitation. For example, the polyamide resin (A) may be prepared by heating a salt composed of a diamine component and a dicarboxylic acid component under pressure in the presence of water, and by allowing melt-polymerization to proceed while removing the added water and released water. The polyamide resin (A) may be prepared alternatively by adding the diamine component directly to the dicarboxylic acid component kept in a molten state, and by subjecting the mixture to polycondensation under normal pressure. In order to keep the reaction system with a uniform liquid condition, the polycondensation in this case is allowed to proceed by continuously adding the diamine component to the dicarboxylic acid component, while heating the reaction system so that the reaction temperature would not fall below the melting points of the oligoamide and polyamide produced therein. During the polycondensation, a small amount of monoamine or monocarboxylic acid may be added as a molecular weight modifier.

[0050] The polyamide resin (A) is preferably a product obtained by polycondensation based on melt polymerization, followed by solid phase polymerization. According to an exemplary method of melt polycondensation, a nylon salt composed of a diamine component and a dicarboxylic acid component is heated under pressure in the presence of water, and the melt is subjected to melt polymerization while eliminating the added water and released water. According to another exemplary method, the diamine component may be added directly to the dicarboxylic acid component kept in a molten state, and the melt is subjected to polycondensation. In order to keep the reaction system with a uniform liquid condition, the polycondensation in this case is allowed to proceed by continuously adding the diamine component to the dicarboxylic acid component, while heating the reaction system so that the reaction temperature would not fall below the melting points of the oligoamide and polyamide produced therein.

[0051] The solid phase polymerization is carried out preferably after the polymer, obtained in the melt polycondensation, is taken out. As a heating apparatus used for the solid phase polymerization, a batch type heating apparatus that excels in air tightness and can substantially isolate the polyamide resin from oxygen is preferred over a continuous type heating apparatus. In particular, heating apparatuses with a rotary drum, such as tumble drier, conical drier and rotary drier; and a conical heating apparatus with an internal rotary blade, called Nauta mixer, are suitably used, but not limited thereto.

[0052] In order to avoid mutual adhesion of polyamide resin pellets or to avoid adhesion of the polyamide resin pellets to the inner wall of apparatus, the solid phase polymerization of polyamide resin is preferably carried out according to: a first step of raising crystallinity of the polyamide resin; a second step of increasing the molecular weight of the polyamide resin; and a third step of cooling the polyamide resin after the solid phase polymerization was allowed to proceed to reach a desired molecular weight. The first step is preferably carried out at a temperature not higher than the glass

transition temperature of the polyamide resin. The second step is preferably carried out under reduced pressure, and at a temperature lower than the melting point of the polyamide resin, but not limited thereto.

<Physical Properties of Polyamide Resin (A)>

[0053] Relative viscosity is widely used as an index of the degree of polymerization of the polyamide resin. The relative viscosity of the polyamide resin (A) used in this invention is preferably 2.2 to 4.0 from the viewpoint of melt viscosity of the water vapor barrier layer (X) and moldability in co-extrusion molding, which is more preferably 2.3 to 3.5, and even more preferably 2.4 to 3.0. Method of measuring the relative viscosity follows a method described later in EXAMPLES.

[0054] The polyamide resin (A) preferably has a melting point of 200 to 250 °C from the viewpoint of moldability or workability, which is more preferably 210 to 245°C, and even more preferably 220 to 240°C.

3-2. Polyamide Resin (B)

[0055] The polyamide resin (B) is a poly(hexamethylene isophthalamide)/poly(hexamethylene terephthalamide) copolymer, and is obtained by polycondensation of terephthalic acid, isophthalic acid, and hexamethylenediamine. The polyamide resin (B) is an amorphous polyamide resin, and acts to reduce crystallization rate of the polyamide resin (A) in the polyamide resin composition (P), to thereby improve the moldability. N-6I/6T may be a block copolymer or may be a random copolymer. N-6I/6T may be any of commercially available products which include "Novamid (registered trademark) X21" (from DSM Japan Engineering Plastics, Inc.), "Selar (registered trademark) PA 3426" (from Du Pont-Mitsui Polychemicals Co., Ltd.), and "Grivory (registered trademark) G21" (from EMS-CHEMIE Japan Ltd.).

[0056] N-6I/6T may contain some other moiety, such as a structural unit other than the structural units derived from terephthalic acid, isophthalic acid and hexamethylenediamine, or a terminal group, without departing from the spirit of this invention. Such other structural unit is exemplified by, but not limited to, lactams such as ϵ -caprolactam, valerolactam, laulolactam and undecalactam; and aminocarboxylic acid-derived structural units such as 11-aminoundecanoic acid and 12-aminododecanoic acid. N-6I/6T used in this invention can also contain trace components such as additives used for the synthesis. In N-6I/6T used in this invention, the structural units derived from terephthalic acid, isophthalic acid and hexamethylenediamine typically account for 95% by mass or more, more preferably 98% by mass or more, and even more preferably 99% by mass or more.

[0057] The content of the polyamide resin (A) and polyamide resin (B) in the polyamide resin composition (P), given in the form of (A) : (B), is 10 to 45% by mass: 90 to 55% by mass, preferably 15 to 40% by mass:85 to 60% by mass, even more preferably 20 to 40% by mass:80 to 60% by mass, yet more preferably 20 to 35% by mass:80 to 65% by mass, and furthermore preferably 25 to 35% by mass:75 to 65% by mass. With the content of the polyamide resin (B) of less than 55% by mass, an effect of delaying crystallization of the polyamide resin (A) will be insufficient, resulting in nonconformities such as blow failure or blushing during injection blow molding due to crystallization. Meanwhile, with the content of the polyamide resin (B) exceeding 90% by mass, heat moldability will be improved, whereas the gas barrier performance will unfortunately degrade. Although it might be preferable, from the viewpoint of improving the oxygen barrier performance, to control the ratio of the polyamide resin (A) above 45% by mass, this invention succeeded in achieving a composition with all-round performance of the medical multilayer vessel, by intentionally employing the above-described ratio of (A) and (B).

[0058] In the polyamide resin composition (P) of this invention, the total content of the polyamide resin (A) and the polyamide resin (B) preferably accounts for 80% by mass or more, more preferably 90% by mass or more, even more preferably 95% by mass or more, and yet more preferably 99% by mass or more.

[0059] Only one species, or two or more species of each of the polyamide resin (A) and the polyamide resin (B) may be contained. When two or more species are contained, the total content preferably falls within the above-described ranges.

[0060] Although the polyamide resin composition (P) in this invention may contain some polyamide resin other than the polyamide resin (A) and the polyamide resin (B), it preferably contains substantially no polyamide resin other than the polyamide resin (A) and the polyamide resin (B). Now the phrase stating "contains substantially no ..." means that the content is 3% by mass or less of the polyamide resin composition (P), which is preferably 1% by mass or less.

3-3. Additive

[0061] The polyamide resin composition (P) may contain freely-selectable additive(s) such as thermoplastic resin besides the polyamide resin, lubricant, matting agent, heat stabilizer, weathering stabilizer, UV absorber, crystal nucleating agent, plasticizer, flame retardant, antistatic agent, anti-coloring agent and antigelling agent, without damaging the effects of this invention.

3-4. Preparation of Polyamide Resin Composition (P)

[0062] The polyamide resin composition (P) may be prepared by employing a freely selectable method of mixing and/or kneading, to thereby mix and/or knead the polyamide resin (A) and the polyamide resin (B). When they are mixed, polyamide resin pellets may be fed into a rotary hollow vessel, or may be fed by predetermined portions through a volumetric feeder into a hopper. The method of kneading is exemplified by melt kneading. It is particularly preferable to blend predetermined amounts of polyamide resin (A) and polyamide resin (B) according to a dry process, and then feeding the mixture all at one into the hopper, to prepare the polyamide resin composition (P). For the case where any additive is blended to the polyamide resin composition, the additive is added to the polyamide resin (A) and/or the polyamide resin (B) before they are mixed and/or kneaded, or may be added at the same time when the polyamide resin (A) and the polyamide resin (B) are mixed and/or kneaded.

4. Optional Layer

[0063] The multilayer vessel of this invention may include, besides the layers (X) and (Y), an optional layer depending on desired performances. The optional layer is exemplified by an adhesive layer.

<Adhesive Layer (AD)>

[0064] When it fails to obtain a practical level of interlayer adhesion strength between two adjacent layers, it is preferable to provide an adhesive layer between the two layers. The adhesive layer preferably contains a thermoplastic resin with an adhesive property. Such adhesive thermoplastic resin is exemplified by acid-modified polyolefin resins obtained by modifying a polyolefin resin such as polyethylene, polypropylene or the like with an unsaturated carboxylic acid such as acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid or the like; and polyester-based thermoplastic elastomer that contains a polyester-based block copolymer as a major ingredient. The adhesive layer preferably uses a resin obtained by modifying a resin equivalent to the water vapor barrier polymer used as the layer (X), from the viewpoint of adhesiveness. The adhesive layer is preferably 2 to 100 μm thick, from the viewpoint of balancing a practical level of adhesion strength and moldability or workability, which is more preferably 5 to 90 μm thick, and even more preferably 10 to 80 μm thick.

5. Medical Multilayer Vessel and Method for Manufacturing the Same

[0065] The medical multilayer vessel of this invention preferably has an oxygen transmission rate (OTR) of 0.00100 mL/(0.21 atm·day·package) or below, more preferably 0.00090 mL/(0.21 atm·day·package) or below, and even more preferably 0.00070 mL/(0.21 atm·day·package) or below. The lower limit value of oxygen transmission rate is typically, but not specified to, 0.00040 mL/(0.21 atm·day·package) or above, and more preferably 0.00045 mL/(0.21 atm·day·package) or above. Even a level of 0.00050 mL/(0.21 atm·day·package) or above is practical enough.

[0066] The medical multilayer vessel of this invention preferably has a water vapor barrier performance (WVTR) of 0.0010 g/(day·package) or below, more preferably 0.0008 g/(day·package) or below, and even more preferably 0.0007 g/(day·package) or below. The lower limit value of the water vapor barrier performance is typically, but not specified to, 0.0005 g/(day·package) or above. Even a level of 0.0006 g/(day·package) or above is practical enough.

[0067] The medical multilayer vessel of this invention, when assumed to be 300 μm thick and treated at 121°C for 30 minutes, preferably has a haze of 10.0% or below, which is more preferably 7.0% or below, even more preferably 5.0% or below, and yet more preferably 4.0% or below. The lower limit value of haze is preferably, but not specified to, 1.0% or above, and more preferably 2.5% or above. Even a level of 3.0% or above is practical enough.

[0068] The medical multilayer vessel of this invention, when assumed to be 300 μm thick and treated at 121°C for 30 minutes, preferably has a total light transmittance of 70% or above, which is more preferably 80% or above, and even more preferably 85% or above. The lower limit value of haze is typically, but not specified to, 95% or below. Even a level of 93% or below is practical enough.

[0069] OTR and WVTR, as well as, haze and total light transmittance after heat sterilization are measured according to methods described later in EXAMPLES.

[0070] The medical multilayer vessel of this invention preferably has a total thickness of 100 to 3000 μm , more preferably 500 to 2000 μm , and even more preferably 810 to 1200 μm .

[0071] In particular in this invention, it is preferable to use the layer (X) that contains, as a major ingredient, the water vapor barrier polymer that contains at least one or more species selected from the group consisting of cycloolefin polymer and cycloolefin copolymer, for the innermost layer of the medical multilayer vessel. With such constitution, the medical multilayer vessel will advantageously have less adhesion of the content to be stored on the inner surface thereof, and will cause less elution from the inner surface thereof. In particular for the case of medical vessel that contains drug or

so, adhesion of an active ingredient to the inner surface of vessel, or elution from the inner surface would adversely affect drug potency. In contrast, with the constitution of this invention, the above-described problem is effectively avoidable.

[0072] The medical multilayer vessel of this invention is preferably manufactured by injection molding or injection blow molding, wherein the injection blow molding is more preferable. According to the injection blow molding, the obtainable multilayer vessel will be less deformable even after sterilization under high pressure steam, will be suppressed from blushing effectively, and will keep a high level of barrier performance. According to the injection blow molding, first a test tube-like preform (parison) is formed by injection molding, the preform that is kept suitably heated is then inserted into dies with a final shape (blow molding dies), then expanded to be fit in the dies using air blown therein through an inlet, and then cooled to solidify into the form of bottle.

[0073] The preform may be formed by a well-known injection molding method. For example, by using an injection molding machine having two or more injection units and injection molding dies, a material for composing the water vapor barrier layer (X) and a material for composing the gas barrier layer (Y) are injected from respective injection cylinders through a hot runner into a die cavity, to thereby manufacture a multilayer preform conforming to the shape of the injection dies.

[0074] Alternatively, a three-layered X/Y/X multilayer preform may be manufactured by first injecting the material for composing the water vapor barrier layer (X) from an injection cylinder, then injecting the material for composing the gas barrier layer (Y) from another injection cylinder, at the same time with the material for composing the water vapor barrier layer (X), and then injecting a necessary amount of the material for composing the water vapor barrier layer (X) to fill the cavity. Still alternatively, a five-layered X/Y/X/Y/X multilayer preform may be manufactured by first injecting the material for composing the water vapor barrier layer (X), then injecting only the material for composing the gas barrier layer (Y), and then finally injecting a necessary amount of the material for composing the water vapor barrier layer (X) to fill the cavity.

[0075] The above-described dies with a final shape is heated to preferably 120 to 170°C, more preferably 130 to 160°C. During blow molding, the outer surface of molded article is kept in contact with the inner surface of the dies for a predetermined duration.

[0076] As another method for manufacturing a blow-molded article, employable is a two-stage blow molding process according to which the above-described multilayer preform is blown in primary stretch blow dies to obtain a primary blow-molded article larger than the final blow-molded article, the primary blow-molded article is then allowed to shrink under heating, and again blown in secondary dies to obtain a final blow-molded article. According to this method for manufacturing a blow-molded article, the obtainable blow-molded article will have a fully stretched and thinned bottom, and will have high deformation and impact resistance during hot filling and heat sterilization.

[0077] The multilayer vessel of this invention may be coated with an evaporated film of inorganic substance or inorganic oxide, or with an amorphous carbon film. The inorganic substance or inorganic oxide is exemplified by aluminum, alumina and silicon oxide. The evaporated film of the inorganic substance or inorganic oxide can block eluates such as acetaldehyde and formaldehyde from the multilayer vessel of this invention. Method of forming the evaporated film is exemplified by, but not specifically limited to, physical vapor deposition methods including vacuum evaporation, sputtering and ion plating; and chemical vapor deposition methods including PECVD (plasma CVD, plasma-enhanced chemical vapor deposition). The evaporated film is preferably 5 to 500 nm thick from the viewpoint of gas barrier performance, light shielding property and flex resistance, which is more preferably 5 to 200 nm thick. The amorphous carbon film is a diamond-like carbon film, which is a hard carbon film also referred to as i-carbon film or hydrogenated amorphous carbon film. An exemplary method for forming the film is such as evacuating a hollow molded article to vacuum, feeding therein a carbon source gas, and applying a plasma generating energy to form a plasma from the carbon source gas. In this way, the amorphous carbon film may be formed over the inner surface of vessel. The amorphous carbon film is capable of not only blocking transmission of low molecular inorganic gas such as oxygen and carbon dioxide to a considerable degree, but of also preventing sorption of various odorous low molecular organic compounds. The amorphous carbon film is preferably 50 to 5000 nm thick, in consideration of an effect of suppressing sorption of low molecular organic compounds, an effect of improving the gas barrier performance, adhesiveness to plastics, durability and transparency.

[0078] The medical multilayer vessel of this invention is particularly suitable for ampule, vial, vacuum blood collecting tube or prefilled syringe (preferably, a barrel (outer cylinder) of prefilled syringe).

[0079] For details of the ampule, vial, vacuum blood collecting tube and prefilled syringe, descriptions in paragraphs [0074] to [0080] of JP-A-2015-048097 may be referred to, the contents of which are incorporated into this specification.

[0080] Substance to be stored in the medical multilayer vessel of this invention is exemplified by, but not specifically limited to, vitamins such as vitamin A, vitamin B2, vitamin B12, vitamin C, vitamin D, vitamin E and vitamin K; alkaloids such as atropine; hormones such as adrenalin and insulin; saccharides such as glucose and maltose; antibiotics such as ceftriaxone, cephalosporin and cyclosporin; benzodiazepine-based drugs such as oxazolam, flunitrazepam, clonazepam and clobazam; and freely-selectable natural products and compounds.

[0081] Methods of heat sterilization of the medical multilayer vessel of this invention include those based on steam

system, hot water reservoir system and shower system. Sterilization temperature preferably falls within the range from 80°C to 140°C, and sterilization time preferably falls within the range from 10 to 120 minutes.

[0082] The medical multilayer vessel of this invention may alternatively subjected to electromagnetic sterilization using ultraviolet radiation, microwave and gamma ray; gas treatment typically using ethylene oxide; or chemical sterilization using hydrogen peroxide, hypochlorous acid and so forth.

EXAMPLES

[0083] This invention will further be detailed below, referring to Examples. This invention is, however, not limited to these Examples. Various methods of measurement in these Examples are as follows.

(1) Relative Viscosity

[0084] Precisely weighed was 0.2 g of a polyamide resin, the resin was then dissolved into 20 mL of a 96% by mass aqueous sulfuric acid solution at 20 to 30°C under stirring. After thorough dissolution of the polyamide resin, 5 mL of the solution was immediately sampled in a viscometer, allowed to stand in a thermostat chamber at 25°C for 10 minutes, and falling time (t) was measured. Also falling time (t₀) of a 96% by mass aqueous sulfuric acid solution as a blank was measured in the same way. Relative viscosity was calculated from t and t₀, according to the equation below. The viscosity was measured using a Cannon-Fenske viscometer.

$$\text{Relative Viscosity} = t/t_0$$

(2) Oxygen Barrier Performance of Multilayer Vessel (OTR)

[0085] Oxygen transmission rate (OTR) of the multilayer vessel was measured at 23°C, under a relative humidity inside the medical multilayer vessel of 100%, and a relative humidity outside the medical multilayer vessel of 50%, in accordance with ASTM D3985 using an oxygen transmission rate measuring instrument. The smaller the measured value, the better the oxygen barrier property. The oxygen transmission rate measuring instrument employed has a model name of "OX-TRAN (registered trademark) 2/61", from Mocon Inc.

(3) Water Vapor Barrier Performance (WVTR) of Medical Multilayer Vessel

[0086] On the 10th day from the start of measurement, water vapor transmission rate (WVTR) of the medical multilayer vessel was measured at 40°C, in an atmosphere with a relative humidity of 100%. For the measurement, a water vapor transmission rate measuring instrument with the model name of "PERMATRAN-W (registered trademark) 3/33G" from Mocon Inc. was used. The smaller the measured value, the better the water vapor barrier performance.

(4) Transparency of Multilayer Vessel after Heat Sterilization (Haze and Total Light Transmittance)

[0087] The multilayer vessel was heat-sterilized (retort-sterilized) in an autoclave at 121°C for 30 minutes, and the thus sterilized medical multilayer vessel was sampled by cutting the side wall thereof for measurement of haze and total light transmittance. The haze was measured in accordance with JIS K7136, and the total light transmittance was measured in accordance with JIS K7375. The above-described time for heat sterilization includes neither heating (temperature elevation) time nor cooling time. The thickness was measured at the spot of measurements, and used for converting the measured results into values expectable from a vessel of 300 μm thick.

[0088] The autoclave employed here was Model "SR-240" from Tomy Seiko Co., Ltd. The measuring instrument employed here was a color and turbidity measuring instrument under the model name of "COH-300A" from Nippon Denshoku Industries Co., Ltd.

(5) Oil Resistance Test of Multilayer Vessel

[0089] Ten milliliters each of an oil (100% medium-chain triglyceride with aliphatic fatty acid residues having 8 to 12 carbon atoms) was poured in the multilayer vessels, and stored at 40°C for 6 months. The multilayer vessels whose appearances were kept unchanged were marked with "○", and those found to cause oil leakage were marked with "×". The oil employed here was Nisshin MCT.

Example 1

[0090] Predetermined amounts of N-MXD6 (under the trade name of "MX-Nylon S6007" from Mitsubishi Gas Chemical Company, relative viscosity =2.65, as polyamide resin (A1)) composed of metaxylylenediamine unit and adipic acid unit, and N-6I/6T (under the trade name of "Novamid (registered trademark) X21" from DSM Japan Engineering Plastics, Inc., as polyamide resin (B1)) were fed into a single screw extruder, kneaded, and pelletized. Polyamide resin composition (P1) composed of 30% by mass of polyamide resin (A1) and 70% by mass of polyamide resin (B1), was thus prepared.

[0091] Next, a three-layered multilayer preform (21.5 g) with an (X)/(Y)/(X) structure was obtained according to conditions below, by injecting a material for composing the layer (X) from an injection cylinder, next by injecting a material for composing the layer (Y) from another injection cylinder, at the same time with the material for composing the layer (X), and then by injecting a necessary amount of the material for composing the layer (X) to fill the cavity. A resin employed for composing the layer (X) was a cycloolefin polymer (under the trade name of "ZEONEX (registered trademark) 690R" from ZEON Corporation). A resin employed for composing the layer (Y) was the polyamide resin composition (P1) described above. The thus obtained preform was cooled to a predetermined temperature, and then transferred to blow forming dies for blow molding that is carried out as the secondary process. A multilayer vial was thus manufactured.

(Geometry of Multilayer Vial)

[0092] The multilayer vial was 45 mm long, 24 mm in outer diameter and 1.0 mm thick, with an outer water vapor barrier layer (X) of 600 μm thick, a gas barrier layer (Y) of 200 μm thick, and the inner water vapor barrier layer (X) of 200 μm thick. The multilayer vial was manufactured using an injection blow integrated molding machine (Model "ASB12N/10T" from Nissei ASB Machine Co., Ltd., four-cavity type).

(Vial molding Conditions)

[0093]

Cylinder temperature for layer (X): 300°C

Cylinder temperature for layer (Y): 280°C

Resin channel temperature within injection molding dies: 300°C

Blow temperature: 150°C

Temperature of cooling water for blow molding dies: 40°C

Example 2

[0094] In a 3-L jacketed reactor equipped with a stirrer, a partial condenser, a cooler, a dropping tank, and a nitrogen gas feeding tube, 4.70 mol of adipic acid (AA) and 0.30 mol of isophthalic acid (IPA) (from A.G. International Chemical Co., Inc.) were placed after precisely weighed, the reactor was thoroughly replaced with nitrogen gas, and the content was allowed to melt at 160°C under stirring while feeding a small amount of nitrogen gas, to prepare a slurry. To the slurry kept under stirring, 4.97 mol of metaxylylenediamine (MXDA) was added dropwise over 160 minutes. During the process, the inner temperature was continuously elevated up to 250°C. Water released as a result of the dropwise addition of metaxylylenediamine was removed out from the system, through the partial condenser and the cooler. After completion of the dropwise addition of metaxylylenediamine, the inner temperature was elevated up to 260°C, and the reaction was allowed to continue for one hour. The obtained polymer was taken out in the form of strands through a nozzle at the bottom of the reactor, cooled in water, and chopped into pellets. Polyamide resin pellets with a molar ratio of adipic acid and isophthalic acid of 94:6 was thus obtained.

[0095] The pellets were then fed into a heating device with a stainless steel rotary drum, which was then rotated at 5 rpm. After thorough replacement with nitrogen gas, the reaction system was further heated from room temperature up to 140°C under a small amount of nitrogen gas flow. When the temperature in the reaction system reached 140°C, the system was then evacuated down to 1 Torr or below, and the temperature in the system was further elevated to 190°C over 130 minutes. After the temperature in the system reached 190°C, the solid phase polymerization was allowed to continue at that temperature for 30 minutes. Upon completion of the reaction, the evacuation was stopped, the temperature in the system was lowered under a nitrogen gas flow, and upon reaching 60°C, the pellets were taken out, to obtain polyamide resin (A2). Polyamide resin (A2) was found to have a relative viscosity of 2.68.

[0096] Polyamide resin composition (P2) was prepared in the same way as in Example 1, except that polyamide resin (A2) was used in place of polyamide resin (A1). A multilayer vial was manufactured in the same way as in Example 1, except that polyamide resin composition (P2) was used in place of polyamide resin composition (P1).

Example 3

5 [0097] Polyamide resin composition (P3) composed of 40% by mass of polyamide resin (A2) and 60% by mass of polyamide resin (B1) was prepared, by altering the ratio of blending of polyamide resin (A2) and polyamide resin (B1) in Example 2, followed by kneading and pelletizing. A multilayer vial was manufactured in the same way as in Example 1, except that polyamide resin composition (P3) was used in place of polyamide resin composition (P1).

Example 4

10 [0098] Polyamide resin composition (P4) composed of 15% by mass of polyamide resin (A2) and 85% by mass of polyamide resin (B1) was prepared, by altering the ratio of blending of polyamide resin (A2) and polyamide resin (B1) in Example 2, followed by kneading and pelletizing. A multilayer vial was manufactured in the same way as in Example 1, except that polyamide resin composition (P4) was used in place of polyamide resin composition (P1).

15 Examples 5 to 8

20 [0099] Multilayer vials were manufactured in the same way respectively as in Examples 1 to 4, except that cycloolefin copolymer (under the trade name of "TOPAS (registered trademark) 6013S-04", from TOPAS Advanced Polymers GmbH) was used in place of cycloolefin polymer (under the trade name of "ZEONEX (registered trademark) 690R", from ZEON Corporation), as a resin for composing the layer (X).

Examples 9 to 12

25 [0100] Multilayer vials were manufactured in the same way respectively as in Examples 1 to 4, except that polypropylene (under the trade name of "Bormed RB845MO", from Borealis AG) was used in place of cycloolefin polymer (under the trade name of "ZEONEX (registered trademark) 690R", from ZEON Corporation), as a resin for composing the layer (X).

Comparative Example 1

30 [0101] A multilayer vial was manufactured in the same way as in Example 1, except that polyamide resin (B1) was used in place of polyamide resin composition (P1).

Comparative Example 2

35 [0102] A multilayer vial was manufactured in the same way as in Example 1, except that polyamide resin (A1) was used in place of polyamide resin composition (P1).

Comparative Example 3

40 [0103] A multilayer vial was manufactured in the same way as in Example 1, except that polyamide resin (A2) was used in place of polyamide resin composition (P1).

Comparative Example 4

45 [0104] Polyamide resin composition (P5) composed of 70% by mass of polyamide resin (A1) and 30% by mass of polyamide resin (B1) was prepared, by altering the ratio of blending of polyamide resin (A1) and polyamide resin (B1) in Example 1, followed by kneading and pelletizing. A multilayer vial was manufactured in the same way as in Example 1, except that polyamide resin composition (P5) was used in place of polyamide resin composition (P1).

50 Comparative Example 5

55 [0105] Polyamide resin composition (P6) composed of 70% by mass of polyamide resin (A2) and 30% by mass of polyamide resin (B1) was prepared, by altering the ratio of blending of polyamide resin (A2) and polyamide resin (B1) in Example 2, followed by kneading and pelletizing. A multilayer vial was manufactured in the same way as in Example 1, except that polyamide resin composition (P6) was used in place of polyamide resin composition (P1).

Comparative Example 6

5 **[0106]** Polyamide resin composition (P7) composed of 90% by mass of polyamide resin (A1) and 10% by mass of polyamide resin (B2) was prepared, by using nylon 6 (under the trade name of "UBE-Nylon", grade 1015B, from Ube Industries, Ltd.) as polyamide resin (B2), in place of polyamide resin (B1), and feeding predetermined amounts of polyamide resin (A1) and polyamide resin (B2) into a single screw extruder, followed by kneading and pelletizing. A multilayer vial was manufactured in the same way as in Example 1, except that polyamide resin composition (P7) was used in place of polyamide resin composition (P1).

10 Comparative Example 7

15 **[0107]** A multilayer vial layer (X) was manufactured in the same way as in Example 1, except that polycarbonate (under the trade name of "Iupilon (registered trademark) S3000", from Mitsubishi Engineering Plastics Corporation) was used in place of cycloolefin polymer (under the trade name of "ZEONEX (registered trademark) 690R", from ZEON Corporation), as a resin for composing the layer (X).

20 **[0108]** The multilayer vials obtained in Examples 1 to 12 and Comparative Examples 1 to 7 were measured regarding the oxygen transmission rate and the water vapor transmission rate according to the methods described above. The multilayer vials obtained in Examples 1 to 8 and Comparative Examples 1 to 7 were heat-sterilized, and the post-treatment haze and total light transmittance were measured. The multilayer vessels obtained in Examples 9 to 12 were heat-sterilized, and the post-treatment total light transmittance was measured. The multilayer vials obtained in Examples 9 to 12 and Comparative Examples 1 to 7 were also subjected to the oil resistance test according to the method described above. Results are summarized in Tables 1 to 3.

[Table 1]

Example											
Inner layer and Outer layer(X)			1	2	3	4	5	6	7	8	
Gas Barrier Layer (Y)	Diamine Unit	Metaxyllylenediamine (mol%) ※ ₁	100	100	100	100	100	100	100	100	
	Polyamide Resin(A)	Dicarboxylic Acid Unit	Adipic Acid (mol%) ※ ₂	100	94	94	94	100	94	94	
											Isophthalic Acid (mol%) ※ ₂
	Polyamide Resin(B)			N-6V6T	N-6I/6T	N-6I/6T	N-6I/6T	N-6I/6T	N-6I/6T	N-6I/6T	N-6I/6T
	Content of Polyamide Resin (A):(B) (Mass Ratio)			30:70	30:70	40:60	15:85	30:70	30:70	40:60	15:85
Haze after treated at 121° C for 30 minutes (%)			6.2	3.8	3.9	3.3	6.1	3.7	3.7	3.0	
Total light transmittance after treated at 121° C for 30 minutes (%)			86.3	89.1	89.3	89.9	87.2	89.3	89.4	90.1	
OTR(mL/(0.21atm·day·package))			0.00058	0.00051	0.00048	0.00072	0.00062	0.00054	0.00058	0.00086	
WVTR(g/(day·package))			0.0006	0.0006	0.0006	0.0006	0.0007	0.0007	0.0007	0.0007	
※ ₁ : mol% in diamine unit (same will apply to Tables below)											
※ ₂ : mol% in dicarboxylic acid unit (same will apply to Tables below)											
COP: cycloolefin polymer (same will apply to Tables below)											
COC: cycloolefin copolymer (same will apply to Tables below)											
PP: polypropylene (same will apply to Tables below)											
N-6I/6T: poly(hexamethylene isophthalamide)/poly(hexamethylene terephthalamide) copolymer (same will apply to Tables below)											

[Table 2]

Example				9	10	11	12
Inner layer and Outer layer(X)				PP	PP	PP	PP
Gas Barrier Layer (Y)	Polyamide Resin (A)	Diamine Unit	Metaxylylenediamine (mol%) ※ ₁	100	100	100	100
		Dicarboxylic Acid Unit	Adipic Acid (mol%) ※ ₂	100	94	94	94
			Isophthalic Acid (mol%) ※ ₂	0	6	6	6
	Polyamide Resin(B)			N-6I/6T	N-6I/6T	N-6I/6T	N-6I/6T
	Contentof Polyamide Resin (A):(B)(Mass Ratio)			30:70	30:70	40:60	15:85
	Total light transmittance after treated at 121° C for 30 minutes (%)			75.3	76.2	75.2	75.3
OTR(mL/ (0.21atm· day· package))				0.00067	0.00065	0.00062	0.00094
WVTR(g/(day·package))				0.0008	0.0008	0.0008	0.0008
Oil Resistance Test				○	○	○	○

[Table 3]

Example		1	2	3	4	5	6	7
Inner layer and Outer layer(X)		COP	COP	COP	COP	COP	COP	PC
Gas Barrier Layer (Y)	Diamine Unit	-	100	100	100	100	100	100
	Polyamide Resin (A)							
	Dicarboxylic Acid Unit		100	94	100	94	100	
	Metaxylylenediamine (mol%) ※ ₁							
	Adipic Acid (mol%) ※ ₂ Isophthalic Acid (mol%) ※ ₂	-	0	6	0	6	0	1000
Polyamide Resin(B)		N-6I/6T	-	-	N-6I/6T	N-6I/6T	Ny6	N-6I/6T
Content of Polyamide Resin (A):(B)(Mass Ratio)		0:100	100:0	100:0	70:30	70:30	90:10	30:70
Haze after treated at 121° C for 30 minutes (%)		5.7	92.1	87.2	76.8	76.8	89.5	6.2
Total light transmittance after treated at 121° C for 30 minutes (%)		89.9	56.8	60.2	68.1	68.1	54.3	86.3
OTR(mL/(0.21atm·day·package))		0.0022	0.00031	0.00032	0.00041	0.00039	0.00033	0.00067
WVTR(g/(day·package))		0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0124
Oil Resistance Test		×	×	×	×	×	×	×
Ny6: nylon 6 PC: polycarbonate								

[0109] In Comparative Example 1 where xylylene group-containing polyamide (polyamide resin (A)) was not used, the vessel was found to have high oxygen transmission rate and poor gas barrier performance. In Comparative Examples 2 and 3 where N-6I/6T (polyamide resin (B)) was not used, the vessels caused blushing after heat sterilization, showing poor transparency. This is supposedly because the N-MXD6 slowly crystallized during the heat sterilization at 121°C, and grown up into a large spherulite.

[0110] Also in Comparative Example 6 where nylon 6, which is a crystalline polyamide, was blended in place of N-6I/6T, the vessel was found to cause blushing after heat sterilization, showing poor transparency. The crystalline polyamide resin has been known to act as a crystal nucleating agent for N-MXD6 during the heat sterilization, and to micronize the spherulite size of N-MXD6, thereby suppressing the blushing during the heat sterilization. This effect was, however, found to be insufficient for suppressing the blushing of the multilayer vessel of this invention after heat sterilization.

[0111] In Comparative Examples 4 and 5 where the content of the polyamide resin (B) was less than 55% by mass, an effect of delaying crystallization of the polyamide resin (A) was found to be insufficient, and the vessel was found to cause blushing due to crystallization, showing poor transparency.

[0112] In Comparative Example 7 where PC was used for the layer (X), the vessel was found to be considerably inferior in water vapor barrier performance.

[0113] In contrast, the multilayer vessels of Examples 1 to 8 were found to excel in water vapor barrier performance and transparency even after heat sterilization. In particular, the vessels of Examples 2 to 4 and 6 to 8, where the polyamide resin (A) that contains the aromatic dicarboxylic acid unit was used, were successful to reduce the haze after heat sterilization to a considerable degree.

[0114] It was also found that the multilayer vessels of Examples 9 to 12 were excel in water vapor barrier performance and oil resistance.

INDUSTRIAL APPLICABILITY

[0115] The multilayer vessel of this invention has water vapor barrier performance and transparency suitable enough for medical packaging materials which are subject to heat sterilization. The multilayer vessel can therefore store the content for a long period, allows the content to be seen through even after heat sterilization, and can be a substitute for glass vessels, with an improved convenience for customers.

Claims

1. A medical multilayer vessel comprising a layer (X) containing, as a major ingredient, a water vapor barrier polymer that contains at least one species or more of polyolefin resin(s), and a gas barrier layer (Y) composed of a polyamide resin composition (P),
the polyamide resin composition (P) comprising:

10 to 45% by mass of polyamide resin (A) that contains a diamine unit with a content of a structural unit derived from xylylenediamine of 70 mol% or more, and a dicarboxylic acid unit with a content of a structural unit derived from a straight-chain aliphatic dicarboxylic acid having 6 to 18 carbon atoms of 70 mol% or more; and,
90 to 55% by mass of a poly(hexamethylene isophthalamide)/poly(hexamethylene terephthalamide) copolymer (B).

2. The medical multilayer vessel of Claim 1, wherein the polyolefin resin is at least one or more species selected from the group consisting of cycloolefin polymer, cycloolefin copolymer and polypropylenes.

3. The medical multilayer vessel of Claim 1, wherein the polyolefin resin is at least one or more species selected from the group consisting of cycloolefin polymer and cycloolefin copolymer.

4. The medical multilayer vessel of any one of Claims 1 to 3, wherein the xylylenediamine is metaxylylenediamine, paraxylylenediamine or a mixture of them, and the straight-chain aliphatic dicarboxylic acid is adipic acid, sebacic acid or a mixture of them.

5. The medical multilayer vessel of any one of Claims 1 to 4, wherein the dicarboxylic acid unit of the polyamide resin (A) contains a structural unit derived from aromatic dicarboxylic acid, and, the molar ratio of the structural unit derived from straight-chain aliphatic dicarboxylic acid and the structural unit derived from aromatic dicarboxylic acid (straight-chain aliphatic dicarboxylic acid/aromatic dicarboxylic acid) is 80/20 to 99/1.

6. The medical multilayer vessel of Claim 5, wherein the aromatic dicarboxylic acid contains isophthalic acid.
7. The medical multilayer vessel of any one of Claims 1 to 3, wherein the polyamide resin (A) contains: a diamine unit with a content of a structural unit derived from metaxylylenediamine of 90 mol% or more; and a dicarboxylic acid unit with a content of an adipic acid-derived structural unit of 90 to 100 mol% and with a content of an isophthalic acid-derived structural unit of 10 to 0 mol%.
8. The medical multilayer vessel of any one of Claims 1 to 7, having the layer (X) as each of an inner layer and an outer layer, and having at least one gas barrier layer (Y) as an intermediate layer.
9. The medical multilayer vessel of any one of Claims 1 to 8, wherein the gas barrier layer (Y) has a thickness that accounts for 2 to 40% of the total thickness of the multilayer vessel.
10. The medical multilayer vessel of any one of Claims 1 to 9, being an ampule, vial, vacuum blood collecting tube or prefilled syringe.
11. The medical multilayer vessel of any one of Claims 1 to 10, being an injection blow molded article.
12. A method for manufacturing a medical multilayer vessel, comprising forming the medical multilayer vessel described in any one of Claims 1 to 10 by injection blow molding.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/079229

A. CLASSIFICATION OF SUBJECT MATTER

A61J1/05(2006.01)i, B32B27/32(2006.01)i, B32B27/34(2006.01)i, B65D81/24(2006.01)i, C08G69/00(2006.01)i, G01N1/10(2006.01)i

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

B. FIELDS SEARCHED

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A61J1/C5, B32B27/32, B32B27/34, B65D81/24, C08G69/00, G01N1/10

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 1996-2016

Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

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

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 64-006056 A (Mitsubishi Chemical Corp.), 10 January 1989 (10.01.1989), page 1, lower left column, line 18 to page 2, lower right column, line 2; page 3, lower left column, line 18 to page 4, lower left column, line 16; examples 4 to 5 (Family: none)	1-12

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

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 2012-201412 A (Mitsubishi Gas Chemical Co., Inc.), 22 October 2012 (22.10.2012), paragraphs [0005], [0017] to [0018], [0025] (Family: none)	5-12
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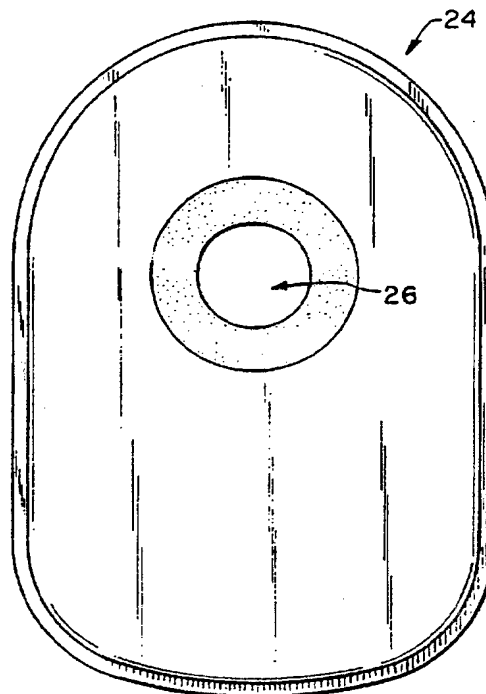
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(54) Title: MULTILAYER BARRIER FILM

(57) Abstract

An oxygen and moisture impermeable multilayer barrier film (10) is provided including a barrier layer (12) comprising a homopolymer of vinylidene chloride or a copolymer of vinylidene chloride and vinyl chloride or methyl methacrylate. The barrier layer is coextruded with or laminated to at least one heat sealable skin layer (14) comprising a thermoplastic polyurethane, a substantially linear copolymer of ethylene and an α -olefin, or a homogeneously-branched linear olefin resin to form the barrier film. The multilayer film may be used for reusable ostomy bags (24), for systems for the transdermal delivery of drugs, and for heat sealable bags used in packaging.



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MULTILAYER BARRIER FILM

5 The present invention relates to an oxygen and moisture impermeable multilayer barrier film, and to articles produced therefrom including ostomy bags, laminates for transdermal delivery of drugs, and heat sealable bags.

Plastic film laminates having oxygen and moisture vapor barrier properties are desirable for current packaging requirements, as well as for use in medical applications such as the fabrication of ostomy bags or transdermal drug delivery systems. Such films have been
10 provided through the use of multi-ply film laminates where at least one of the plies is oxygen and moisture vapor impermeable. Typically, the films comprise chlorinated polyethylene films or plasticized polyvinyl chloride films, polyvinylidene chloride copolymer films, or multilayered structures such as ethylene vinyl acetate-polyvinylidene chloride/ethylene vinyl acetate combination films.

15 Several other methods for producing barrier films have been proposed. For example, Manne et al, U.S. Patent 3,753,828 describes a method of preparing oxygen impermeable film packaging materials using an adhesive-containing Saran resin which is applied to one ply of a two-ply laminate and then cured. However, the process requires the addition of an adhesive and involves curing steps which require the use of a printing press or
20 laminator.

Lustig et al, U.S. Patent 4,348,437 relate to a coextruded multilayer food packaging film comprising a first layer of an ethylene vinyl acetate copolymer, a second layer comprising a polyvinylidene chloride copolymer or an ethylene vinyl alcohol copolymer, and a third layer comprising a blend of a polyurethane polymer and an ethylene vinyl acetate
25 copolymer. However, the film does not provide other desirable physical properties such as softness and low noise characteristics which are required for ostomy applications.

Accordingly, the need still exists for multilayer barrier films which may be produced by simple and inexpensive conventional processes and for films which are impermeable to moisture and oxygen, provide odor barrier, softness, and low noise properties,
30 and which have a heat sealable surface for forming bags or the like.

The present invention meets that need by providing an oxygen and moisture impermeable multilayer barrier film which may be produced by coextrusion or lamination techniques. The film provides excellent adhesion between layers, odor barrier and softness characteristics, and provides a heat sealable surface for the fabrication of bags.

35 According to one aspect of the present invention, an oxygen and moisture impermeable multilayer barrier film having a heat seal strength of at least 1.0 lb/inch of film

width, and preferably greater than 1.5 lb/inch of film width, is provided. By "oxygen impermeable", it is meant that the film has an oxygen transmission rate of equal to or less than 90 cc/m²/day-atm. By "moisture impermeable", it is meant that the film has a water vapor transmission rate of equal to or less than 5 gm/m²/day.

5 In one embodiment, the film comprises a barrier layer with at least one heat sealable skin layer thereon. The barrier layer comprises, for example, any suitable barrier layer material which will provide the desired oxygen and moisture impermeability while being compatible with the heat sealable skin layer or layers. A preferred barrier material is a copolymer of vinylidene chloride with vinyl chloride or methyl methacrylate. Where the barrier
10 layer includes a copolymer of vinylidene chloride with vinyl chloride or methyl methacrylate, the barrier layer may also optionally include from 0 to 6 percent by weight of a copolymer of ethylene and vinyl acetate, and more preferably from 4-6 percent as a processing aid.

In one embodiment of the invention, the barrier layer is coextruded with at least one heat sealable skin layer. To provide the desired softness characteristics, the heat sealable
15 skin layer preferably has a 2 percent secant modulus of less than 15,000 psi in both the machine (MD) and transverse (TD) directions. The heat sealable skin layer preferably comprises either a thermoplastic polyurethane, a substantially linear copolymer of ethylene and an α -olefin having a density in the range of from 0.87-0.92, or a homogeneously-branched linear polyolefin resin. To aid in processing of the film, the skin layer or layers may contain from 0 to
20 10 percent by weight of a copolymer of ethylene and vinyl acetate, and more preferably, from 0.5-5 percent of the copolymer as a processing aid. In addition, the skin layer may optionally contain from 0.5 to 6 percent by weight of a slip additive/antiblocking agent package. Where the skin layer is a substantially linear copolymer of ethylene and an α -olefin, it may be desirable to coextrude an adhesive tie layer of a copolymer of ethylene and vinyl acetate between the
25 skin and barrier layers to improve adhesion of those layers.

In a preferred embodiment of the invention, the barrier layer is coextruded between two heat sealable skin layers, where the skin layers comprise 70 percent by volume (thickness) of the film and the barrier layer comprises 30 percent by volume (thickness) of the film. This construction may be used to form reusable ostomy bags or pouches. The barrier and
30 skin layer or layers may also be formed separately and then laminated together using suitable adhesive polymers, liquid adhesives, or hot melt adhesives. The multilayer barrier films of the present invention exhibit a noise of less than 85 dB when subjected to flexing through a 65° angle at 0.45 Hz, preferably exhibit a noise of less than 83 dB when subjected to flexing through a 65° angle at 0.45 Hz, and most preferably exhibit a noise of less than 81 dB when
35 subjected to flexing through a 65° angle at 0.45 Hz.

In another embodiment of the invention, additional layers may be added to the barrier film to form a system for transdermal delivery of drugs. The system preferably comprises a backing layer of the barrier film which functions as a barrier to the drug system. An

adhesive containing an active drug is preferably adhered to one surface of the film. Adjacent the adhesive is a controlled release membrane which is adapted to contact a patient's skin and to controllably release the drug.

5 In another form of this embodiment, the backing layer may form a reservoir for containing the active drug with the controlled release membrane covering the opening of the reservoir to control the diffusion of the drug into a patient's skin. A peripheral or overall adhesive may be used to adhere the transdermal delivery system to a patient's skin. Preferably, a release liner overlies the adhesive and membrane to protect the construction prior to use.

Accordingly, it is a feature of the present invention to provide an oxygen and
10 moisture impermeable multilayer barrier film which may be produced using coextrusion or lamination processes. Further features of the invention include odor barrier, softness, and low noise properties. Additionally, a heat sealable surface for use in forming bags and pouches is provided. These, and other features and advantages of the present invention will become apparent from the following detailed description, the accompanying drawings, and the
15 appended claims.

Fig. 1 is a schematic cross-section of one embodiment of the multilayer barrier film of the present invention;

Fig. 2 is a schematic cross-section of another embodiment of the multilayer barrier film of the present invention;

20 Fig. 3 is a schematic cross-section of one embodiment of a transdermal drug delivery system in accordance with the present invention;

Fig. 4 is a schematic cross-section of another embodiment of a transdermal drug delivery system in accordance with the present invention; and

Fig. 5 is a front elevational view of an ostomy bag or pouch formed from the
25 multilayer barrier film of Figs. 1 or 2 of the present invention.

In one embodiment, the multilayer barrier film of the present invention may be produced using standard extrusion techniques such as feedblock coextrusion, multi-manifold die coextrusion, or combinations of the two. The volume (thickness) of each individual layer may be controlled as it is extruded. Thus, the overall thickness of the multilayer structure may
30 be controlled. Alternatively, the individual layers may be formed separately and laminated together using suitable adhesive bonding layers.

The polymers in the films are not intentionally stretched or oriented other than as a natural consequence of their manufacture to preserve their low noise characteristics. For example, films produced by a blown process will inherently have some orientation in both the
35 machine (MD) and transverse (TD) directions, while cast films will remain unoriented in the transverse direction. Generally, the less orientation which is introduced into the films, the less

noisy they will be. The multilayer barrier films of the present invention exhibit a noise of less than 85 dB when subjected to flexing through a 65° angle at 0.45 Hz, preferably exhibit a noise of less than 83 dB when subjected to flexing through a 65° angle at 0.45 Hz, and most preferably exhibit a noise of less than 81 dB when subjected to flexing through a 65° angle at
5 0.45 Hz

Additionally, to provide the desired softness characteristics, the heat sealable skin layer preferably has a 2 percent secant modulus of less than 15,000 psi in both the machine (MD) and transverse (TD) directions. 2 percent secant modulus is a measure of the stiffness or softness of a film. We have found that the lower the value for 2 percent secant modulus for the
10 heat sealable skin layer, the softer the resulting film will be. Generally, it is desirable for the 2 percent secant modulus of the film to be as low as possible and yet still remain processable by conventional equipment. For the overall multilayer film, it is preferable that the 2 percent secant modulus be 30,000 psi or below. The resulting multilayer films possess low oxygen and vapor transmission rates, as well as having the odor barrier, softness, and low noise properties
15 needed for ostomy applications.

Referring now to Fig. 1, an oxygen and moisture impermeable multilayer barrier film 10 is illustrated. The film 10 includes a barrier layer 12 which may be of a copolymer of vinyl chloride (15-20 percent by weight) and vinylidene chloride (80-85 percent by weight) or a copolymer of vinylidene chloride (93-94 percent by weight) and methyl methacrylate (6-7
20 percent by weight). Examples of suitable barrier materials include Saran® 469 and Saran® MA, commercially available from The Dow Chemical Company. Where a Saran® barrier layer material is used, the barrier layer may also include from 0 to 6 percent by weight of a copolymer of ethylene and vinyl acetate, and more preferably from 4-6 percent by weight of the copolymer as a processing aid. A suitable class of ethylene/vinyl acetate copolymer
25 compositions are those copolymers sold commercially as Elvax® resins by E.I. du Pont de Nemours & Co., Inc.

As shown, the barrier layer is preferably coextruded with or laminated between two heat sealable skin layers 14 comprising either a thermoplastic polyurethane, a substantially linear copolymer of ethylene and an α -olefin having a density in the range of from 0.87-0.92
30 gm/cc, or a homogeneously-branched linear polyolefin resin. Suitable thermoplastic polyurethanes include those based on the reaction of a polyisocyanate (aromatic or aliphatic) with polyester, polyether, or polycaprolactone polyols. Chain extenders such as diols and diamines may also be used in the reaction. Such thermoplastic polyurethanes are commercially available from the B.F. Goodrich Co. under the trademark Estane® and from The Dow Chemical
35 Company under the trademark Pellathane®. A preferred thermoplastic polyurethane composition is Pellathane® 2355-95AE.

To aid in processing of the thermoplastic polyurethane skin layers, the skin layers may contain from 0 to 10 percent by weight of a copolymer of ethylene and vinyl acetate, and

more preferably, from 0.5-5 percent by weight. In addition, the skin layers may contain from 0.5-6 percent by weight of a slip additive and/or antiblocking agent such as Akzo 16LB15, commercially available from Akzo Chemicals Inc. The thermoplastic polyurethane skin layers used in the present invention typically will provide a heat seal strength in the range of from 7 to 9 lb/inch of film width (measured in accordance with ASTM D 903).

A suitable substantially linear copolymer resin of ethylene and an α -olefin is taught in commonly-assigned published PCT application PCT/US92/08812, published April 27, 1993, the disclosure of which is hereby incorporated by reference. These copolymer resins are commercially available from The Dow Chemical Company as polymer resins made using Insite™ constrained geometry catalyst technology (CGCT). The constrained geometry catalysts are described in commonly-assigned copending U.S. application Serial Nos. 545,403, filed July 3, 1990; 758,654, filed September 12, 1991; 758,660, filed September 12, 1991; and 720,041, filed June 24, 1991. The catalysts may be generally characterized as comprising a metal coordination complex of a metal of Groups 3-10 or the Lanthanide series of the Periodic Table of Elements and a delocalized α -bonded moiety substituted with a constrain-inducing moiety.

Such substantially linear copolymers have the strength and toughness of linear low density polyethylene (LLDPE) but with processability similar to highly branched low density polyethylene (LDPE). Thus, the polymers have processing indices (PI's) less than or equal to 70 percent of those of a comparable linear olefin polymer and a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at onset of surface melt fracture of a traditional linear olefin polymer at the same I_2 and M_w/M_n , where I_2 is the melt index measured according to ASTM D-1238, Condition 190°C/2.16 kg (formerly known as "Condition E"), M_w is the weight average molecular weight, and M_n is the number average molecular weight of the polymer. The substantially linear copolymers will have from 0.01 to 3 long chain branches/1000 carbon atoms along the polymer backbone, where long chains are defined as a chain length of at least 6 carbon atoms. The substantially linear copolymers also have homogeneous branching distributions. Copolymers having homogeneous branching distributions are those in which the comonomer is randomly distributed within a given molecule and wherein all the copolymer molecules have the same ethylene/comonomer ratio, as described in U.S. Patent No. 3,645,992, to Elston, the disclosure of which is incorporated herein by reference.

Moreover, these substantially linear copolymers have desirable quietness for use in ostomy applications. Such substantially linear ethylene/ α -olefin copolymers typically will provide a heat seal strength in the range of from 2 to 3 lb/inch of film width (ASTM D 903). Thus, these substantially linear copolymers are preferred for use in the present invention because they possess a unique combination of processability, quietness, and heat seal strength.

A suitable homogeneously-branched linear polyolefin resin is commercially available from Exxon Corporation under the trademark Exact® or from Mitsui Chemical Co.

under the trademark Tafmer[®]. These resins also provide good heat seal strength and have desirable quietness properties.

The barrier film 10 may be used to form a reusable ostomy bag or pouch by folding the film and heat sealing either the thermoplastic polyurethane, substantially linear ethylene/ α -olefin copolymer, or homogeneously-branched linear polyolefin resin skin layers to each other. Preferably, the bag will have an oxygen permeability of less than 90 cc/m²/day·atm (1.8 cc/100 in²/day·atm). The barrier film 10 may have a total thickness of between 35 and 100 micrometers, with the barrier layer 12 making up from 10 to 30 percent of the total thickness of the film. The skin layers (and adhesive layers, if needed) will typically make up 70 to 90 percent of the total thickness of the film.

The multilayer barrier films of the present invention may also be formed by lamination techniques using suitable adhesives. For example, the barrier and skin layer or layers may be formed separately and then laminated together using adhesive polymers, liquid adhesives, or hot melt adhesives. Suitable adhesive polymers to bond the barrier and skin layers include, but are not limited to, ethylenically unsaturated copolymers of vinyl acetate, ethyl acrylate, ethyl methacrylate, methyl acrylic acid, acrylic acid, and carbon monoxide. Other examples include ionomers of ethylene and methyl acrylic acid or acrylic acid and grafted anhydride copolymers. Suitable liquid or hot melt adhesives include, but are not limited to, adhesives based on urethanes, copolyesters, and copolymers of amide acrylates.

Fig. 2 schematically illustrates a five-layer oxygen and moisture impermeable barrier film 10. The film 10 includes a barrier layer 12 of a suitable barrier material as discussed above. The barrier layer is preferably coextruded with two outer heat sealable skin layers 14 with adhesive layers 13 sandwiched therebetween. The heat sealable skin layers in this five layer embodiment may comprise the substantially linear copolymer of ethylene and an α -olefin of published PCT application No. PCT/US92/08812 or homogeneously branched linear polyolefin resins such as the Exact[®] and Tafmer[®] resins. Suitable adhesives for layers 13 include copolymers of ethylene and vinyl acetate which improve the adherence of the barrier and skin layers to each other.

Fig. 3 illustrates another embodiment of the invention in which additional layers are included with the barrier film to form a system 16 for transdermal delivery of drugs. In its simplest form, the barrier layer 12 and skin layers 14 of the film serve as a backing film that is a barrier to the drug system. The barrier film further includes an adhesive layer 18 containing an active drug blended in a matrix therein adhered to one surface of the film. The adhesive which is selected should be compatible with the active drug and permeable to the drug. There are many active drugs which can be administered to a patient in this manner including, for example, estrogen, nitroglycerin, nicotine, and scopolamine. In theory, almost any drug may be administered in this manner.

A controlled release membrane 20 adapted to contact a patient's skin and to controllably release the drug overlies adhesive layer 18. An additional adhesive layer 22, which may be applied peripherally or over the entire surface of membrane 20, may also be present to secure the transdermal delivery system 16 to a patient's skin. The adhesives used in the practice of this embodiment of the invention should be medical grade adhesives such as silicone, acrylic, or vinyl acetate adhesives. Generally, in this embodiment, the system 16 will be sealed in a package or secured to a second barrier film which is removed prior to use.

Fig. 4 illustrates an alternative form of a transdermal drug delivery system 16 in accordance with the present invention. Barrier layer 12 and skin layer 14 form a barrier film which is formed into a reservoir to contain active drug 17 therein. The opening to the reservoir is covered by a controlled release membrane 20. An adhesive 18, which may either be peripherally applied or applied over the entire area of membrane 20, acts to secure system 16 to a patient's skin. Again, the adhesive which is selected should be compatible with the active drug and permeable to the drug. Preferably, a release liner 23 or the like covers and protects the adhesive 18 and membrane 20 prior to use.

Fig. 5 illustrates a typical reusable ostomy bag 24 including an opening 26 formed from the multilayer barrier films of either Figs. 1 or 2. The bag may be formed by folding and heat sealing the edges of multilayer film 10. The film is preferably folded and sealed such that one heat sealable skin layer provides the inner surface of the bag or pouch 24. The barrier film of the present invention provides softness and quietness features which are desirable for ostomy applications, as well as moisture resistance and odor and oxygen barrier properties. As will be appreciated by those skilled in the art, the barrier films of the present invention may also find use in other packaging applications where moisture and oxygen barrier properties are required.

In order that the invention may be more readily understood, reference is made to the following examples, which are intended to be illustrative of the invention, but are not intended to be limiting in scope.

Example 1

A five-layer barrier film was produced in accordance with the present invention and included a core barrier layer, two outer skin layers, and two intermediate tie layers joining the core and outer skin layers together. The layers were coextruded using conventional techniques. The core barrier layer was Saran® 469, commercially available from The Dow Chemical Company and included 4 percent by weight of a processing aid (Elvax® 3180 resin available from E.I. du Pont de Nemours & Co., Inc.). The two outer skin layers comprised a thermoplastic polyurethane (Pellathane® 2355-95AE, available from The Dow Chemical Company) which included 5 percent by weight of a slip additive (Akzo 16LB15, commercially available from Akzo Chemicals Inc.). The two intermediate tie layers were also a thermoplastic polyurethane (Pellathane® 2355-95AE).

The resulting multilayer barrier film had a thickness of approximately 2.0 mils and an ultimate tensile strength (ASTM D-882) of 12,330 (MD) and 7,492 (TD) psi, respectively. The film had an oxygen transmission rate (ASTM D-3985) of 0.39 cc/100 in²/day·atm and a water vapor transmission rate (Permatran W) of 0.181 gm/100 in²/day. The film also had a 2 percent secant modulus (ASTM method D-882 using an Instron tensile tester) of 18,450 psi (MD) and 21,180 psi (TD).

Example 2

Three different five-layer barrier films were produced in accordance with the present invention, and each film included a core barrier layer, two outer skin layers, and two intermediate tie layers joining the core and outer skin layers together. The layers were coextruded using conventional techniques. The core barrier layer in each instance was Saran[®] 469, commercially available from The Dow Chemical Company and included 4 percent by weight of a processing aid (Elvax[®] 3180 resin (28 percent vinyl acetate, 25 melt index) available from E.I. du Pont de Nemours & Co., Inc.). The two outer skin layers comprised the polyolefin resins reported in Table 1 below. The two intermediate tie layers were copolymers of ethylene and vinyl acetate available from Exxon Corp. under the designation Exxon LD 740.16 (23 percent vinyl acetate, 5 melt index).

The resulting multilayer barrier films had nominal thicknesses of approximately 3.0 mils, with the core layer and tie layers making up approximately 10 percent of the film thickness and the outer skin layers making up approximately 90 percent. The films also had a 2 percent secant modulus (ASTM method D-882 using an Instron tensile tester) as reported below.

These films were tested for quietness by forming a 4"x4" piece of the film into a cylinder and flexing the film through an angle of 65° at a frequency of 0.45 Hz and measuring the sound level in decibels (dB). Data are reported in Table 1 below. The noise levels show the improved quietness for the substantially linear α -olefin polymers (Samples 2 and 3) of the present invention versus conventional low density polyethylene (Sample 1).

Example 3

Three samples of four-layer barrier films were produced in accordance with the present invention, and each film included a core barrier layer, a tie layer and a seal layer, and an outer skin layer. The layers were coextruded using conventional techniques. The core barrier layer in each instance was Saran[®] 469, commercially available from The Dow Chemical Company and included 4 percent by weight of a processing aid (Elvax[®] 3180 resin (28 percent vinyl acetate, 25 melt index) available from E.I. du Pont de Nemours & Co., Inc.). The outer skin layer comprised the polyolefin resins reported in Table 2 below. The intermediate tie layer and seal layer were copolymers of ethylene and vinyl acetate available from Exxon Corp. under the designation Exxon LD 740.16 (23 percent vinyl acetate, 5 melt index). The resulting multilayer barrier films had nominal thicknesses of approximately 4.0 mils, with the core layer and tie layer making up

TABLE 1

Sample # (psi)	Polymer Resin	Noise (dB)	2% secant Modulus	
			MD (psi)	TD
1	Low density polyethylene (0.9245 g/cc, 1.9 MI)	89	23,000	23,000
2	Blend of 50% CGCT substantially linear ethylene/ α -olefin copolymer (0.909 g/cc, 3.2 MI)/50% CGCT substantially linear ethylene/ α -olefin copolymer (0.870 g/cc, 1.0 MI)	81	9,500	11,000
3	Blend of 25% CGCT substantially linear ethylene/ α -olefin copolymer (0.909 g/cc, 3.2 MI)/75% CGCT substantially linear ethylene/ α -olefin copolymer (0.870 g/cc, 1.0 MI)	81	8,600	9,000

approximately 10 percent of the film thickness. The seal layer represented approximately 20 percent of the film thickness, while the outer skin layer made up the remainder of the structure.

These films were tested for quietness by forming a 4"x4" piece of the film into a cylinder and flexing the film through an angle of 65° at a frequency of 0.45 Hz and measuring the sound level in decibels (dB). Data are reported in Table 2 below. The noise levels show the improved quietness for the substantially linear α -olefin polymers (Sample 2) of the present invention versus conventional low density polyethylene (Sample 1). Comparable noise levels are shown in comparison to a commercial film with a chlorinated polyethylene resin (Sample 3).

TABLE 2

Sample # (psi)	Polymer Resin	Noise (dB)	2% secant Modulus	
			MD (psi)	TD
1	Low density polyethylene (0.925 gm/cc, 1.9 MI)	86	27,000	28,000
2	Blend of 50% CGCT substantially linear ethylene/ α -olefin copolymer (0.909 g/cc, 3.2 MI)/50% CGCT substantially linear ethylene/ α -olefin copolymer (0.870 g/cc, 1.0 MI)	81	17,000	17,000
3	Chlorinated polyethylene	80	17,000	17,000

Example 4

To demonstrate the quietness of the skin layers used in the multilayer barrier films of the present invention, a number of monolayer films were prepared using a cast film process. Monolayer films of a thermoplastic polyurethane and a substantially linear ethylene/ α -olefin copolymer of the present invention were cast and tested for comparison purposes against prior art chlorinated polyethylene and homogeneously-branched polyethylene films.

The monolayer films were tested for quietness by forming a 4"x4" piece of the film having a 2.0 mil thickness into a cylinder and flexing the film through an angle of 65° at a frequency of 0.45 Hz and measuring the sound level in decibels (dB). Data are reported in Table 3 below. The data show that the films using the thermoplastic polyurethane (Samples 6 and 7) and constrained geometry catalyst technology (CGCT) linear ethylene/ α -olefin copolymers (Samples 3-5) of the present invention were at least comparable in quietness to chlorinated polyethylene (Sample 8) and better than other conventional low density polyethylene films (Samples 1 and 2) in commercial use. The films also had a 2 percent secant modulus (ASTM method D-882 using an Instron tensile tester) as reported below.

TABLE 3

Sample # (psi)	Polymer Resin	Noise (dB)	2% secant Modulus	
			MD (psi)	TD
1	Ultra low density polyethylene (Dow Attane [®] 4202, 0.912 g/cc, 3.2 MI)	86	16,000	16,500
2	Linear low density polyethylene (Dow Dowlex [®] 2047, 0.917 g/cc, 2.3 MI)	85	18,000	18,500
3	CGCT substantially linear ethylene/ α -olefin copolymer (0.9096 g/cc, 4.7 MI)	79.5	11,500	11,500
4	CGCT substantially linear ethylene/ α -olefin copolymer (0.9015 g/cc, 4.5 MI)	83.5	8,500	8,000
5	CGCT substantially linear ethylene/ α -olefin copolymer (0.8966 g/cc, 1.9 MI)	80.5	6,500	6,500
6	Thermoplastic polyurethane (Dow Pellathane [®] 2355-95AE)	81.5	7,000	7,000
7	Thermoplastic polyurethane (Dow Pellathane [®] 2363-90AE)	79.5	5,000	5,000
8	Chlorinated polyethylene	79.5	4,000	4,000

While certain representative embodiments and details have been shown for purposes of illustrating the invention, it will be apparent to those skilled in the art that various changes in the methods and apparatus disclosed herein may be made without departing from the scope of the invention, which is defined in the appended claims.

CLAIMS

1. An oxygen and moisture impermeable multilayer barrier film having a heat seal strength of at least 1.0 lb/inch width of said film, said film comprising a barrier layer and at least one heat sealable skin layer, said skin layer comprising a thermoplastic polymer having a 2 percent secant modulus of less than 15,000 psi in both the machine and transverse directions, said barrier film exhibiting a noise of less than 85 dB when subjected to flexing through a 65° angle at 0.45 Hz.
2. The multilayer barrier film of claim 1 wherein said skin layer comprises either a thermoplastic polyurethane, a substantially linear copolymer of ethylene and an α -olefin resin having a density in the range of from 0.87-0.92 gm/cc and from 0.01 to 3 long chain branches/1000 carbon atoms along the polymer backbone, or a homogeneously-branched linear olefin resin.
3. The multilayer barrier film of claim 1 wherein said heat sealable skin layer comprises a thermoplastic polyurethane, and said skin layer contains from 0 to 10 percent by weight of a copolymer of ethylene and vinyl acetate.
4. The multilayer barrier film of claim 1 wherein said barrier layer is selected from the group consisting of a homopolymer of vinylidene chloride, a copolymer of vinylidene chloride with vinyl chloride or methyl methacrylate.
5. The multilayer barrier film of claim 1 wherein said film has an oxygen transmission rate of less than 90 cc/m²/day-atm.
6. The multilayer barrier film of claim 1 wherein said barrier layer is positioned between two heat sealable skin layers.
7. The multilayer barrier film of claim 6 wherein said skin layers comprise 70 percent by weight of said film and said moisture barrier layer comprises 30 percent by weight of said film.
8. The multilayer barrier film of claim 1 wherein said skin layers contain from 0.5-5 percent by weight of a slip additive/antiblocking agent package.
9. The multilayer barrier film of claim 3 wherein said skin layers contain from 1-10 percent by weight of a copolymer of ethylene and vinyl acetate.
10. The multilayer barrier film of claim 1 wherein said skin layer is a substantially linear copolymer of ethylene and an α -olefin having a density in the range of from 0.87-0.92 gm/cc, from 0.01 to 3 long chain branches/1000 carbon atoms along the polymer backbone.
11. The multilayer barrier film of claim 10 including an intermediate tie layer of a copolymer of ethylene and vinyl acetate between said barrier layer and said skin layer.

12. The multilayer barrier film of claim 1 wherein said barrier layer comprises a homopolymer of vinylidene chloride or a copolymer of vinylidene chloride with vinyl chloride or methyl methacrylate, and from 1-6 percent of a copolymer of ethylene and vinyl acetate.

13. The multilayer barrier film of claim 1 wherein said barrier film further
5 includes:

a) an adhesive containing an active drug adhered to one surface of said barrier film; and

b) a controlled release membrane adjacent said adhesive and adapted to controllably release said drug to a patient's skin.

14. The multilayer barrier film of claim 13 further including an adhesive
10 adhered to a least a portion of said controlled release membrane and a release liner overlying said adhesive and release membrane to form a system for transdermal delivery of drugs.

15. The multilayer barrier film of claim 13 wherein said at least one skin layer is heat sealed along its edges to form a bag or pouch.

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FIG-1

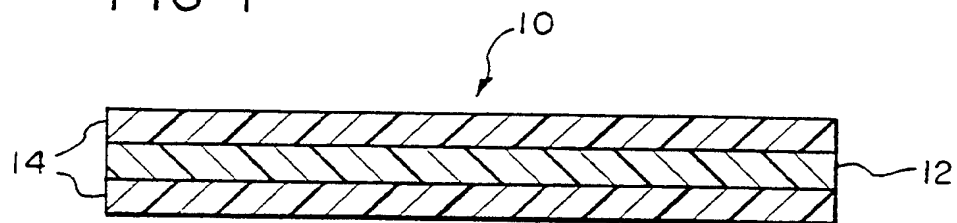


FIG-2

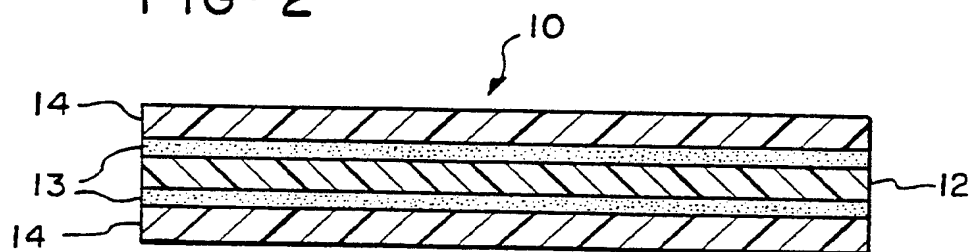


FIG-3

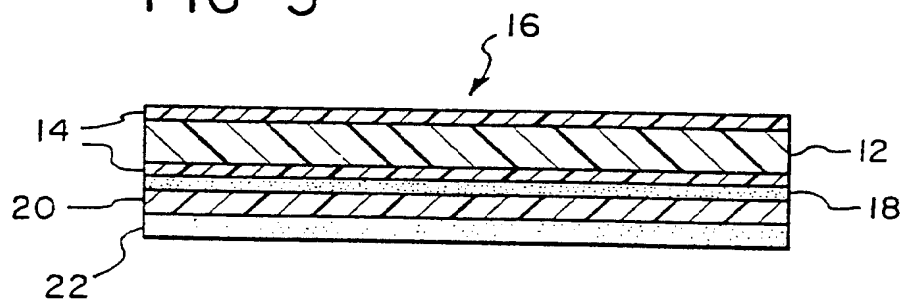


FIG-4

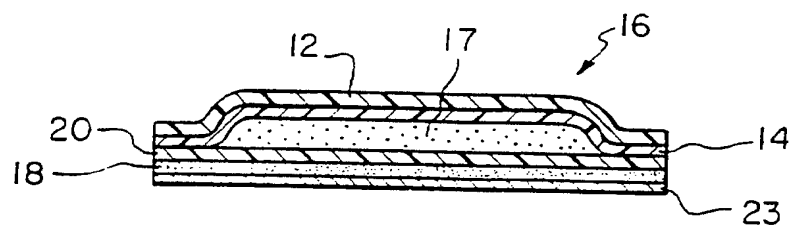
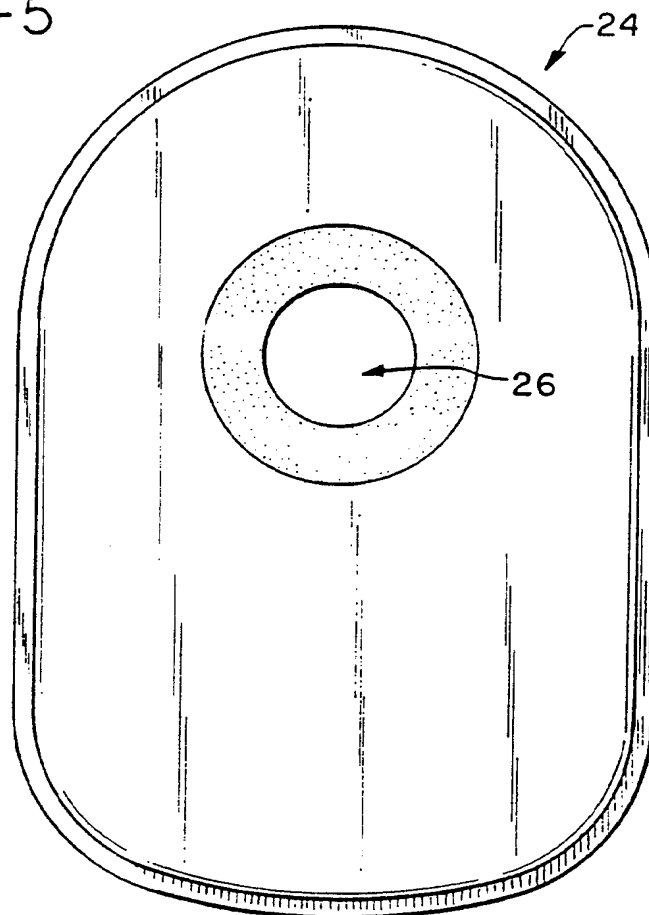


FIG-5



INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 94/09229

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B27/08 B65D65/40 A61F5/445

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)

IPC 6 B32B A61F

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 318 025 (W.R. GRACE & CO.) 31 May 1989	1,4-8,15
Y	see column 1, line 1 - line 25 see column 1, line 40 - line 52 see column 2, line 7 - line 12 see column 2, line 42 - column 3, line 1 see column 3, line 7 - line 18 ---	3
A	DATABASE WPI Week 8831, Derwent Publications Ltd., London, GB; AN 88-218087 see abstract & RESEARCH DISCLOSURE, RD290014, 6 October 1988, HAVANT GB ANONYMOUS 'STRETCHED SILANE CROSSLINK PLASTIC PRODUCT' --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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

2 December 1994

Date of mailing of the international search report

23.12.94

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De Jonge, S

INTERNATIONAL SEARCH REPORT

Internat. Application No.

PCT/US 94/09229

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 435 792 (AMERICAN NATIONAL CAN COMPANY) 3 July 1991 see abstract see page 2, line 38 - page 3, line 1 see page 4, line 1 - page 5, line 12 see example 1 see page 9, line 48 - line 51 see figure 1B ---	1,4-7,15
X	EP,A,0 366 802 (KURARAY CO. LTD.) 9 May 1990 see page 2, line 22 - page 3, line 14 see page 11, line 10 - line 26 see page 13, line 3 - line 21 see page 14, line 13 - line 19 see page 19, line 6 - line 19 see table 1 ---	1,4-7, 11-15
X	WO,A,93 11938 (MINNESOTA MINING AND MANUFACTURING) 24 June 1993 see claims 1-8,18,21,25 see page 4, line 36 - page 5, line 23 see page 6, line 17 - line 23 see page 7, line 9 - line 18 see page 14, line 4 - line 40 see page 15, line 1 - line 7 see page 15, line 28 - line 39 see page 16, line 18 - line 29 ---	1,5-7,9, 13-15
Y	EP,A,0 240 886 (WOLFF WALSRODE AKTIENGESELLSCHAFT) 14 October 1987 see claim 1 ---	3
A	EP,A,0 524 775 (DOW CORNING CORPORATION) 27 January 1993 see claims 1-4 -----	13,14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/09229

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EP-A-0435792	03-07-91	NONE	
EP-A-0366802	09-05-90	WO-A- 8908464	21-09-89
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EP-A-0240886	14-10-87	DE-A- 3612160 AU-B- 587541 AU-A- 7146687 JP-A- 62244635 US-A- 4830918	15-10-87 17-08-89 15-10-87 26-10-87 16-05-89
EP-A-0524775	27-01-93	US-A- 5300299 JP-A- 5202349 US-A- 5352722	05-04-94 10-08-93 04-10-94

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES
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Internationales Büro



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Zur Erklärung der Zweibuchstaben-Codes, und der anderen
Abkürzungen wird auf die Erklärungen ("Guidance Notes on
Codes and Abbreviations") am Anfang jeder regulären Ausgabe
der PCT-Gazette verwiesen.

(54) Title: POLYMER MIXTURE CONTAINING AN AMORPHOUS POLYOLEFIN WHICH CONTAINS CYCLOALIPHATIC
OLEFINS

(54) Bezeichnung: POLYMERGEMISCH ENTHALTEND EIN AMORPHES POLYOLEFIN ENTHALTEND CYCLOALIPHA-
TISCHE OLEFINEN

(57) Abstract: The invention relates to a novel transparent polymer mixture with modified relaxation and contraction characteris-
tics, containing cycloolefinic polymers. The inventive polymer mixture contains at least one amorphous polyolefin and is used for
producing mono- or biaxially oriented foils, blister packs, films and mixtures with other plastics, especially polyolefins. The polymer
mixture is used in injection moulding, injection-blow moulding and blow extrusion moulding.

(57) Zusammenfassung: Die vorliegende Erfindung beschreibt eine neue transparente Polymermischung mit verändertem Relaxa-
tions- und Schrumpfverhalten enthaltend Cycloolefinpolymere. Die Polymermischung enthält mindestens ein amorphes Polyolefin.
Die Polymermischung wird zur Herstellung von mono- oder biaxial orientierten Folien, Blisterverpackungen, Filmen, Gemischen
mit anderen Kunststoffen, besonders Polyolefinen verwendet. Die Polymermischung wird beim Spritzguss, Spritzblasen und Blas-
extrusion verwendet.



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Beschreibung

POLYMERGEMISCH ENTHALTEND EIN AMORPHES POLYOLEFIN ENTHALTEND CYCLOALIPHATISCHE OLEFINEN

Die vorliegende Erfindung betrifft eine neue transparente Polymermischung mit verändertem Relaxations- und Schrumpfverhalten enthaltend Cycloolefinpolymere.

- 5 Das Relaxationsverhalten von Polymeren beschreibt die Veränderung des Elastizitätsmoduls als Funktion von Temperatur und Frequenz. Das Relaxationsverhalten eines Cycloolefinpolymers oder bekannten Cycloolefingemisches zeigt einen steilen Abfall des Elastizitätsmoduls innerhalb eines engen Temperaturbereiches, dem sogenannten Glasumwandlungs- oder
- 10 Erweichungsbereich.

Das Schrumpfverhalten beschreibt die Längenänderung mono- oder biaxial orientierter Probekörper als Funktion von Temperatur oder Zeit.

- In Delfolie et al, Makromolecules 32, 1999, 7781 - 7789, wird die Mischbarkeit von Ethylen-Norbornen-Copolymeren untersucht. Die Grenzen der Mischbarkeit werden
- 15 mittels DSC aufgezeigt: Das Auftreten einer einzelnen Glasumwandlungstemperatur wird als Maß für Mischbarkeit angesehen, während die Unmischbarkeit sich im Auftreten zweier separierter Glasstufen äußert.

- In Utracki, Polymer Alloys and Blends-Thermodynamics and Rheology, 2nd edition, Munich, Hanser 1989, 3ff, wird allgemein der Elastizitätsmodulus als Funktion der
- 20 Temperatur für 50/50 Polymermischungen in der Nähe der Glasumwandlungstemperatur beschrieben. Für homogen mischbare Polymere wird ein steiler Abfall des Modulus bei einer mittleren Glasumwandlungstemperatur beobachtet. Für unmischbare Polymere werden zwei Sprünge im Elastizitätsmodul und somit zwei Glasumwandlungstemperaturen beobachtet, die denen der
- 25 Ausgangsstoffe entsprechen. Für teilweise mischbare Polymere werden zwei Sprünge im Elastizitätsmodul und somit zwei Glasumwandlungstemperaturen beobachtet, die von denen der Ausgangsstoffe leicht abweichen. Für unmischbare

Polymere mit feiner Dispersion unter 15 nm sog. verträgliche Polymere wird ein breites Gebiet der Glasumwandlungstemperatur mit einem leichten Abfall des Elastizitätsmodulus beobachtet

In Hsiue und Ye, J. Appl. Pol. Sci. 37, 1989, 2803 – 2836, wird das

- 5 Schrumpfverhalten von verstreckten Polyesterfolien oberhalb der Glastemperatur beschrieben. Es wird aufgezeigt, daß das Schrumpfverhalten amorpher Polymere in diesem Bereich durch die Verschlaufung der Polymerketten bestimmt wird. Eine Erhöhung des Molekulargewichtes und eine Absenkung der Verstreckungstemperatur führen zu einem stärkeren Schrumpfen.
- 10 In US-A-5,824,398 und US-A-5,589,126 wird aufgezeigt, daß durch Zugabe eines Weichmachers zu Polyester die Temperatur des Schrumpfbeginns orientierter Folien zu tieferen Temperaturen verschoben wird.

Ein wesentlicher Nachteil des steilen Abfalles des Elastizitätsmoduls mit der Temperatur ist, daß die Dehnung von Probekörpern nur in einem engen

- 15 Temperaturbereich möglich ist. Das ist beispielsweise relevant beim mono- oder biaxialen Verstrecken von Folien. Der steile Abfall des Elastizitätsmoduls als Funktion der Temperatur bewirkt darüber hinaus eine schnell Änderung des Schrumpfes von verstreckten Folien mit der Temperatur. Dadurch können hergestellte Folien nur unzureichend auf ungleichmäßig geformte Probekörper
- 20 aufgeschrumpft werden. Die starke Längenänderung orientierter Probekörper mit der Temperatur übt zusammen mit einem hohen Verschlaufungsgrad der Polymerketten eine starke Schrumpfkraft auf dem Probekörper aus, was bei einer geringen Wandstärke zu einer unerwünschten Volumenänderung führen kann. Daher bestand seit langem die Bestrebung, einen Weg zu finden, um die Temperaturabhängigkeit
- 25 des Elastizitätsmoduls im Glasübergangsbereich und des Schrumpfes unter gleichzeitiger Wahrung der Transparenz zu beeinflussen.

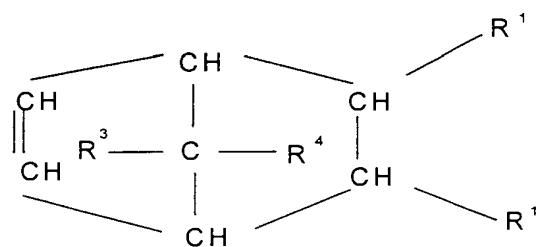
Die Aufgabe der vorliegenden Erfindung liegt darin, eine neue transparente Polymermischung, enthaltend Cycloolefinpolymere, mit verändertem Relaxations- und Schrumpfverhalten bereitzustellen.

Die Aufgabe der vorliegenden Erfindung wird gelöst durch ein Polymergemisch enthaltend mindestens ein amorphes Polyolefin. Die Zugabe eines amorphen Polyolefins bewirkt überraschend eine unerwartete Änderung des Elastizitätsmoduls und des Schrumpfverhaltens mit der Temperatur.

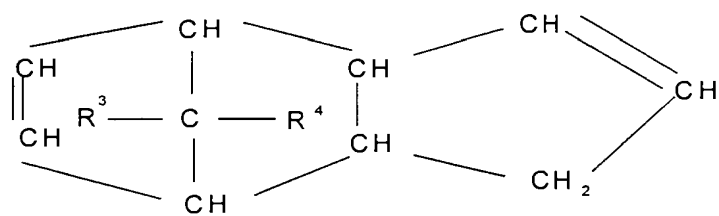
- 5 Das erfindungsgemäße Gemisch enthält bevorzugt mindestens ein Cycloolefinpolymer. Die Zugabe mindestens eines amorphen Polyolefins zum Cycloolefinpolymer bewirkt gute Ergebnisse bei der Änderung des Elastizitätsmoduls und des Schrumpfverhaltens mit der Temperatur.

- 10 Das erfindungsgemäße Gemisch enthält bevorzugt mindestens ein amorphes Cycloolefinpolymer. Die Zugabe mindestens eines amorphen Cycloolefinpolymer zu einem Cycloolefinpolymer bewirkt besonders gute Ergebnisse bei der Änderung des Elastizitätsmoduls und des Schrumpfverhaltens mit der Temperatur.

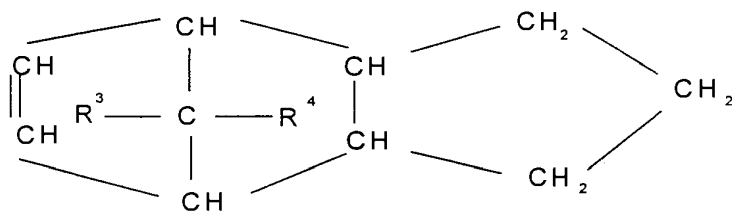
- 15 Das erfindungsgemäße Gemisch enthält mindestens ein Cycloolefinpolymer, enthaltend 0,1 Gew.-% bis 100 Gew.-%, bevorzugt 0,1 Gew.-% bis 99,9 Gew.-%, bezogen auf die Gesamtmasse des Cycloolefincopolymers, polymerisierte Einheiten, welche sich ableiten von mindestens einem polycyclischen Olefin der Formeln I, II, II', III, IV, V oder VI



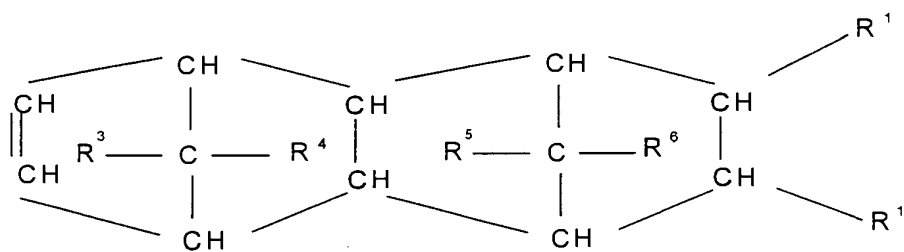
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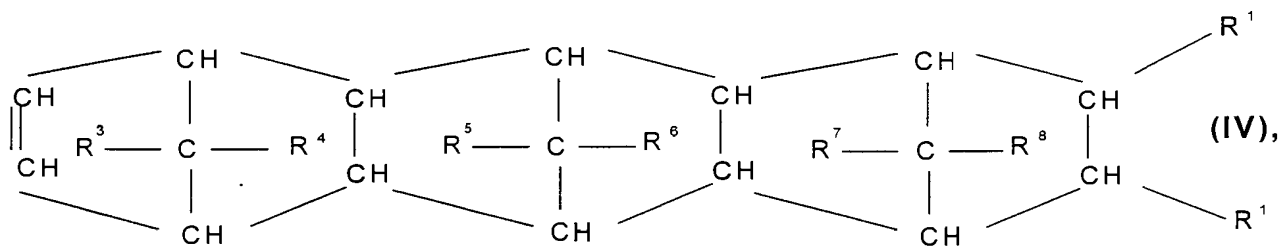
(II),



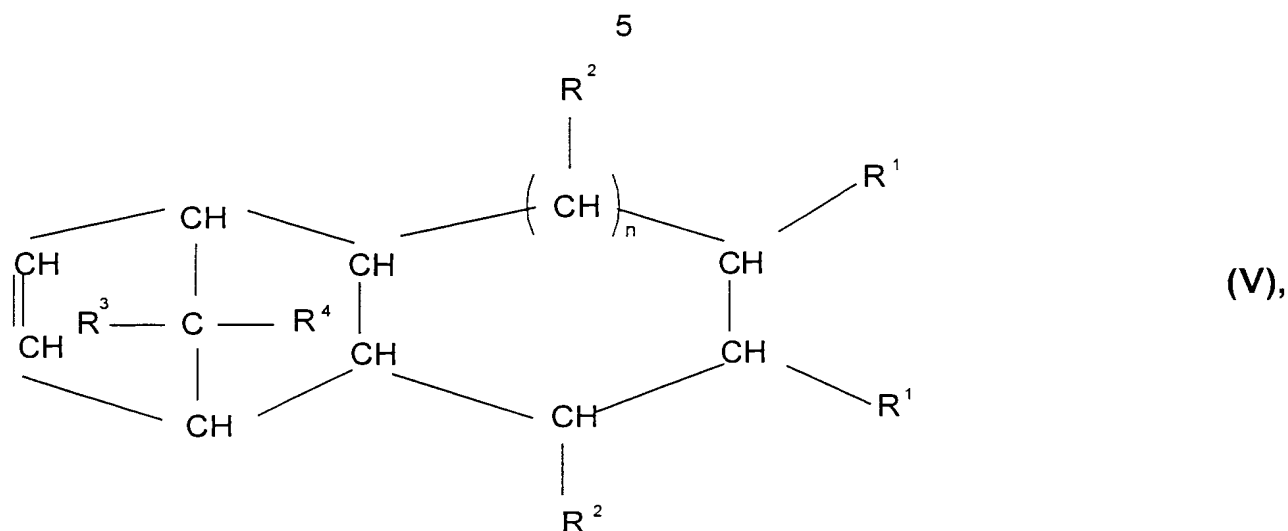
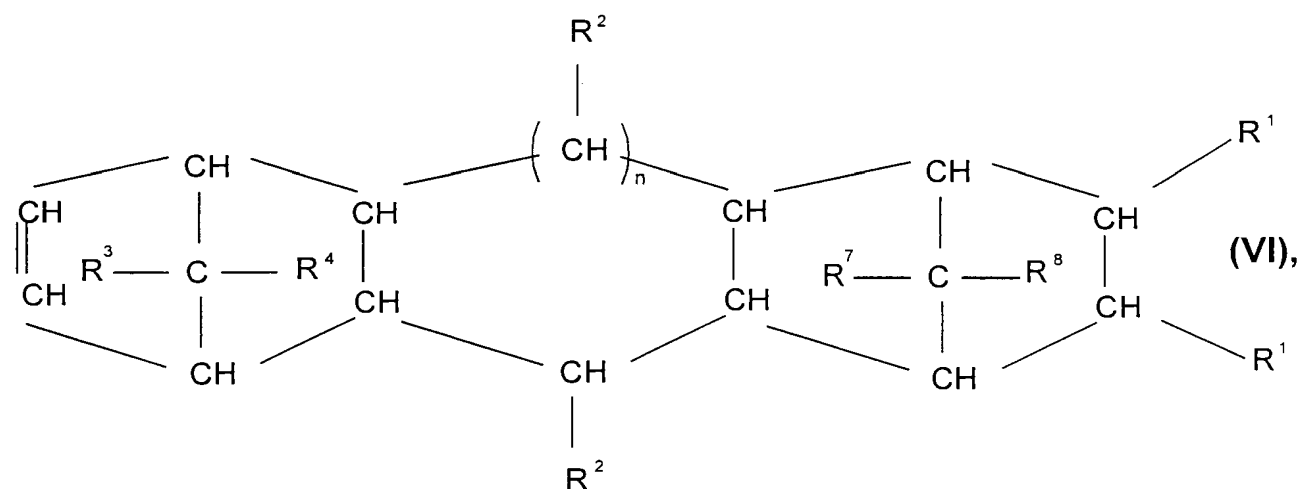
(II'),



(III),



(IV),



worin R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 und R^8 gleich oder verschieden sind und ein Wasserstoffatom oder einen C_1 - C_{20} -Kohlenwasserstoffrest, wie einen linearen oder verzweigten C_1 - C_8 -Alkylrest, C_6 - C_{18} -Arylrest, C_7 - C_{20} -Alkylenarylrest, einen cyclischen oder acyclischen C_2 - C_{20} -Alkenylrest bedeuten, oder einen gesättigten, ungesättigten oder aromatischen Ring bilden, wobei gleiche Reste R^1 bis R^8 in den verschiedenen Formeln I bis VI eine unterschiedliche Bedeutung haben können, worin n Werte von 0 bis 5 annehmen kann, und enthaltend 0 bis 99,9 Gew.-%, bevorzugt 0,1 bis 99,9 Gew.-%, bezogen auf die Gesamtmasse des Cycloolefincopolymers, polymerisierte Einheiten, welche sich ableiten von einem oder mehreren acyclischen Olefinen der Formel VII



worin R^9 , R^{10} , R^{11} und R^{12} gleich oder verschieden sind und ein Wasserstoffatom, einen linearen, verzweigten, gesättigten oder ungesättigten C_1 - C_{20} -Kohlenwasserstoffrest wie einen C_1 - C_8 -Alkylrest oder einen C_6 - C_{18} -Arylrest bedeuten.

Außerdem können die erfindungsgemäß verwendeten Cycloolefincopolymere 0 bis 45 Gew.-%, bezogen auf die Gesamtmasse des Cycloolefincopolymers, polymerisierte Einheiten enthalten, welche sich ableiten von einem oder mehreren monocyclischen Olefinen der Formel VIII



10 worin m eine Zahl von 2 bis 10 ist.

Bei den cyclischen Olefinen sind ebenfalls Derivate dieser cyclischen Olefine mit polaren Gruppen, wie Halogen-, Hydroxyl-, Ester-, Alkoxy-, Carboxy-, Cyano-, Amido-, Imido- oder Silylgruppen, eingeschlossen.

15 Bevorzugt im Sinne der Erfindung sind Cycloolefincopolymere, die polymerisierte Einheiten enthalten, welche sich ableiten von polycyclischen Olefinen der Formeln I oder III, und polymerisierte Einheiten, welche sich ableiten von acyclischen Olefinen der Formel VII.

Besonders bevorzugt sind Cycloolefincopolymere, die polymerisierte Einheiten enthalten, welche sich ableiten von Olefinen mit Norbornengrundstruktur, ganz

besonders bevorzugt von Norbornen und Tetracyclododecen und gegebenenfalls Vinylnorbornen oder Norbornadien.

Besonders bevorzugt sind auch Cycloolefincopolymere, die polymerisierte Einheiten enthalten, welche sich ableiten von acyclischen Olefinen mit endständigen

- 5 Doppelbindungen wie α -Olefinen mit 2 bis 20 C-Atomen, ganz besonders bevorzugt Ethylen oder Propylen. Außerordentlich bevorzugt sind Norbornen/ Ethylen- und Tetracyclododecen/ Ethylen-Copolymere.

Bei den Terpolymeren sind besonders bevorzugt Norbornen/Vinylnorbornen/ Ethylen-, Norbornen/Norbornadien/Ethylen-, Tetracyclododecen/Vinylnorbornen/ Ethylen-,

- 10 Tetracyclododecen/Vinyltetracyclododecen/Ethylen-Terpolymere oder Norbornen/Dicyclopentadien/Ethylen. Der Anteil der polymerisierten Einheiten, die sich ableiten von einem Polyen, bevorzugt Vinylnorbornen oder Norbornadien, liegt bei 0,1 bis 50 mol-%, vorzugsweise bei 0,1 bis 20 mol-%, der Anteil des acyclischen Monoolefins der Formel VII beträgt 0 bis 99,9 mol-%, bevorzugt 5 bis 80 mol-%,
- 15 bezogen auf die Gesamtzusammensetzung des Cycloolefinpolymers. In den beschriebenen Terpolymeren liegt der Anteil des polycyclischen Monoolefins bei 0,1 bis 99,9 mol-%, bevorzugt 3 bis 75 mol-%, bezogen auf die Gesamtzusammensetzung des Cycloolefinpolymers.

Weitere geeignete Polymere werden in EP-A-317262 beschrieben. Hydrierte

- 20 Polymere und Copolymere, wie von Styrol oder Dicyclopentadien und anderen amorphen Polyolefinen sind ausdrücklich ebenfalls geeignet.

Abmischungen dieser Polymere mit typischen Kunststoffadditiven wie Antioxidantien, Metalldesaktivatoren, Lichtschutzmitteln, Weichmachern, Gleitmitteln,

Verarbeitungshilfsmitteln, Antistatika, Optische Aufheller, Biostabilisatoren

- 25 Brandschutzmittel, Pigmente, Farbstoffe sowie Füll- und Verstärkungsmittel (siehe auch Gächter, Müller, Plastics Additive Handbook, 4th edition, 1993, München, Hanser) sind ausdrücklich ebenfalls geeignet.

Die erfindungsgemäß verwendeten Cycloolefincopolymere können hergestellt werden bei Temperaturen von -78 bis 200 °C und einem Druck von 0,01 bis 200 bar,

in Gegenwart eines oder mehrerer Katalysatorsysteme, welche mindestens eine Übergangsmetallverbindung und gegebenenfalls einen Cokatalysator und gegebenenfalls ein Trägermaterial enthalten. Als Übergangsmetallverbindungen eignen sich Metallocene, insbesondere stereorigide Metallocene. Beispiele für

5 Katalysatorsysteme, welche für die Herstellung der erfindungsgemäßen Cycloolefincopolymere geeignet sind, sind beschrieben in US-A-5,008,356, EP-A-0 407 870, EP-A-0 485 893 und EP-A-0 503 422. Auf diese Referenzen wird hiermit ausdrücklich Bezug genommen. Die Offenbarung dieser Referenzen ist somit Bestandteil der vorliegenden Patentanmeldung.

10 Beispiele für eingesetzte Übergangsmetallverbindungen sind:

rac-Dimethylsilyl-bis-(1-indenyl)-zirkondichlorid,
 rac-Dimethylgermyl-bis-(1-indenyl)-zirkondichlorid,
 rac-Phenylmethylsilyl-bis-(1-indenyl)-zirkondichlorid,
 rac-Phenylvinylsilyl-bis-(1-indenyl)-zirkondichlorid,

15 1-Silacyclobutyl-bis-(1-indenyl)-zirkondichlorid,
 rac-Diphenylsilyl-bis-(1-indenyl)-hafniumdichlorid,
 rac-Phenylmethylsilyl-bis-(1-indenyl)-hafniumdichlorid,
 rac-Diphenylsilyl-bis-(1-indenyl)-zirkondichlorid,
 rac-Ethylen-1,2-bis-(1-indenyl)-zirkondichlorid,

20 Dimethylsilyl-(9-fluorenyl)-(cyclopentadienyl)-zirkondichlorid,
 Diphenylsilyl-(9-fluorenyl)-(cyclopentadienyl)-zirkondichlorid,
 Bis(1-indenyl)-zirkondichlorid,
 Diphenylmethylen-(9-fluorenyl)-cyclopentadienylzirkondichlorid,
 Isopropylen-(9-fluorenyl)-cyclopentadienyl-zirkondichlorid,

25 rac-Isopropyliden-bis-(1-indenyl)zirkondichlorid,
 Phenylmethylen-(9-fluorenyl)-cyclopentadienyl-zirkondichlorid,
 Isopropylen-(9-fluorenyl)-(1-(3-isopropyl)cyclopentadienyl)-zirkondichlorid,
 Isopropylen-(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)-zirkondichlorid,
 Diphenylmethylen-(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)-zirkondichlorid,

30 Methylphenylmethylen-(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)-zirkondichlorid,
 Dimethylsilyl-(9-fluorenyl)(1-(3-methyl)-cyclopentadienyl)-zirkondichlorid,

Diphenylsilyl-(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)-zirkondichlorid,

- Diphenylmethylen-(9-fluorenyl)(1-(3-tert.-butyl)cyclopentadienyl)-zirkondichlorid,
 Isopropylen-(9-fluorenyl)(1-(3-tert.-butyl)cyclopentadienyl)-zirkondichlorid,
 Isopropylen-(cyclopentadienyl)-(1-indenyl)-zirkondichlorid,
 Diphenylcarbyl-(cyclopentadienyl)-(1-indenyl)-zirkondichlorid,
 5 Dimethylsilyl-(cyclopentadienyl)-(1-indenyl)-zirkondichlorid,
 Isopropylen-(methylcyclopentadienyl)-(1-indenyl)-zirkondichlorid, 4-(η^5 -
 cyclopentadienyl)-4,7,7-trimethyl-(η^5 -4,5,6,7-tetrahydroindenyl)-zirkondichlorid,
 [4-(η^5 -cyclopentadienyl)-4,7,7-triphenyl-(η^5 -4,5,6,7-
 tetrahydroindenyl)]zirkondichlorid,
 10 [4-(η^5 -cyclopentadienyl)-4,7-dimethyl-7-phenyl-(η^5 -4,5,6,7-
 tetrahydroindenyl)]zirkondichlorid,
 [4-(η^5 -3'-tert.-butylcyclopentadienyl)-4,7,7-triphenyl-(η^5 -4,5,6,7-
 tetrahydroindenyl)]zirkondichlorid,
 [4-(η^5 -3'-tert.-butylcyclopentadienyl)-4,7-dimethyl-7-phenyl-(η^5 -4,5,6,7-
 15 tetrahydroindenyl)]zirkondichlorid,
 [4-(η^5 -3'-methylcyclopentadienyl)-4,7,7-trimethyl-(η^5 -4,5,6,7-
 tetrahydroindenyl)]zirkondichlorid,
 [4-(η^5 -3'-methylcyclopentadienyl)-4,7,7-triphenyl-(η^5 -4,5,6,7-
 tetrahydroindenyl)]zirkondichlorid,
 20 [4-(η^5 -3'-methylcyclopentadienyl)-4,7-dimethyl-7-phenyl-(η^5 -4,5,6,7-
 tetrahydroindenyl)]zirkondichlorid,
 [4-(η^5 -3'-isopropylcyclopentadienyl)-4,7,7-trimethyl-(η^5 -4,5,6,7-
 tetrahydroindenyl)]zirkondichlorid,
 [4-(η^5 -3'-isopropylcyclopentadienyl)-4,7,7-triphenyl-(η^5 -4,5,6,7-
 25 tetrahydroindenyl)]zirkondichlorid,
 [4-(η^5 -3'-isopropylcyclopentadienyl)-4,7-dimethyl-7-phenyl-(η^5 -4,5,6,7-
 tetrahydroindenyl)]zirkondichlorid,
 [4-(η^5 -cyclopentadienyl)(η^5 -4,5-tetrahydropentalen)]zirkondichlorid,
 [4-(η^5 -cyclopentadienyl)-4-methyl-(η^5 -4,5-tetrahydropentalen)]zirkondichlorid,
 30 [4-(η^5 -cyclopentadienyl)-4-phenyl-(η^5 -4,5-tetrahydropentalen)]zirkondichlorid,
 [4-(η^5 -cyclopentadienyl)-4-phenyl-(η^5 -4,5-tetrahydropentalen)]zirkondichlorid,
 [4-(η^5 -3'-methyl-cyclopentadienyl)(η^5 -4,5-tetrahydropentalen)]zirkondichlorid,

[4-(η^5 -3'-isopropylcyclopentadienyl)(η^5 -4,5-tetrahydropentalen)]zirkondichlorid,

[4-(η^5 -3'-benzyl-cyclopentadienyl)(η^5 -4,5-tetrahydropentalen)]zirkondichlorid,

[2,2,4Trimethyl-4-(η^5 -cyclopentadienyl)-(η^5 -4,5-tetrahydropentalen)]-

zirkoniumdichlorid,

- 5 [2,2,4Trimethyl-4-(η^5 -(3,4-Di-isopropyl)cyclopentadienyl)-(η^5 -4,5-tetrahydropentalen)]-zirkoniumdichlorid.

Die Herstellung der Cycloolefincopolymere kann auch auf anderen, nachfolgend kurz skizzierten Wegen erfolgen: Katalysatorsysteme basierend auf Mischkatalysatoren aus Titansalzen und Aluminiumorganylen werden in DD-A-109 224 und DD-A-237
10 070 beschrieben. EP-A-0 156 464 beschreibt die Herstellung mit Katalysatoren auf Vanadiumbasis.

Die Cycloolefincopolymere können auch durch ringöffnende Polymerisation mindestens eines der Monomere mit den Formeln I bis VI und anschließender Hydrierung der erhaltenen Produkte.

- 15 Die Polymerisation kann auch mehrstufig erfolgen, wobei auch Blockcopolymere entstehen können (DE-A-42 05 416).

- Cycloolefincopolymere sind bevorzugt amorphe, transparente Werkstoffe. Die Wärmeformbeständigkeiten der Cycloolefincopolymere lassen sich in einem weiten Bereich einstellen. Als Anhaltspunkt für die Wärmeformbeständigkeit, wie sie nach
20 ISO 75 Teil 1 und Teil 2 an Spritzgußformkörpern bestimmt werden kann, läßt sich für Cycloolefincopolymere die Glasübergangstemperatur heranziehen gemessen nach DIN EN ISO 11357-1 mit Hilfe einer DSC. Die beschriebenen Cycloolefincopolymere weisen Glasübergangstemperaturen zwischen -50 und 250 °C auf. Bevorzugt sind Glasübergangstemperaturen zwischen 0 und 220 °C,
25 besonders bevorzugt sind Glasübergangstemperaturen zwischen 40 und 200 °C.

Die mittlere Molmasse der Cycloolefincopolymere läßt sich durch Wasserstoff-Dosierung, Variation der Katalysatorkonzentration oder Variation der Temperatur in

bekannter Weise steuern. Die in den erfindungsgemäßen mikrostrukturierten Bauteilen enthaltenen Cycloolefincopolymere weisen massenmittlere Molmassen M_w zwischen 1.000 und 10.000.000 g/mol auf. Bevorzugt sind massenmittlere Molmassen M_w zwischen 5.000 und 5.000.000 g/mol, besonders bevorzugt sind massenmittlere Molmassen M_w zwischen 5.000 und 1.200.000 g/mol. Diese mit Hilfe der Gelpermeationschromatographie (GPC) in Chloroform bei 35°C mit Hilfe eines RI Detektors bestimmten Molmassen sind relativ und beziehen sich auf eine Eichung mit engverteilten Polystyrolstandards.

Die hier beschriebenen Cycloolefincopolymere weisen gemäß DIN 53 728

Viskositätszahlen zwischen 5 und 5.000 ml/g auf. Bevorzugt sind Viskositätszahlen zwischen 5 und 2000 ml/g, besonders bevorzugt sind Viskositätszahlen zwischen 5 und 1000 ml/g.

Die optischen Eigenschaften der Polymermischungen wurden an 1 mm dicken Preßplatten mit dem Auge qualitativ beurteilt.

Die erfindungsgemäßen, transparente Polymermischung, enthaltend Cycloolefinpolymere, mit verändertem Relaxations- und Schrumpfverhalten können besonders für folgende Produkte eingesetzt werden. Mono- oder biaxial orientierte Folien mit geändertem Schrumpfverhalten. Produkte, bei denen durch erfindungsgemäßen Abmischungen ein zu den Ausgangsprodukten geänderte Wärmeformbeständigkeit erreicht wurde. Blisterverpackungen, bei denen durch die erfindungsgemäßen Abmischungen ein verändertes Thermoformbarkeit erreicht wurde. Mischungen mit anderen Kunststoffen, besonders Polyolefine bei denen durch die erfindungsgemäßen Abmischungen ein verändertes Relaxationsverhalten, Schrumpfverhalten oder Wärmeformbeständigkeit erzielt wurde. Durch Mono- oder biaxiale orientierte Folien, bei denen durch die erfindungsgemäßen Abmischungen ein breites Arbeitsfenster beim Verstrecken ermöglicht wird. Durch Spritzblasen hergestellte Probekörper wie Fläschchen bei denen durch die erfindungsgemäße Abmischungen ein breites Arbeitsfenster beim Aufblasen ermöglicht wird. Durch

Blasextrusion hergestellte Filme, bei denen durch die erfindungsgemäße Abmischungen ein breites Arbeitsfenster ermöglicht wird.

Die Erfindung wird nun anhand von Beispielen und Diagrammen näher erklärt.

Beispiel 1

- 5 500 g eines Norbornen-Ethylen Copolymer Granulates mit einer Glasstemperatur von 69 °C, einer VZ von 90 ml/g und $M_w = 120000$ g/mol (Handelsname Topas® 8006, Ticona GmbH, Frankfurt) wurden mit 500 g eines Norbornen-Ethylen Copolymer Granulates mit einer Glasstemperatur von 145 °C, einer VZ von 65 ml/g und $M_w = 70000$ g/mol (Handelsname Topas® 6013, Ticona GmbH, Frankfurt) auf einem
- 10 Rollstand homogenisiert. Das homogenisierte Gemisch wurde auf eine Spritzgußmaschine gegeben und bei einer Schmelzetemperatur von 250 °C Probekörper hergestellt. Die Probekörper waren transparent.

- An den Probekörpern wurden Glasstemperaturen bestimmt gemessen nach DIN EN ISO 11357-1 mit Hilfe einer DSC (TAInst 2920) bei einer Heizrate von 20 K/min in der
- 15 zweiten Heizkurve. Die Glasstemperatur (T_g) betrug 87 °C und der Temperaturunterschied zwischen Beginn und Mittelpunkt (T_g -Breite) 8,3 °C.

- Das Elastizitätsmodul und Tang Delta als Funktion der Temperatur wurden mit einem Torsionspendel bei einer Frequenz von 5 Hz und einer Heizrate von 5/min an Probekörpern der Abmessungen 50*10*1 mm bestimmt. Das Maximum von Tang
- 20 Delta (tang d max) wurde bei 97 °C beobachtet.

- Aus den Probekörpern wurden mittels einer Presse Folien mit einer Dicke von 1 mm hergestellt. Daraus wurden Proben von 20 mm 20 mm zugeschnitten. Diese Folien wurden mittels eines Zug-Dehnungs Meßgeräts (Instron) mit einer
- 25 Zuggeschwindigkeit von 500 mm/min bei 125 °C auf die fünffache Länge gedehnt und unter Zugspannung abgekühlt. Anschließend wurde die Längenänderung dieser verstreckten Folien als Funktion der Temperatur bestimmt. Bis zu einer

Temperaturen unter 90°C wurden die verstreckten Folien für 30 s im Wasserbad gelagert, oberhalb von 90 °C erfolgte die Lagerung für 180 s im

Umlufttrockenschrank auf Sand. Der Schrumpf ist die Längenänderung vor und nach der Warmlagerung geteilt durch die Ausgangslänge.

In der folgenden Tabelle sind weitere Beispiele und Vergleichsbeispiele zusammengefaßt:

	Bsp.2	V-Bsp.1	V-Bsp.2	V-Bsp.3	V-Bsp 4
Komponente 1	8006	8006	8006	8006	8006
Anteil / %	75	100	50	75	75
Komponente 2	6013	-	Zeonor 1060	Kraton G 1560	Topas TM
Anteil / %	25	0	50	25	25
Herstellung	Spritzguß	Spritzguß	Spritzguß	Extrusion	Extrusion
Transparenz	transparent	transparent	trüb	opak	transparent
Tg / °C	80	69	70/102	68	67
Tg-Breite / °C	6,8	4,7	5,9	6,3	7,4
Tan d max / °C	86	73	70/102	71	71
Verstreck T / °C	110	90	Nicht möglich	90	90

- 5 Zeonor 1060 ist ein amorphes Cycloolefinpolymer von Nippon Zeon Co. Ltd. (Japan) mit einer Glasumwandlungstemperatur von 106 °C.

Kraton G 1650 ist ein thermoplastisches lineares S-E/B-S Elastomer der Deutsche Shell Chemie GmbH, Eschborn.

Topas TM ist ein Norbornen-Ethylen Copolymer mit einer Glasstemperatur von 65 °C, einer VZ von 15 ml/g und $M_w = 10000$ g/mol der Ticona GmbH, Frankfurt.

- 5 Die vorliegende Erfindung wird anhand der Figuren 1 und 2 näher erläutert. Figur 1 zeigt die Elastizitätsmoduli der Beispiele und Vergleichsbeispiele als Funktion der Temperatur.

Figur 2 zeigt den Schrumpf der Beispiele und Vergleichsbeispiele als Funktion der Temperatur.

- 10 Beispiele 1 und 2 zeigen das gewünschte veränderte Relaxations- und Schrumpfverhalten unter Wahrung der Transparenz.

Vergleichsbeispiel 1 zeigt das bekannte Relaxations- und Schrumpfverhalten amorpher Polyolefine.

- 15 Vergleichsbeispiel 2 ist ein trübes Produkt, welches zwei separate Glasumwandlungstemperaturen aufweist. Die beiden Stoffe sind also nicht homogen mischbar. Ein Verstrecken war bei keiner Temperatur möglich.

Vergleichsbeispiel 3 ist eine opake Polymermischung, welche das bekannte Relaxations- und Schrumpfverhalten amorpher Polyolefine zeigt.

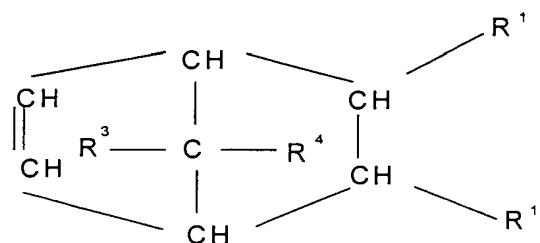
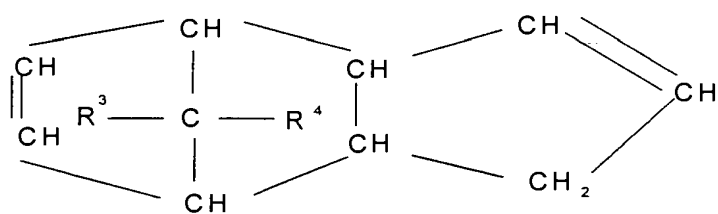
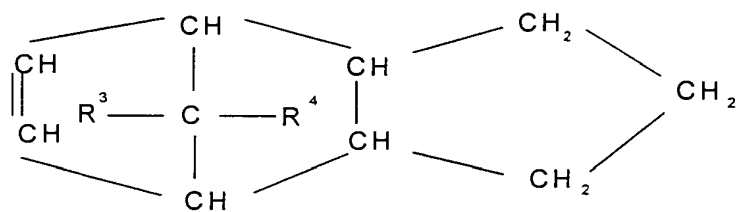
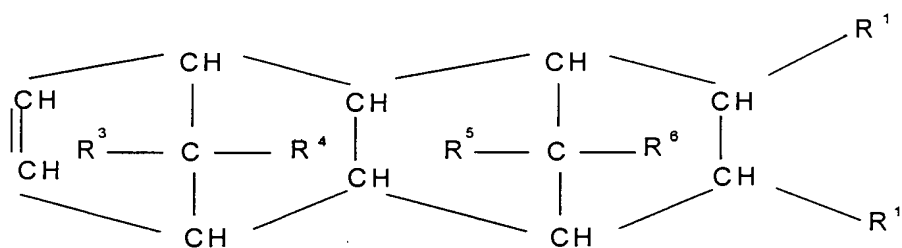
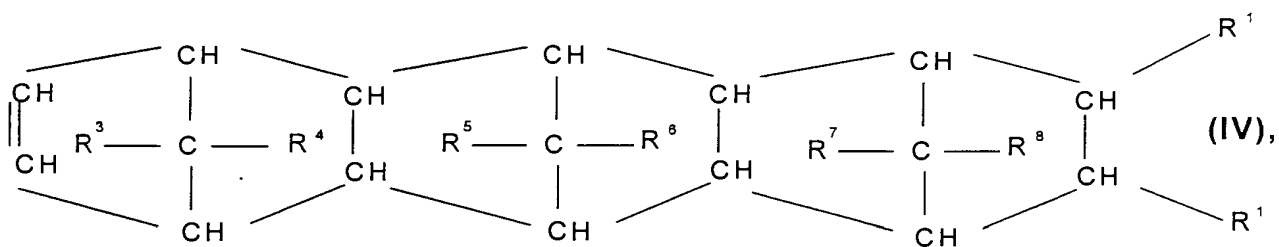
- 20 Vergleichsbeispiel 4 ist eine transparente Mischung amorpher Polyolefine, welche das bekannte Relaxations- und Schrumpfverhalten amorpher Polyolefine zeigt.

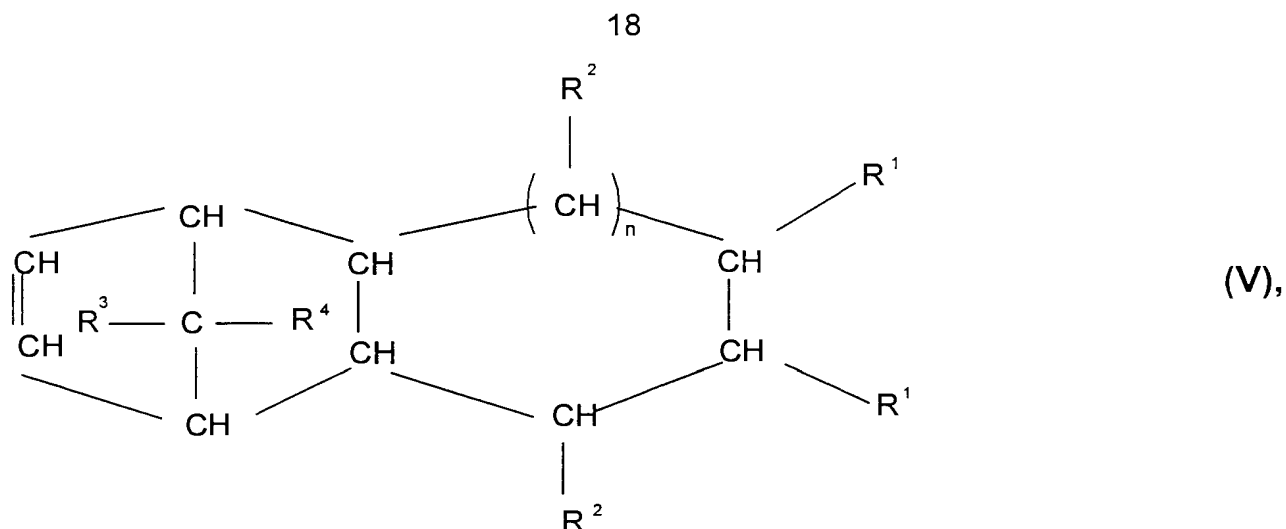
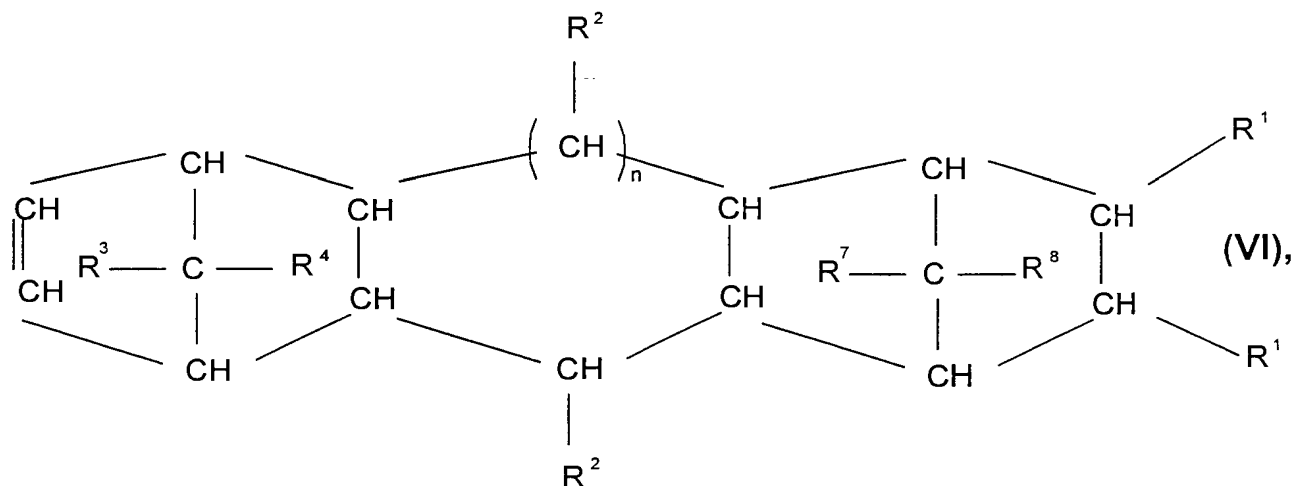
- Weiterhin können Weichmacher, wie Phthalsäureester, Phosphorsäureester, Ester der Adipin-, Azelanin- und Sebacinsäure, Fettsäureester, Epoxidierte Fettsäureester, Zitronensäureester, nieermolekulare Polyester, und Chlorierte Kohlenwasserstoffe, zugesetzt werden um die Glasumwandlungstemperatur und somit den Abfall des
- 25 Elastizitätsmoduls und den Schrumpfbeginn zu tieferen Temperaturen zu verschieben. Ausdrücklich besonders geeignet sind hochsiedende medizinischen

Weißöle wie Ondina 9xx (Deutsche Shell), Cobersol (Cölner Benzin Raffinerie) und Enerpar (BP Schmierstoffe), welche selbst eine geringe Eigenfärbung aufweisen und mit amorphen Polyolefinen transparente, farblose Mischungen ergeben.

Patentansprüche

1. Polymergemisch enthaltend mindestens ein amorphes Polyolefin.
2. Polymergemisch nach Anspruch 1, enthaltend mindestens ein Cycloolefinpolymer.
- 5 3. Polymergemisch nach Anspruch 1 oder 2, mindestens ein amorphes Cycloolefinpolymer.
4. Polymergemisch nach einem oder mehreren der Ansprüche 1 bis 3, enthaltend mindestens ein Cycloolefinpolymer, enthaltend 0,1 bis 100 Gew.-%, bevorzugt 0,1 bis 99,9 Gew.-%, bezogen auf die Gesamtmasse des
10 Cycloolefincopolymers, polymerisierte Einheiten, welche sich ableiten von mindestens einem polycyclischen Olefin der Formeln I, II, II', III, IV, V oder VI





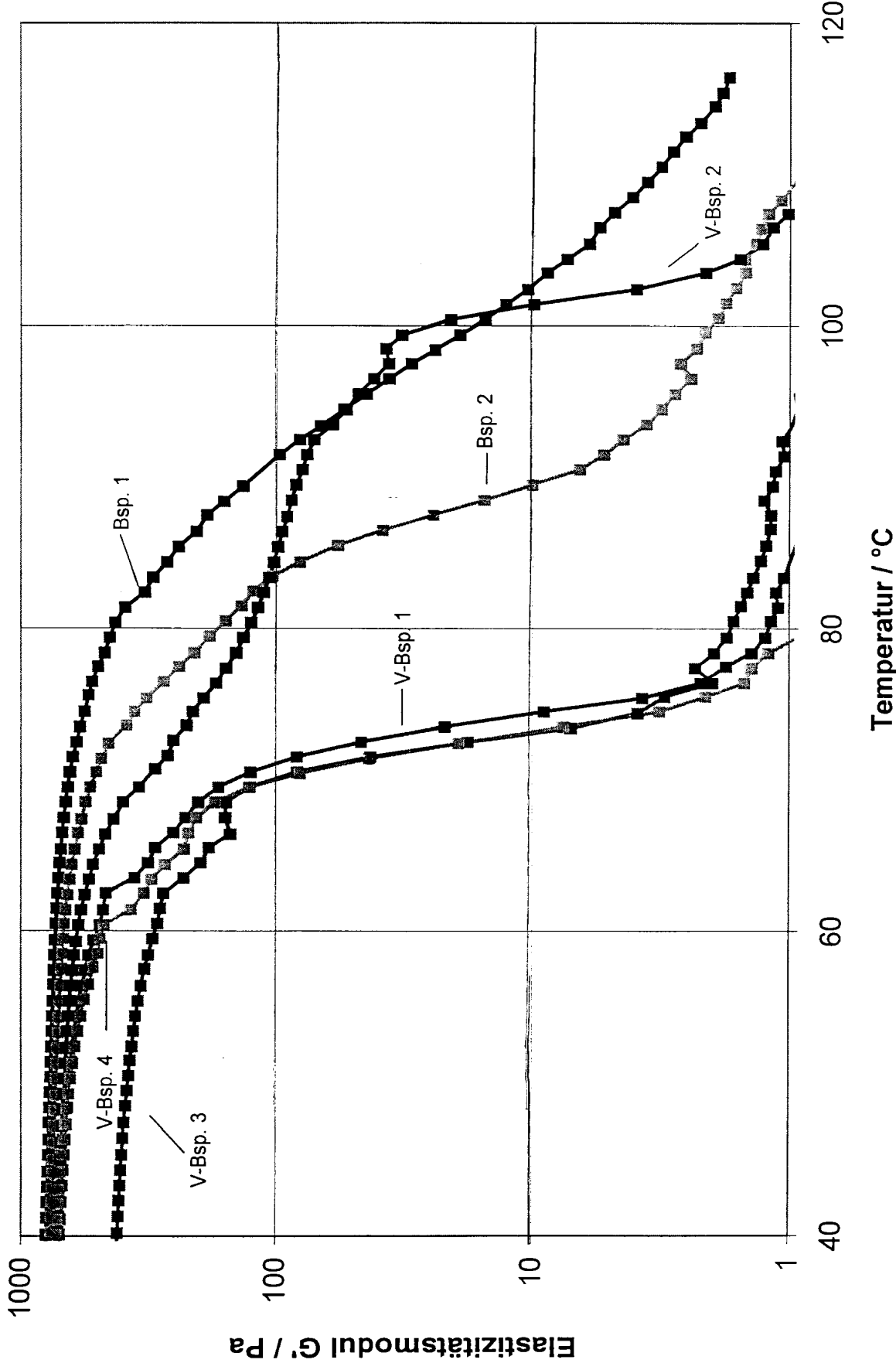
worin R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 und R^8 gleich oder verschieden sind und ein Wasserstoffatom oder einen C_1 - C_{20} -Kohlenwasserstoffrest, wie einen linearen oder verzweigten C_1 - C_8 -Alkylrest, C_6 - C_{18} -Arylrest, C_7 - C_{20} -Alkylenarylrest, einen cyclischen oder acyclischen C_2 - C_{20} -Alkenylrest bedeuten, oder einen gesättigten, ungesättigten oder aromatischen Ring bilden, wobei gleiche Reste R^1 bis R^8 in den verschiedenen Formeln I bis VI eine unterschiedliche Bedeutung haben können, worin n Werte von 0 bis 5 annehmen kann, und enthaltend 0 bis 99,9 Gew.-%, bevorzugt 0,1 bis 99,9 Gew.-%, bezogen auf die Gesamtmasse des Cycloolefincopolymers, polymerisierte Einheiten, welche sich ableiten von einem oder mehreren acyclischen Olefinen der Formel VII



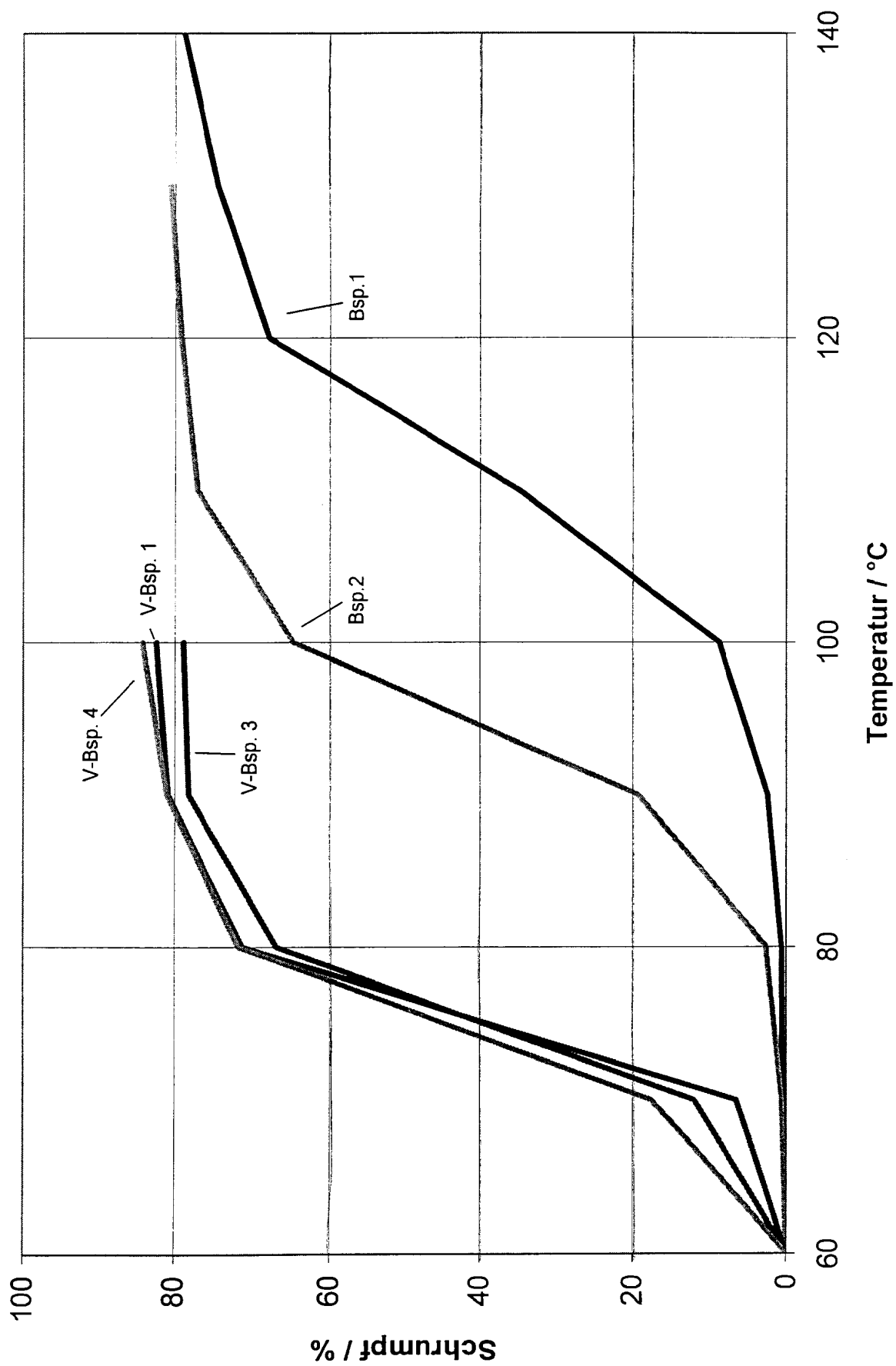
worin R^9 , R^{10} , R^{11} und R^{12} gleich oder verschieden sind und ein Wasserstoffatom, einen linearen, verzweigten, gesättigten oder ungesättigten C_1 - C_{20} -Kohlenwasserstoffrest wie einen C_1 - C_8 -Alkylrest oder einen C_6 - C_{18} -Arylrest bedeuten.

5. Verwendung eines Polymergemischs nach einem oder mehreren der Ansprüche 1 bis 4 zur Herstellung von mono- oder biaxial orientierten Folien, Blisterverpackungen, Filmen, Gemischen mit anderen Kunststoffen, besonders Polyolefinen.
- 10 6. Verwendung eines Polymergemischs nach einem oder mehreren der Ansprüche 1 bis 4 beim Spritzguß, Spritzblasen und Blasextrusion.

Figur 1



Figur 2



INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/02012

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L45/00 C08L65/00 C08F232/08 B32B27/32 B65D65/40

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)

IPC 7 C08L C08F B32B B65D

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, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 96 37528 A (GOODRICH CO B F) 28 November 1996 (1996-11-28) page 3-5 -page 24-25; examples 1-8, 24, 25, 34, 36, 37 ---	1-4
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Further documents are listed in the continuation of box C.



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Date of the actual completion of the international search

3 May 2001

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Inte. .ionales Aktenzeichen

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A. KLASIFIZIERUNG DES ANMELDUNGSGEGENSTANDES

IPK 7 C08L45/00 C08L65/00 C08F232/08 B32B27/32 B65D65/40

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Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)

IPK 7 C08L C08F B32B B65D

Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

EPO-Internal, PAJ, WPI Data

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	DE 196 33 641 A (HOECHST AG) 26. Februar 1998 (1998-02-26) das ganze Dokument ---	1-6
X	WO 96 37528 A (GOODRICH CO B F) 28. November 1996 (1996-11-28) Seite 3-5 -Seite 24-25; Beispiele 1-8,24,25,34,36,37 ---	1-4
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☒ Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

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Bevollmächtigter Bediensteter

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C.(Fortsetzung) ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
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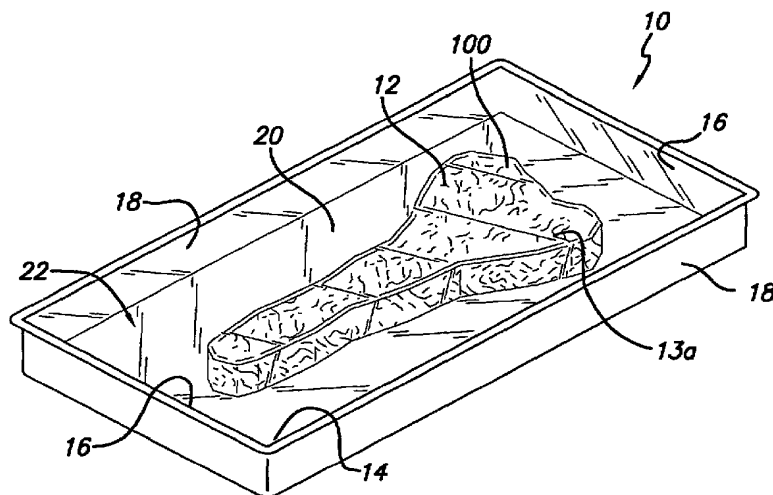
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(54) Title: IMPROVED PACKAGING METHOD THAT CAUSES AND MAINTAINS THE PREFERRED RED COLOR OF FRESH MEAT



(57) Abstract: The present invention is a method for improving the visual appearance of a food product (12) and a film (22) utilized in the method. The film includes an effective amount of a nitrogen-containing compound contained within or applied to one side of the film and adapted to contact a food item held within a food packaging container (10). Upon contacting the food item within the container, the nitrogen-containing compound forms nitrous oxide gas within the container, because of the contact of the compound with and dissolution into the juices of the food product. Thus, the physical contact of the packaging film with the food product causes a preferred reddish bloom to appear on the viewing surface (100) of the food item without effecting the appearance, performance or color of the interior of the food product.



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**IMPROVED PACKAGING METHOD THAT CAUSES AND MAINTAINS THE
PREFERRED RED COLOR OF FRESH MEAT**

FIELD OF THE INVENTION

The present invention relates to food packaging, and more specifically to a method and packaging film adapted to transfer a material to a food surface to promote an attractive appearance of the food product contained in the packaging.

BACKGROUND AND SUMMARY OF THE INVENTION

By itself, color remains the single most important quality characteristic of meat that affects its merchandizability. Consumers use color as an indicator of freshness. The color of meat comes from myoglobin. This is a complex pigmented protein present in the muscle tissue of all animals. Its biological function is for oxygen storage and delivery. It achieves this function by reversibly binding molecular oxygen, thereby creating an intracellular source of oxygen for the mitochondria. Pork and poultry contain lower amounts of myoglobin than beef and thus are lighter in color than beef.

Myoglobin consists of a non-protein portion called heme and a protein portion called globin. The protein portion is a large polypeptide chain that determines the three dimensional configuration of the myoglobin molecule. The heme portion consists of an iron atom in a planar ring. The globin portion surrounds the heme group and interacts with it in a manner that stabilizes the molecule. The heme group is the reactive center of myoglobin. It has an open binding site that attracts a ligand. The ligand must be small enough to fit into the heme pocket and have the proper electron configuration to bond to the iron atom. Oxygen meets these requirements perfectly and this is how myoglobin carries out its biological function to transport oxygen from the blood to the mitochondria.

When oxygen enters the heme pocket, its electron configuration changes the shape of the globin portion of the molecule in a manner that affects light absorption characteristics. It is the presence or absence of a ligand in the heme pocket, and the ligand itself that affects visible color changes of myoglobin.

When there is no ligand in the heme pocket, myoglobin is in its native state. This form of the molecule is called deoxymyoglobin. Its color is purple. When oxygen is present at high concentrations such as the level in the earth's atmosphere, it is pulled into the heme pocket and deoxymyoglobin becomes oxymyoglobin. Its color is red. If oxygen tension becomes low it tends to dissociate from the oxymyoglobin molecule. When this occurs there is a tendency for the oxygen to take an electron from the iron atom and leave it in the ferric state. As this occurs, a water molecule moves into the heme pocket and becomes the ligand that affects light absorption. The oxidized form of myoglobin with H₂O in the prosthetic heme group is referred to as metmyoglobin and its color is brown. When the chemical state of iron changes from ferrous (Fe⁺²) to ferric (Fe⁺³), the three-dimensional structure of the globin part changes in a manner that allows water into the heme pocket. The oxidation of the iron atom always causes a brown color.

Other variables that affect the stability of the globin portion also affect the affinity of the heme group for oxygen and the tendency of the chemical state of the iron atom to become oxidized. Acidity and high temperature, such as that associated with cooking, can denature the globin part thus leading to instability of the heme group. In the absence of stabilizing ligands the oxidation of the heme iron is automatic when the globin is denatured.

In fresh meat (postmortem muscle tissue) oxygen is continually associating and disassociating from the heme complex. Thus, it is the relative abundance of three forms of the muscle pigment that determines the visual color of fresh meat. In summary they include deoxymyoglobin (reduced myoglobin), which is purple; oxymyoglobin (oxygenated myoglobin) which is red; and metmyoglobin (oxidized myoglobin) which is brown.

The deoxymyoglobin form dominates immediately after the animal is slaughtered. Thus, freshly cut meat has a purple color. This purple color can persist for a long time if the pigment is not exposed to oxygen. Cutting or grinding exposes the pigment to oxygen in the atmosphere, and the purple color quickly converts to either bright red (oxymyoglobin) or brown (metmyoglobin). Even though deoxymyoglobin is technically fresher, it is the red or bloomed meat color that consumers use as their primary criterion for perceiving freshness.

Changes in the relative percentage of each of these forms continue to occur the longer fresh meat is exposed to oxygen. The immediate conversion of the purple color to the desirable bright red or undesirable brown depends upon the partial pressure of oxygen at the surface. The purple color is favored at the very low oxygen levels. It dominates at levels of 0-0.2%. The brown color is favored when the partial pressure of oxygen is only slightly higher (0.2% to 5.0%). Consumer discrimination begins when the relative amount of metmyoglobin is 20%. A distinctly brown color is evident at 40% metmyoglobin, which typically renders the meat unsaleable.

There are biochemical reactions that occur in muscle tissue after death that are important to fresh meat color. These reactions are caused by the presence of active glycolytic enzymes that convert oxygen to carbon dioxide. The effect on meat color is the presence of reducing coenzymes that continually convert metmyoglobin back to deoxymyoglobin. These reducing coenzymes are called metmyoglobin reductases, and their activity is called "MRA" which is an abbreviation for metmyoglobin reducing activity. MRA can be described as the ability of muscle to reduce metmyoglobin back to its natural deoxymyoglobin state. It is lost when the oxidizable substrates are depleted or when heat or acid denatures the enzymes. When the enzymes lose their activity or are denatured, the iron of the heme pigment automatically oxidizes to the metmyoglobin form, and the brown color stabilizes and dominates.

MRA persists for a period of time after death depending on the amount of exposure of the meat tissue to oxygen. During this time oxygen is continually consumed by the meat tissue. The oxygen consumption rate is referred to as "OCR". When meat that has a high OCR is exposed to oxygen, the oxygen tension is reduced so rapidly that the metmyoglobin is favored below the viewing surface. If it is close to the viewing surface, the perceived color of the meat is affected. The MRA is important to minimize this layer of metmyoglobin that forms between the bloomed surface and purple interior. As the MRA wears out, the brown metmyoglobin layer thickens and migrates toward the surface, thus terminating display life. When the MRA is high, the metmyoglobin layer is thin and sometimes not visible to the naked eye.

There is a practical relationship of MRA and OCR to the specifications of a package intended for retail sale in order to prolong the desirable appearance of meat as long as possible. Hermetically sealed packages with films that are a barrier to oxygen

will cause a low oxygen tension on the meat surface. Thus, metmyoglobin formation occurs and the viewing surface changes to an undesirable brown color. However, if the OCR is high enough to keep ahead of the oxygen that migrates across the packaging film, and the MRA is good enough to reduce metmyoglobin that forms on the surface, then native deoxymyoglobin replaces metmyoglobin. After a period of time, the perceived color changes from brown to purple. Both of these colors are unacceptable to the consumer. For this reason, vacuum packaging by itself has historically been an unacceptable format for case ready fresh meat. On the other hand, vacuum packaging is the format of choice for cooked and cured processed meats where the myoglobin pigment is denatured by heat and stabilized by the presence of nitrite. When oxygen is eliminated from a cured processed meat package, the product's color and flavor deteriorate slower than when oxygen is present.

Some fresh meat applications are suited to vacuum packaging because of its inherent advantages in protecting product quality. For example vacuum packaging is commonly used for wholesale primals and subprimals as well as for frozen steaks. The product's color is not critical in these applications. However, the color of retail cuts is very critical and the color caused by vacuum packaging is unacceptable. Thus, the industry has not been able to capitalize on the benefits of vacuum packaging for case ready applications.

As mentioned previously, the prosthetic heme group is responsible for color. Relevant literature teaches us that ligands other than oxygen or water also affect meat color. For example, cyanide and fluorine cause a brown color, carbon monoxide (CO) causes the preferred bright red color and nitric oxide (NO) causes a dull red color. In particular, methods of treating fresh meat with carbon monoxide have been developed for case ready packaging applications. The bright red myoglobin complex is referred to as carboxymyoglobin.

Sodium nitrite also affects color when added to meat. This approved additive is a commonly known preservative used in the curing process for products such as hams, lunchmeat, bologna and hot dogs. Its effects on meat color and bacterial growth are the basis for its wide spread use in the meat industry. Almost immediately after its addition, the raw meat color changes to a grayish brown. This is a commonly experienced occurrence. The pigment associated with the characteristic brown color of

raw cured meat is sometimes referred to as nitric oxide metmyoglobin. It has been shown that nitrite is reduced to nitric oxide gas upon dissolution into meat juices. Nitric oxide is the simplest known thermally stable paramagnetic molecule (i.e. a molecule with an unpaired electron). Upon contact with raw meat in the presence of oxygen, nitrite and nitric oxide turn the color brown by encouraging the disassociation of oxygen from the oxymyoglobin complex. The presence of oxygen oxidizes available nitric oxide to nitrite thus reducing its availability to associate with the myoglobin molecule. During these conversion processes, the heme group losses an electron thus forming brown metmyoglobin.

Upon cooking in the presence of nitric oxide, the globin portion of the metmyoglobin molecule denatures and nitric oxide is attracted to the heme pocket. Since nitric oxide has an unpaired electron, its presence in the heme group encourages the reduction of the iron atom back to its ferrous state. The color changes to pink or maroon depending on the relative amount of myoglobin in the muscle tissue. Cooked cured pork or poultry is pink and cooked cured beef is more of a maroon color.

The denatured (cooked) myoglobin complex with nitric oxide as its ligand is called nitrosohemochrome. In the absence of oxygen this pigment is very stable, however the presence of oxygen eventually oxidizes the nitrosohemochrome and the color changes to grayish brown. As a result, the packaging format of choice for processed meat is vacuum packaging with a high barrier film. This protects the nitrosohemochrome from oxidation by oxygen so that the color is stable for months.

The conventional packaging format used by the retail grocer for fresh meat is to stretch a thin PVC film around a foam tray that supports the product. The film is permeable to oxygen so that the initial color of the meat is bright red. However, the shelf life for the bright red color is only about three days. Thus, this packaging format is undesirable because the color often becomes unacceptable before it can be displayed or sold. As a result, a packaging format that maintains the fresh meat color for a longer period of time is required for the centralized packaging operation.

As an alternative, a high oxygen content-modified atmosphere tray can be utilized. Presently, it is the most commonly used case-ready packaging format. Pre-formed oxygen barrier trays of this type are filled and sealed on high-speed equipment.

The tray is typically either formed of foam with an oxygen barrier layer or of a rigid oxygen barrier plastic. An oxygen rich gas is then flushed into the tray before hermetically sealing a clear film on the top of the tray. In this case, the film used for the lid also has an oxygen barrier film as well as some slight shrink properties. The product is loose inside the package, as the film does not contact the meat such that there is considerable space between the film and the product (headspace) allowing the gas to affect the meat color. Centralized or regional packers currently manufacture whole muscle cuts and ground beef with this type of package. The high oxygen content atmosphere in the package creates a thick bloomed color that lasts longer when compared to meat that is exposed to only atmospheric levels of oxygen. The maximum attainable shelf life is about 14 days for ground beef and 10 days for whole muscle cuts. As it pertains to the modified atmosphere inside these packages, the most common approach is to use a blend that contains 60-80% oxygen and the balance carbon dioxide. The partial pressure of oxygen at the meat surface supplies enough oxygen for enzyme activity as well as reactions with myoglobin. The surface myoglobin pigment is converted to oxymyoglobin before tissue respiration consumes the excess oxygen, and the result is the formation of a thicker layer of surface oxymyoglobin and consequently an extension of display life. However, as the MRA is depleted toward the end of color display life, the thick, oxymyoglobin layer oxidizes to metmyoglobin.

The high oxygen packaging format has additional shortcomings as well. More specifically, the actual display life is much shorter than 14 days because exposure to light actually catalyzes or speeds up the oxidation of the bright red color to the undesirable brown. Further, whole muscle cuts fade more quickly than ground products when exposed to light. As a result, they are priced and printed with a three day sell-by-date at the store level, greatly reducing the available selling time for the meat. Also, oxidative rancidity, core metmyoglobin development and premature browning are quality issues due to the long exposure to an elevated level of oxygen. Furthermore, the characteristic headspace in the individual package takes up room in the box, thereby increasing shipping and storage costs. The headspace is less attractive to the consumer than the tightly wrapped piece of meat.

Recently the use of carbon monoxide was approved as a component of the gas used for the modified atmosphere case ready package. It has been shown to effectively

extend the shelf life. As mentioned previously, when carbon monoxide is the ligand of the myoglobin complex, the bright red preferred color develops. This is a very suitable method to extend the color life and as such a number of commercial applications are presently being pursued by the industry. This type of modified atmosphere package will have no oxygen and only 0.4% carbon monoxide to produce the desired effect. A headspace is required by this method and development of the preferred bright red color will be thwarted any place there is contact between the meat and the film. U.S. Patents 4,522,835, 6,113,962, 6,270,829 and 6,521,275 describe methods utilizing carbon monoxide and other gases to cause and maintain the desirable fresh meat color.

Another approach used by some packers to permit centralized packing and have economy of scale is to use the conventional PVC wrapped format with its oxygen permeable film inside another oxygen barrier package. One or more of the conventional packages are over wrapped in a masterpack that is flushed with either a low or high oxygen gas to extend shelf life of the packages contained therein. If low oxygen gas is used, the meat blooms when the individual trays are removed from their masterpack. It does a good job extending color life, but sometimes bloom is difficult because atmospheric levels of oxygen do not adequately penetrate the film that covers the meat surface. The high oxygen gas approach is limited to a regional level of distribution because the shelf life is shorter than the low oxygen modified atmosphere packages described above. As such, the masterpack approach is more commonly used for pork and poultry.

Other packaging formats to enhance the appearance of the packaged food products have also been disclosed by others in the industry. For example, one such format uses carbon monoxide (CO) as part of the gas that is flushed into a secondary or outer master package. The carbon monoxide penetrates the permeable inner package and affects the color of the food product in a manner similar to oxygen, causing the food product to bloom. However, since there is no oxygen present in the gas including the carbon monoxide that is flushed into the package to oxidize the myoglobin, the red color developed by carbon monoxide is more stable. Therefore, it lasts longer than the red color caused by oxygen. This extension of the time before the red color turns brown consequently increases the attractiveness of the food product to a consumer and the likelihood of the sale of the product to a consumer. However, the oxygen free/carbon

monoxide format requires special packaging equipment and an additional outer package to accomplish the desired effect.

In addition to the previously mentioned formats, a variety of other additives and gases have been used and disclosed in prior art to enhance or extend the bacteriological and color shelf life of case ready fresh meat. For example, U.S. Patent 4,683,139 describes a method to enhance and maintain fresh meat color for up to two weeks. The method utilizes direct additives that include phosphate salts, ascorbic acid, or alkali metal salts, and a sequestering agent, such as citric acid, in combination with a modified package atmosphere. This patent, and references cited therein, refers to stabilizing the color of fresh meat that is caused by the presence of oxygen.

Several patents also describe the use of pressurized gases as a means to treat meat prior to packaging so as to intensify and stabilize the preferred red color. U.S. Patent 6,716,464 discloses use of the oxygen gas in this manner. Again, these methods emphasize the importance of the red color of fresh meat.

Other methods that actively exchange the package atmosphere to cause the meat color to change are described in U.S. Patent 5,481,852, and U.S. Patent 5,989,613. The display life of the packages formed by these methods is very short and oxygen is used as the agent to cause the color change. Similarly, the method described in U.S. Patents 5,866,184 and 5,711,978 uses perforations in the tray or lid of a modified atmosphere package to allow for a passive ingress of oxygen into meat surface at a time just prior to retail display. U.S. Patents 5,759,650, 5,591,468 and 4,055,672 describe methods where an exterior barrier film layer is removed leaving behind a permeable layer of film. When the barrier layer is removed just prior to display, atmospheric oxygen diffuses into the meat surface thereby causing the preferred color change. Further, U.S. patents 5,989,610, 5,597,599 and 5,352,467 describe the use of a variety of gases and additives. All of these methods are attempts to cause and maintain the oxygenated (red) form of the meat pigment for an extended period of time.

U.S. Patents 6,046,243, 5,965,264 and 5,888,528 relate to the encapsulation and subsequent release of biocidal gases for the purpose of retarding, controlling, killing or preventing microbiological contamination. Nitrite and nitric oxide are mentioned in the patents as agents to achieve these specific effects. Applications to

meat packaging are also mentioned more specifically with regard to chlorine dioxide as the active antibacterial agent. U.S. Patent Application 2004/0137202 discloses a method for coating a contact film surface of a food wrap with active ingredients or agents that carry out a variety of secondary effects or functions. Nitrite is mentioned in this method for a preservative function

Further, several patents disclose use of nitrite in the packaging material as an inhibitor of corrosion. They include U.S. Patent Nos. 6,533,962, 6,465,109, 6,033,599 and 5,281,471. U.S. Patent No. 5,271,471 is a broad disclosure which also mentions vacuum packaging and packaging food.

Prior technologies relate to methods of affecting meat color using passive or active treatments of the meat with gases or chemicals. Some of these methods also employ physical properties of the package to assist in transforming the color of fresh meat which include peelable barriers, perforations, and packages with multiple film layers. However, none of these technologies teach us anything about selecting for the preferred red color of fresh meat using nitrite, nitrate or nitric oxide. Furthermore, none of these methods are able to create and maintain the preferred red color of fresh meat in a vacuum package.

Therefore, it is desirable to develop a novel packaging format that creates and maintains the red display color of the meat food product and has the appearance that more closely resembles the packaging format traditionally offered to the consumer.

SUMMARY OF THE INVENTION

It is a primary object of the present invention to cause and maintain the preferred red color on the surface of fresh meat. The color of interest is that typically associated with fresh meat that has been exposed to oxygen to create the oxygenated red form of the meat pigment. The present method achieves this goal by using nitrite or nitrate compounds in a packaging format that significantly extends the desirable color of a meat food product. More specifically, the present invention causes and maintains the preferred red color by using nitrite or nitrate in a manner that allows reaction with the myoglobin pigment of meat to form nitroxymyoglobin as defined herein.

The present method accomplishes the objectives by creating conditions inside the meat food package that allow nitroxymyoglobin to form. More specifically, it has been found that when raw meat is exposed to sodium nitrite after vacuum packaging in a barrier film, its color changes from red to brown within minutes. However, surprisingly and unexpectedly after a period of time (1-5 days) the color changes back to bright red. Thus, during this time period the predominate pigment on the meat surface changes from oxymyoglobin to metmyoglobin to nitroxymyoglobin. This is because the elimination of oxygen and reduction of metmyoglobin allow for nitroxymyoglobin to form. The vacuum that is applied during the packaging step is not able to eliminate oxygen that absorbed into the meat surface because it was bound into the heme pocket of the myoglobin complex. However, the OCR and MRA of the meat are able to eliminate this oxygen and reduce the remaining metmyoglobin pigments. Several days may be needed to allow enough time for this change to occur. Once the metmyoglobin pigments are reduced, nitroxymyoglobin pigments begin to dominate and the color on the meat product surface turns to the preferred bright red.

It is another object of the present invention to create conditions that allow the nitroxymyoglobin to form on the visible surfaces of meat without extending throughout the meat's thickness. More specifically, a nitrite or nitrate is sprayed onto or incorporated into the packaging film that forms the sealant layer for the film that is positioned directly over and in contact with the food product. The amount of nitrite to affect the efficient conversion of surface deoxymyoglobin to nitroxymyoglobin is related to the concentration of myoglobin molecules that are naturally present in the meat product being packaged. This amount varies greatly between meat types with beef and lamb being greater than pork and poultry. Furthermore, there are variances in the myoglobin molecule concentration between individual animals, and their age, sex or breed. Individual muscle type and slaughtering conditions further affect the rate and efficiency of the conversion of the myoglobin molecules. Thus, the present invention is utilized to cause nitroxymyoglobin formation only on the viewing surface of the fresh meat leaving the center of the product in its natural myoglobin state. Specifically, the desired depth of improved color penetration provided by the method is preferably less than about 10mm (0.375 inch), and more preferably less than about 6mm (0.25 inch).

Numerous other objects, features and advantages of the present invention will be made apparent from the following detailed description taken together with the drawing figures.

BRIEF DESCRIPTION OF THE DRAWINGS

The drawings illustrate the best mode currently contemplated as practicing the present invention.

In the drawings:

FIG. 1 is an isometric view of a package incorporating the packaging film containing an oxide of nitrogen;

FIG. 2A is a cross-sectional view of the packaging film FIG. 1 where the nitrogen-containing compound is sprayed onto the film;

FIG. 2B is a cross-sectional view of the packaging film of FIG. 1 where the oxide of nitrogen is incorporated into the film; and

FIG. 3 is an isometric view of a vacuum package incorporating the packaging film of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The undenatured (raw) nitric oxide myoglobin complex is of major significance to the present inventive method and packaging film. The current scientific teachings describe “nitric oxide metmyoglobin” as the pigment that forms from the exposure of raw meat to nitrite. Little research has been done on the reduced form of this pigment. Terminology for the pigment is inconsistent. Researchers refer to it as “nitric oxide myoglobin”, “nitrosomyoglobin”, or “nitrosylhaemochromagen” among others. In order to avoid confusion, in this writing the undenatured and reduced form of the nitric oxide myoglobin complex will be referred to as nitroxymyoglobin.

As previously mentioned, the viewing surface of untreated fresh meat is actually the combination three forms of myoglobin. Pigments on the surface and subsurface contribute to the color. When meat is exposed to the atmosphere, oxymyoglobin dominates the relative percentage of the pigments and the color is a bright red. When the raw fresh meat is exposed to nitric oxide, metmyoglobin dominates on the surface and the color is brown. However, below the surface the meat color is dull red and deep in the core the color is bright red. The perceived color of nitrite treated meat is a combination of four pigments that include nitroxymyoglobin. If no oxygen is present and the metmyoglobin is reduced to deoxymyoglobin, the nitroxymyoglobin form will

begin to outnumber the other three forms. Conditions have to be just right for all of the metmyoglobin to be reduced. The results of experiments with the method of the present invention suggest that the color of nitroxymyoglobin is the same as oxymyoglobin and carboxymyoglobin. Thus, when nitroxymyoglobin is the predominant form of the myoglobin pigment on the meat surface, the perceived color is bright red.

With reference now to the drawing figures in which like reference numerals designate like parts throughout the disclosure, a food package according to the present invention, such as a tray, is illustrated in FIG. 1 generally at 10. The package 10 can have any desired shape depending upon the size and configuration of the food product 12 having a viewing surface 100 to be contained therein. In accordance with this invention, the method may advantageously be employed with any myoglobin or hemoglobin containing tissue and has special relevance to food products harvested from: livestock such as beef, pork, veal, lamb, mutton, chicken or turkey; game such as venison, quail, and duck; and fish, fishery or seafood products. The phrases "meat food product" or "food product" used throughout this application refer to any of the above referenced types of meat. The meat can be in a variety of forms including primals, subprimals, and retail cuts as well as ground, comminuted or mixed.

Furthermore, the package 10 can be formed of any number of suitable materials, such as foam and plastic materials, which are well known for use in forming food packages or trays 10. Indeed the film alone may be used to package the food by means of a pouch or bag which is vacuum packed about the meat, and the film may be heat shrinkable or not. In a particular preferred embodiment, the food product 12 is a meat such as fresh red meat having a top meat surface 13a, and opposing bottom surface(not shown) connected by a continuous meat side wall surface 13b which is packaging by a film according to the present invention. In a preferred package, food is vacuum skin packaged in a tray such as package tray 10 which includes a bottom wall 14, a pair of side walls 16 extending upwardly from the bottom wall 14, and a pair of end walls 18 extending upwardly from the bottom wall 14 and connected to the side walls 16. The respective walls 14, 16 and 18 forming the package tray 10 form an enclosure 20 within which the food product 12 can be positioned. The food product 12 is retained within the package tray 10 by a packaging film 22 positioned over the food product 12 and tray 10, and secured at each end to the tray 10. The package film 22 can be secured

to the package tray 10 in any suitable manner, such as by heat shrinking, heat sealing, an adhesive or any other suitable method.

Referring now to FIGS. 2A and 2B, the packaging film 22 can be formed from any suitable and preferably at least generally transparent packaging material, and can be formed to have one or more layers. In a preferred embodiment, the film 22 includes a number of layers to enable the film 22 to function movably for its intended purposes. In a particularly preferred embodiment, the packaging film 22 includes an inner sealing layer 24 having a meat contact surface 25, and an outer layer 26. Additionally, one or more inner layers 28a and 28b can be incorporated into the packaging film 22. The invention contemplates use of films having 1, 2, 3, 4, 5, 6, 7, 8, 9, or more layers.

The sealing layer 24 includes an amount of an oxide of nitrogen, a nitrite or a nitrate compound 30 that is used to control the exhibited color of the food product 12. Then nitrate or nitrite compound 30 is applied to or incorporated in the formation of the layer 24, and optionally layers 26 and 28. The compound 30 can be applied to the meat contact surface 25 of layer 24 or incorporated into the sealing layer 24 in any conventional manner, so long as it is evenly dispersed over the contact surface 25 of the layer 24 and/or throughout the entire layer 24 to enable any length of film 22 incorporating the layer 24 to include approximately similar amounts of the compound 30 within the sealing layer 24 for a uniform transfer to meat via surface 25. In the embodiment where the compound 30 is incorporated within the sealing layer 24, the thickness of the sealing layer 24 is adjusted to optimize the migration of the compound 30 from layer 24 upon contact with the top and side surfaces 13a and 13b of food product 12. The layer thicknesses and/or amount of compound 30 for the layer 24 can be adjusted so as to vary the speed of the migration of the compound 30 out of the layer 24, as desired. Also, the film 22 may also be formed with an adhesive layer 34 disposed between layers 24 and 28 of the film 22. The adhesive 34 may contain the nitrogen-containing compound 30 in order to release the compound 30 through the layer 24 in a controlled manner depending upon the materials used in forming the layer 24.

EXPERIMENTAL

The packaging film 22 of this invention was developed using experiments in which a variety of chemicals were sprayed onto raw meat prior to vacuum packaging. The chemicals used were various reducing agents and oxidizing agents, which were tested in an attempt to affect the myoglobin reducing activity (MRA) and oxygen consumption rate (OCR) of the raw meat. The objective was to stabilize the respiratory conditions of the meat so as to retard myoglobin oxidation after exposure to oxygen. Commonly used meat additives were evaluated as well. The chemicals included a variety of phosphates, sulfites, acids and alkalis, salts, different forms of ascorbic acid, antioxidants, oxygen sequestering agents, plant extracts such as rosemary extract, and others that are beyond the scope of, and not necessarily related to this disclosure.

In the course of these experiments, sodium nitrite and sodium nitrate were tested. It was found that very small amounts of nitrite or nitrate affected the color of vacuum packaged meat. More specifically, when nitrite was coated onto the inner contact film surface of a vacuum package, the color would turn brown immediately after evacuating oxygen away from the viewing surface. However, unexpectedly and surprisingly in some experiments the preferred red color gradually displaced the brown color and remained stable for several months.

As a result of the testing performed, it is believed, without wishing to be bound by the belief, that nitric oxide (NO) gas forms as a result of the reduction of the nitrite on the package and this gas affects the color of the meat food product. The nitric oxide gas is believed to have a similar effect on bloom as carbon monoxide gas. Trials where meat food products were contacted with nitrite found that the bloomed color occurs only in the absence of oxygen. It is the initial small amount of residual oxygen that causes initial browning of the food product. It was found that when residual oxygen is high, a longer time is required for the initial brown color to be replaced by the preferred red color. In the initial experiments, five days were needed for the red color to fully develop. The freshness of the muscle and the specific cut affects this "bloom time" as well. Also, when a poor barrier film is used for the packaging material, the time necessary to achieve the desired bloom is extended. This is because oxygen migrates through the film causing and maintaining the brown or dark color of the meat inside.

In efforts to shorten the bloom time, extended vacuum times were used during packaging of the food product. It was observed that when a high vacuum level was applied, the bloom time decreased. With higher vacuum levels, it was also observed that when the food product surface was sprayed, dusted or otherwise coated with a water-based solution of nitrite, the bloom time could be reduced to approximately 60 hours. When the nitrite solution was sprayed, dusted or otherwise applied onto the inside surface of the package and allowed to dry before packaging the bloom time was reduced to approximately 48 hours. Additionally, it was observed that in general bloom time is shorter for pork than beef. Less than 24 hours was required for pork. Enhanced pork (pork with about 10% or less added mixture of water, salt and phosphate) exhibited a shorter bloom time than non-enhanced pork. Beef that was more than 20 days postmortem appeared to require the longest bloom time of up to 72 hours. On the other hand, 10 day postmortem beef bloomed in 24 hours. This illustrated that the higher oxygen consumption rate of fresher meat is important to minimize bloom time.

The red color developed by the application of the nitrite or nitrate in this manner is very stable, and does not turn brown during cooking. The uncontrolled addition of nitrite or nitrate can be a problem in that a visually perceptible "well done" indication of cooking for the food product is hard to achieve when the nitric oxide gas (or color changing material) penetrates intact muscle or ground meat to depths that almost reach the center of the individual portion. Therefore, it is important to control the level of nitrite utilized so that only enough is used to achieve a very shallow penetration by the color effect (believed to be caused by nitric oxide penetration) of the viewing surface of the food product. As the depth of the nitric oxide gas penetration increases, the internal color is no longer affected by cooking temperatures that normally turn the color brown or grey. When this occurs it is not possible to cook the product to the normal appearance of a well-done level. Thus, it is important to minimize the amount of nitrite exposure to the meat-viewing surface.

This objective can be achieved by adding nitrite to the contact surface 32 of the sealing layer 24 or the packaging film 22. After vacuum packaging, the film 22 contacts the viewing surface 100 of the food product 12. Nitrite from the film surface 24 dissolves into the meat juices and breaks down into nitric oxide to achieve the desired result. Best results occur when the level of nitrite is controlled so that only enough nitric

oxide is released to affect the pigments within the viewing surface 100 of the food product 12. The nitrite level required for this result is less than one-tenth (1/10) of the nitrite commonly used for curing. In fact, it is part of the focus of the present method to controllably deliver only enough nitric oxide to affect the viewing surface 100 of the meat 12. Nitrite levels typically associated with curing are so high that their effect on the color lasts after cooking. In a preferred embodiment the level of nitrite that can be used in the present inventive method is so small that in most embodiments it is not analytically detectable as nitrite or nitrate in the finished product by commonly used test methods. Furthermore, the amount is insufficient to effectively cure the entire product 12.

More specifically, in one example of the present invention the immediate 0.25 inches of beef that was exposed to the film containing the proper level of nitrite was tested for nitrite. It is an important observation that after short (about 48 hours) and long (about 7-10 days) periods of exposure, no nitrite was measured in the meat (minimum detection level = 2.0 ppm). Thus, a very small amount of sodium nitrite is needed for its desired affect. While the preferred depth of penetration of the nitrite is about 0.25 inch (~6 mm), it is also acceptable for the nitrite to penetrate deeper into the viewing surface to a maximum of about 0.375 inch (~10 mm).

In earlier studies when nitrite was coated onto the film surface, concentrations of levels higher than 20 ppm were observed. At these levels, the nitrite appeared to penetrate the viewing surface very deeply. Upon cooking it was not possible to achieve a "well done" appearance level of odor in the meat. The pink color created from the nitroxymyoglobin was present in the core of the meat cut. These trials evaluated film that contacted both sides of the cut of meat. Subsequent evaluations with a tray that did not contain nitrite on the meat contact surface still found a significant depth of penetration when the higher levels of nitrite were evaluated. However, when the 20,000 ppm sealant film was used on the skin pack package, the penetration was less than 3/16th inch. It was found that at this level, subsequent cooking performance is similar to the control after 30 days of refrigerated storage prior to cooking. Both the core and surface of the meat browned during cooking. A thin layer of pink color often remains between the surface and core.

The preferred embodiment of this method is to use the treated film 22 for

a vacuum package 10', as shown in FIG. 3. During vacuum packaging all air is removed from the inside of the package 10' so that the film 22 intimately contacts top surface 13a and side surface 13b i.e. the viewing surface 100 of the meat 12. Best results are achieved when the contact packaging film 22 effectively prevents the ingress of oxygen from the atmosphere after packaging. This is because small amounts of oxygen accelerate unacceptable discoloration as described previously. Thus, it is desirable to minimize the time of exposure by the raw meat to oxygen during the cutting or grinding procedures that occur prior to packaging. Residual oxygen that absorbed into the meat surface during the cutting and grinding operations is eliminated by the postmortem respiratory activities of the raw meat tissue. Since time is required for this to occur, the method works best when the nitrite dissolution into the meat juices occurs gradually. It was found that incorporating the nitrite compound 30 into the thin polymer sealing layer 24 of a multi layer packaging film 22 gave better results than coating or dusting the nitrite compound 30 onto the inner film surface 24 where all of the compound 30 is immediately available to the viewing surface 100. In one embodiment of the invention encapsulating the nitrite compound 30, or otherwise protecting it in a manner that controls or delays the release of nitric oxide, is contemplated as beneficial to the present method.

One of the best appearing types of vacuum packages is referred to in the industry as a "skin pack". This type of package generally uses a rigid tray that supports the product. The clear top film is formed around the product during the vacuum packaging procedures. The thin film forms a skin around the entire viewing surface of the product. It appears as though there is no film on the product surface. Thus, an excellent fresh meat appearance can be achieved when this method is used with a skin packaging film.

It is contemplated that oxygen barrier trays with or without the nitrite or nitrate containing surfaces may be employed with packaging films according to the present invention. The oxygen barrier tray may keep a fresh purple color on the meat to tray contact surface which will bloom red after unwrapping and exposure to oxygen or the tray may contain nitrite or nitrate on its surface as is done with the inventive film.

Another application of the present method is to utilize it with the vacuum packaging of cured processed meats such as ham, lunchmeat, bologna and hot dogs.

They are most commonly vacuum packaged with barrier films to maintain their characteristic color. This color is much more stable than fresh meat and typically lasts more than 60 days. When color fading occurs, it is attributable to an oxidation of the nitrosohemachrome pigment. This most likely occurs because of the depletion of residual nitrite and ingress of very small amounts of oxygen through the packaging film. The present method advantageously maintains a residual nitrite level at the film 22 to meat contact surface thereby extending color life.

To control the rate and amount of nitric oxide gas that releases from the internal film surface after packaging, impregnating or permeating the nitrite or nitrate compound 30 in the polymer that comprises the film contact surface layer 24 would enable a slow and controlled release of the compound. Polymer films for this purpose were prepared using 0, 1,000, 5,000, 10,000, 20,000 and 25,000 parts per million of sodium nitrite incorporated into surface layer 24 (based on the weight of the surface layer 24). It was found that even the lowest amount of nitrite tested induced the preferred red color formation in the food product. Further, different types of food products showed different results with different levels of nitrite present in the film 22. For example, pork showed the best results with a film having 10,000 ppm of nitrite, where beef had the best results with a 20,000 ppm nitrite level in the film 22. Thus, the level of nitrite needed in the film 22 to produce the desirable and stable color is related to the level of myoglobin present in the food product.

Although the description of the present invention has been described with respect to nitrite it will be appreciated that the invention contemplated use of a sodium or potassium salt of nitrite or nitrate or blends thereof and these commonly available materials or less common oxides of nitrogen may be usefully employed in the present invention.

Preferably, the surface of the film will have 0.01 mg per square inch or less, and more preferably 0.0077 mg per square inch or less, of the nitrogen oxide agent, for example nitrite, to avoid an undesirably deep penetration of the agent into a meat during contact. This amount minimizes haze to produce a beneficially transparent package. Beneficially, the nitrogen-oxide containing film will have good optical properties and be transparent. Advantageously, the film will preferably have a haze value of less than 25 percent, preferably less than 20 percent, and more preferably less

than 15 percent as measured by ASTM D-1003-52. Preferably, the surface will have at least 0.0008 mg per square inch and beneficially at least 0.0016 mg per square inch in a transferable amount in order to effect a suitable color change within 96 hours after contact with an uncooked meat in an oxygen barrier vacuum packaged environment.

Advantageously, for use with beef an amount of at least 1 ppm (based on the weight of the beef) available on the nitrite or nitrate treated surface of the film may be advantageously used. Similarly for pork only 0.5 ppm (based on the weight of the pork) may be used to similar effect. It has been found that film containing 10,000 ppm (0.106 mg per square inch) of nitrite (in the form of sodium nitrite) after 48 hours will make available for transfer 0.0017 mg per square inch to the surface of meat. At 20,000 ppm (0.211 mg/ square inch) 0.0077 mg/ square inch is available for transfer at 48 hours.

Although the description of the invention above relates to its application to fresh red meat, this method also offers benefits when applied to fresh fish. More specifically, when the packaging film and method is applied to vacuum packaged fresh fish, it improves its bacteriological safety. Currently the safety of a low oxygen fresh fish package is at more risk than an oxygen permeable or high oxygen content package because low content oxygen packaging creates conditions that favor the growth of certain bacteria, such as *Clostridium botulinum*. The higher oxygen content packaging is preferred for this reason and is actually mandated by regulatory agencies. However, the presence of increased levels of oxygen also allows the faster growing bacteria to degrade the product more quickly. Nitrite or nitrate and nitric oxide gas inhibit the ability of the *Clostridium* bacteria to produce its toxin. Therefore, its presence at the surface of a vacuum package reduces this risk and extends the bacteriological shelf life for the fish.

Food products, such as pork, beef, etc., that have been enhanced also work well with the method and film of the present invention. More specifically, common ingredients of enhancements that include antioxidants such as rosemary extract or erythorbate help to accelerate the break down of nitrite to nitric oxide. Other ingredients of these types of enhancements such as sodium phosphate help to stabilize the myoglobin pigment and elevate the oxygen consumption rate of the meat tissues.

Various alternative embodiments of the present invention are contemplated as being within the scope of the following claims particularly pointing out and distinctly claiming the subject matter regarded as the invention.

CLAIMS

I claim:

1. A food packaging film for use in creating and stabilizing a desirable color on a viewing surface of a raw myoglobin-containing food product without deleteriously affecting the subsurface color of the food product, the film comprising:
 - a) a food contact layer capable of contacting the food product held within a package formed with the film; and
 - b) an effective amount of a nitrogen oxide -containing compound applied to the food contact layer and capable of interacting with the myoglobin-containing food product to produce the desirable color.
2. The packaging film of claim 1 wherein the food packaging film is a barrier to oxygen.
3. The packaging film of claim 1 wherein the nitrogen oxide -containing compound forms nitric oxide when contacted with the food product.
4. The packaging film of claim 3 wherein the nitrogen oxide -containing compound is a nitrite.
5. The packaging film of claim 4 wherein the nitrogen oxide -containing compound is a sodium nitrite.
6. The packaging film of claim 1 wherein the nitrogen oxide -containing compound is present in an amount sufficient to affect the viewable surface of the food product.
7. The packaging film of claim 6 wherein the nitrogen oxide -containing compound is applied to the surface of the food contact layer.
8. The packaging film of claim 6 wherein the nitrogen oxide -containing compound is incorporated into the food contact layer.
9. The packaging film of claim 1 further comprising at least one additional layer positioned on the food contact layer.

10. The packaging film of claim 9 wherein the food contact layer is an adhesive.
11. The packaging film of claim 10 wherein the at least one additional film layer is disposed on the food contact layer.
12. The food packaging film of claim 1 wherein the film is adapted to vacuum package the food item.
13. A food packaging container comprising:
 - a) a tray adapted to hold a food item therein; and
 - b) a film positioned over the tray to maintain the food item therein, the film including an effective amount of a nitrogen-containing compound and adapted to be in contact with the food item held within the tray.
14. The food packaging container of claim 13, wherein the film is used to vacuum package the food item in the tray and substantially eliminate the presence of oxygen between the film and the tray.
15. The food packaging container of claim 13 wherein the nitrogen-containing compound is applied to the tray.
16. A method of packaging a food item to prolong a desirable appearance for the food item, the method comprising the steps of:
 - a) providing a film including an oxide of nitrogen; and
 - b) contacting the film with the food item to form a package for the food item.
17. The method of claim 16 further comprising the step of evacuating oxygen from between the film and the food item after contacting the film with the food item.
18. The method of claim 17 further comprising the step of introducing other gases or mixture of gases between the film and the food item after evacuating the oxygen.
19. The method of claim 16 wherein the step of providing the film having the oxide of nitrogen comprises the steps of:
 - a) providing a packaging film; and
 - b) applying the oxide of nitrogen to the film.

20. The method of claim 19 wherein the step of applying the oxide of nitrogen to the film comprises permeating the film with the oxide of nitrogen.

21. The method of claim 19 wherein the step of applying the oxide of nitrogen to the film comprises applying the oxide of nitrogen to the film in an amount sufficient to affect the viewable surface of the food item.

22. The method of claim 18 wherein the step of applying the oxide of nitrogen to the film comprises applying the oxide of nitrogen to a contact surface of the film which contacts the food item.

23. The method of claim 16 further comprising the step of evacuating oxygen from between the film and the food item prior to contacting the film with the food item.

24. The method of claim 16 further comprising the step of treating the food item with the oxide of nitrogen prior to contacting the film with the food item.

25. A method for creating and stabilizing a desirable color in a food product, the method comprising the step of contacting a viewable surface of the food product with an effective amount of a nitrogen-containing compound.

26. The method of claim 25 wherein the step of contacting the viewable surface comprises releasing the nitrogen-containing compound into contact with the food product in a controlled manner.

27. A vacuum packaged meat comprising an uncooked meat product vacuum packaged in a multilayer polymeric film having a first oxygen barrier polymeric layer and a second surface layer containing an oxide of nitrogen, selected from a group consisting of sodium nitrite, sodium nitrate, potassium nitrite, potassium nitrate and blends thereof, in an amount sufficient to transfer between 0.0008 and 0.016 milligram per square inch to the uncooked meat product within 96 hours.

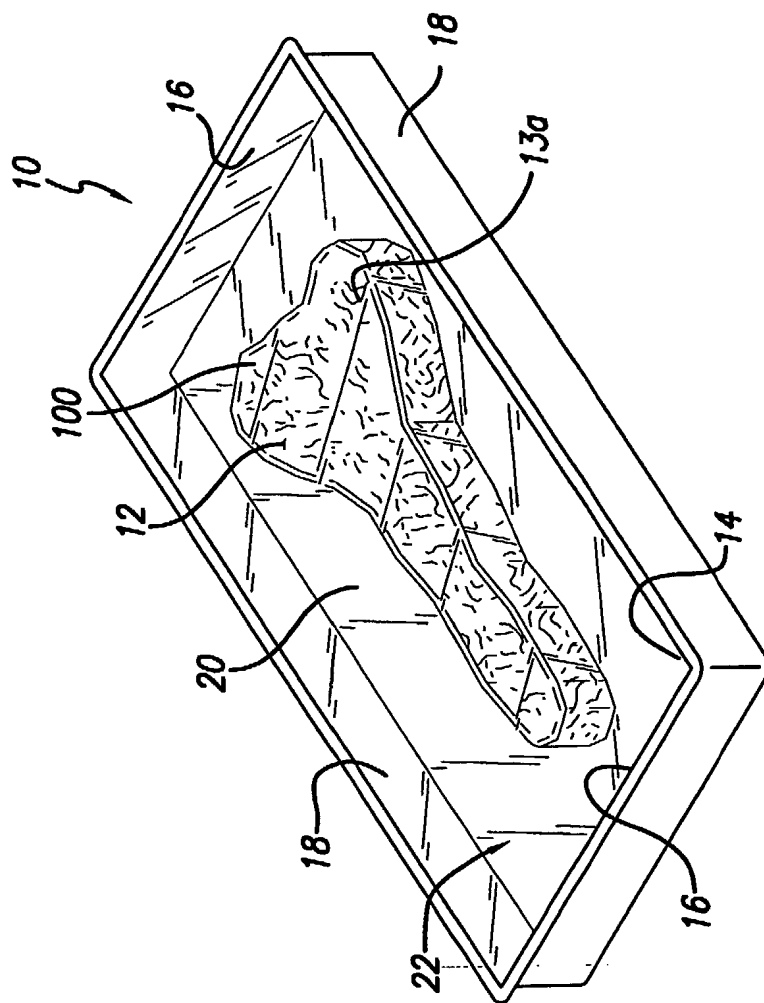


FIG. 1

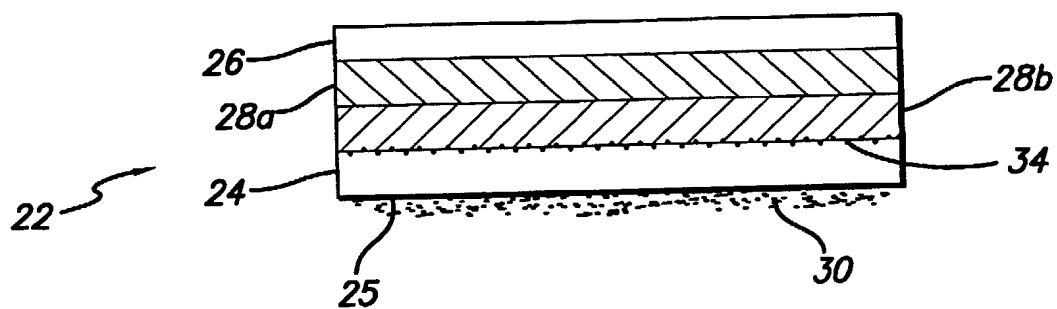


FIG. 2A

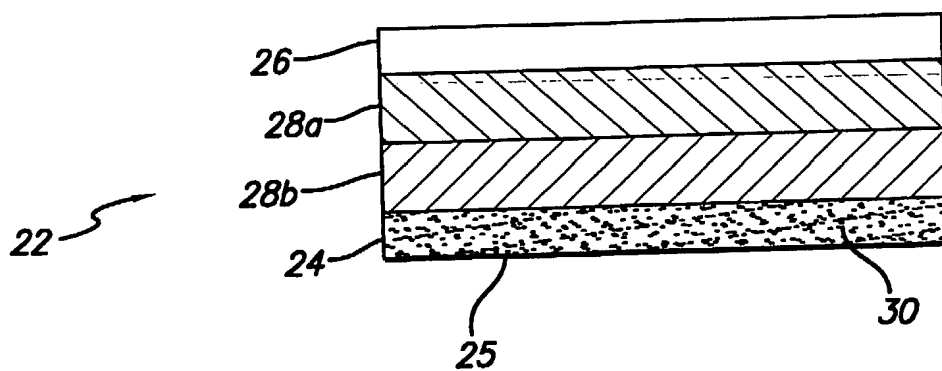


FIG. 2B

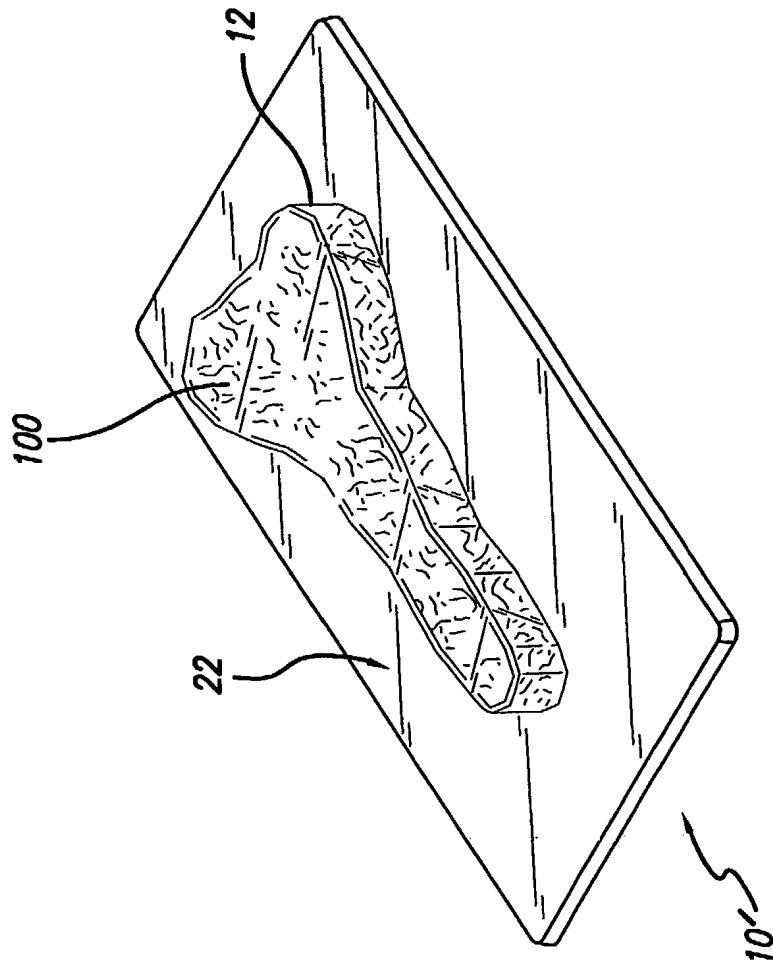


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US05/11387

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B32B 9/04

US CL : 428/34.1, 35.2, 35.4, 35.7, 35.9, 36.9, 36.91, 704; 426/124, 129, 278

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)

U.S. : 428/34.1, 35.2, 35.4, 35.7, 35.9, 36.9, 36.91, 704; 426/124, 129, 278, 415

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6,632,773 B2 (MEIER et al) 23 September 2003, column 1, lines 20-42; column 3, lines 40-67	1-10
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Y		11-27
X	US 2,925,346 A (HARPER) 16 February 1960, column 2, lines 3-72; column 3, lines 1-2.	25
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Y		1-24, 26-27
Y	2,621,129 A (RAMSBOTTOM) 09 December 1952, column 3, lines 22-38.	1-27

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

☐ See patent family annex.

* Special categories of cited documents	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent published on or after the international filing date	"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
"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)	"&"	document member of the same patent family
"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		

Date of the actual completion of the international search

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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))

(54) Title: MULTILAYER SHRINK FILMS, LABELS MADE THEREFROM AND USE THEREOF

(57) Abstract: A multilayer heat shrink film including a core layer including one or more alpha-olefin polymer and at least one skin layer including one or more cyclic olefin copolymers (COC) process for its preparation and uses thereof.



**MULTILAYER SHRINK FILMS, LABELS MADE THEREFROM AND
USE THEREOF**

CROSS-REFERENCE TO RELATED APPLICATIONS

5 [0001] The application claims priority from U.S. Provisional Application Serial No. 61/108,334, filed October 24, 2008, the contents of which are incorporated by reference in their entirety.

FIELD OF INVENTION

10 [0002] The present disclosure relates to multilayer shrink films comprising at least one core layer comprising an alpha-olefin polymer and at least one skin layer comprising a cyclic olefin polymer. More specifically the disclosure relates to labels made from these films, in particular sleeve labels, and to the use of such films and labels in packaging.

BACKGROUND OF THE INVENTION

15 [0003] Shrink labels represent a high proportion of labelling applications. High shrink labels are the fastest growing segment in the labelling business due to the trend toward using contoured containers and shrink sleeve labels with 360° graphics for high customer appeal.

[0004] Application of heat to a shrink label around a contour container causes the label to shrink preferentially in the direction extending circumferentially around the container to conform to the outside container shape.

20 [0005] Shrink labels fall into two categories: roll-on-shrink-on (ROSO) labels and sleeve labels. ROSO labels are supplied from a reel, cut into sheets, applied around a container and seamed around the container during the labelling step using hot melt to form a seam, with the machine direction (MD) of the film extending circumferentially around the container. ROSO label films primarily shrink in the MD direction and generally employ biaxially oriented polypropylene (BOPP) films.

[0006] In contrast sleeve labels are solvent seamed into a tube and supplied from that tube placed around a container, with the transverse direction (TD) of the film extending circumferentially around the container. Application of heat causes the label to shrink preferably in the direction extending circumferentially around the container and to conform to the container. Sleeve labels primarily shrink in the TD direction.

30 [0007] Current high shrink sleeve labels are sleeves made of a TD shrink film that is solvent seamed into a folded tube. These high shrink labels provide more than 60% shrinkage and are usually made of polyvinyl chloride (PVC), polyethylene terephthalate (PET), polyethylene terephthalate glycol (PETG), polylactic acid (PLA) or oriented polystyrene

(OPS). PVC and PET labels are not easily separated from PET bottle flakes using the flotation technique in the recycling process as the films have a density higher than 1 kg/dm³. OPS film requires transportation and storage under controlled conditions due to high natural shrinkage phenomenon occurring gradually at a storage temperature in a warehouse. Natural shrinkage causes deformation problems in a roll form.

[0008] While ROSO labels offer a cost advantage, the sleeve labels enjoy an advantage in the extent of shrink percentage that can be obtained. Sleeve labels typically shrink up to 60-70% around the circumference of the container whereas commercial ROSO films shrink only up to 20%.

[0009] Currently, no "all polyolefin" shrink films are known to be solvent seamed to form a tube, due to the inability of solvent to swell semi-crystalline materials. Solvent sealable material like polystyrene (PS) or PET may be coextruded on the polyolefin based film, but it will require an expensive tie layer to bond the solvent sealable skin on the polyolefin core layer. Such combination of a solvent sealable skin on a polyolefin core layer using an adhesive tie layer has other disadvantages like the development of haze on film after shrinkage or poor optics when the film is recycled.

[0010] It is therefore desirable to identify a polyolefin based film suitable for sleeve labelling that can be seamed on the current available solvent seamed machines and shrink around a container to at least 50%, has low natural shrinkage and can be easily separated from PET flakes for recycling. Shrinkage in a steam tunnel for high heat efficiency would be preferred.

[0011] WO2006/071826 discloses multilayer heat shrink film having a core layer comprising a blend of (i) at least one polyterpene and (ii) a syndiotactic polypropylene or a cyclic olefin copolymer (COC) and skin layers comprising one or more polyolefins having an ultimate shrinkage of at least 25% at 135°C. These films suffer from low stability and stiffness.

[0012] EP 1632343 discloses a multilayer heat shrinkable film composed of at least three layers comprising skin layers made of resin composition comprising 55 to 95% by mass of cyclic olefin based resin and from 45 to 5% by mass of a linear low-density polyethylene and an intermediate layer composed of a resin composition comprising 95 to 55% by mass of propylene- α -olefin random copolymer and from 5 to 45% by mass of the cyclic olefin based resin. The density and cost of such films are high.

[0013] It has now been discovered that combining a polyolefin core layer with one or two skin layers composed of solvent sealable or swellable polymer such as cyclic olefin copolymer (COC) provides a film that can be used for shrink sleeve labelling with up to about 70% shrink at temperature compatible with steam tunnel. The COC is solvent sealable using the standard solvent used in sleeve labelling. The films and/or labels made from the films have high stiffness for good dispensing. Their low natural shrinkage provides good storage stability and usually avoids transportation and storage under controlled conditions. Finally the multilayer films according to the disclosure are particularly suitable to produce labels that are easily separated from the PET containers.

10 **SUMMARY OF THE INVENTION**

[0014] Accordingly, in some embodiments, the present disclosure relates to a multilayer heat shrink film comprising a core layer comprising one or more alpha-olefin polymers and at least one skin layer comprising one or more cyclic olefin polymers or amorphous polyesters or polylactic acids.

15 [0015] In other embodiments, the film is a three layers film comprising one core layer and two skin layers.

[0016] The film may also be a five layers films comprising one core layer, two skin layers on each side of the core layer and a tie layer between the core layer and each skin layer.

20 **DETAILED DESCRIPTION**

[0017] Various specific embodiments, versions, and examples are described herein, including exemplary embodiments and definitions that are adopted for purposes of understanding the claimed invention. While the following detailed description gives specific preferred embodiments, those skilled in the art will appreciate that these embodiments are exemplary only, and that the invention can be practiced in other ways. For purposes of determining infringement, the scope of the invention will refer to any one or more of the appended claims, including their equivalents, and elements or limitations that are equivalent to those that are recited. Any reference to the "invention" may refer to one or more, but not necessarily all, of the inventions defined by the claims.

30 [0018] As used herein, "polymer" may be used to refer to homopolymers, copolymers, interpolymers, terpolymers, etc.

[0019] As used herein, the term "COC" means random copolymers of ethylene or propylene and cyclic olefin. Examples of cyclic olefins are norbornene and/or its derivatives, and/or tetracyclododecene and/or its derivatives.

CORE LAYERS

5 [0020] As described above, the core layer comprises one or more alpha-olefin polymers. The alpha-olefins polymers used for the core layer preferably have melting points as determined by differential scanning calorimeter (DSC) in the range of from 60°C to 125°C, more preferably from 60°C to 100°C. Propylene and ethylene homopolymers and copolymers and combination thereof are usually used for forming the core layer of the films according to
10 the disclosure. Core layers include propylene based elastomers, ethylene based plastomers, metallocene catalysed linear low density polyethylenes as defined hereafter and combinations thereof provide good results.

PROPYLENE-BASED ELASTOMERS

[0021] Propylene-based elastomers have a heat of fusion (Hf) less than or equal to 75 J/g
15 and a triad tacticity of three propylene units, as measured by ¹³C NMR, of 75% or greater, or even 90% or greater. The lowered Hf may result from stereo- or regio errors and/or from the incorporation of one or more units derived from a comonomer of a C₂ or C₄-C₂₀ alpha-olefin and optionally diene-derived units. Such propylene-alpha-olefin elastomers can comprise between 6 to 25 wt.% alpha-olefin and more preferably more than 7 wt.% alpha-olefin.
20 Polypropylene-based elastomers comprising from 8 to 12 wt.% ethylene are particularly suitable.

[0022] Triad tacticity is determined according to the method as disclosed in US-A-20040236042. The propylene-alpha-olefin elastomers may have a Hf which is greater than or equal to 0.5 J/g and preferably less than or equal to about 50 J/g. The Hf is determined using
25 ASTM E-794-95 (version E-794-01). Preferred propylene-alpha olefin elastomers have a Mooney viscosity [ML (1+4) @ 125°C], determined according to ASTM D1646, of less than 100, preferably less than 60 or less than 30 MU. The molecular wt. distribution index (Mw/Mn) of the propylene-alpha olefin elastomers may be from 1.8 to 3 as determined by Gel Permeation Chromatography (GPC). Propylene-based elastomers may be produced by
30 different types of single site catalysts such as bridged metallocenes (see WO199907788), pyridine amines (see WO03/040201) and unbridged metallocenes (see US5969070), preferably in a solution process. Propylene-based elastomers that may be useful in accordance with this disclosure are commercially available from ExxonMobil Chemical

Company under the trade name of Vistamaxx™. Some of these materials are further available from the Dow Chemical Company under the trade name Versify™.

ETHYLENE BASED PLASTOMERS

[0023] Ethylene based plastomers are very low density linear polyethylenes (VLDPE) having a density between 0.85 g/cm³ to 0.91 g/cm³ determined according to ASTM D1505. Ethylene-based plastomers contain a sufficient quantity of units derived from a C₃ to C₁₀ comonomer, preferably C₄ to C₈ alpha-olefins to, among other things, achieve required density. Ethylene-based plastomers are preferably produced in solution or under high pressure conditions using single site catalysts such as biscyclopentadienyl or monocyclopentadienyl metallocenes.

[0024] Such plastomers are commercialized by ExxonMobil under the trade name of Exact™, by Dow under the trade name of Affinity™ and by Mitsui under the trade name of Tafmer™.

METALLOCENE CATALYSED LINEAR LOW DENSITY POLYETHYLENES

[0025] In LLDPE, Metallocene linear low density polyethylenes (LLDPE's) have a density of from 0.91 g/cm³ to 0.94 g/cm³ determined according to ASTM D1505. They may be produced in solution, slurry or gas phase conditions using a single site catalyst, such as a metallocene activated by methods well known for such components, for example with aluminoxane or a non-coordinating anion. Low melt index ratio linear polyethylene polymer is a linear polyethylene with a shear sensitivity expressed as melt index ratio I_{21.6} / I_{2.16} ratio (MIR) of less than 30 as determined by ASTM-1238 (2.16 kg and 21.6 kg at 190°C). The low MIR indicates no or a low level of long chain branches as well as a narrow molecular wt. distribution. High MIR linear polyethylenes include LLDPE's with an MIR of more than 30 which in combination with a relatively low Mw/Mn value is generally accepted to be indicative of the presence of long chain branching. These polymers may be referred to as "homogeneously branched linear polyethylenes". The branches are believed to be linear in structure and may be present at a level where no peaks can be specifically attributed to such long chain branches in the ¹³C NMR spectrum.

[0026] Metallocene LLDPE's are commercialized by ExxonMobil Chemical Company under the trade name of Exceed™ and Enable™ and by Dow Chemical Company under the trade name of Elite™.

[0027] Core layers including propylene-based elastomers such as Vistamaxx™, metallocene linear low density polyethylene such as Exceed™, ethylene based plastomer such as Exact™, or blend thereof provide improved properties like gradual shrink curve and low shrink initiation temperature.

5 [0028] In some embodiments, the core layer consists essentially of alpha-olefin polymer(s). In other embodiments, the core layer comprises polymer blend(s) of alpha-olefin polymer with other polymers, preferably with different alpha-olefin polymer(s).

[0029] Polymer blends containing (i) from 50 to 98 wt.% of at least one polymer selected from of propylene based elastomers, ethylene plastomers, metallocene catalysed linear low
10 density polyethylenes or blend thereof and (ii) from 50 to 2 wt.% of at least one other alpha-olefin polymer polymers having a higher melting point and more preferably a higher Hf generally provide films that can be easily oriented on a tenter frame with uniform film flatness and web integrity.

[0030] In a preferred embodiment the core layer contains from 5 to 20 wt.% of low
15 density polyethylene (LDPE). According to the present description, LDPE have a density range of 0.910 - 0.940 g/cm³ and are produced using a high pressure process via free radical polymerisation.

[0031] Another preferred embodiment uses polymer blends containing from 50 to 95 wt.% of ethylene based plastomer and 50 to 5 wt.% of metallocene linear low density
20 polyethylene.

[0032] Core layer comprising polymer blends of propylene based elastomer and copolymer of propylene with ethylene and optionally butene (copolymer or terpolymer) having a melting point preferably lower than 145°C provide easily orientable films. These copolymers have preferably a melting point of higher than 100°C, more preferably higher
25 than 125°C. In an embodiment of such films to be preferably used in steam shrink tunnels, the polymer blends contain from 50 to 95 wt.% of propylene based elastomers and 50 to 5 wt.% of copolymer of propylene with ethylene and optionally butene (copolymer or terpolymer) having a melting point preferably lower than 145°C. Polymer blends containing from 5 to 50 wt.% of propylene based elastomers and 50 to 95 wt.% of said copolymer or
30 terpolymer are used more often in hot air shrink tunnels.

[0033] Copolymers of propylene with ethylene and optionally butene copolymer can be manufactured in any conventional manner using Ziegler-Natta or metallocene catalysts or any other suitable catalyst systems. Examples of suitable commercially available resins include:

XPM-7794 and XPM-7510 both C₂-C₃-C₄ terpolymers available from Japan Polypropylene Corp; EP-8573 a C₃-C₂ copolymer available from Total Petrochemical Company; PB0300M and Adsyl 3C30FHP available from Basell. Copolymers of propylene with ethylene are preferably used.

5 [0034] The core layer may contain cyclic olefin copolymer (COC) as defined below. Films comprising a core layer having up to 30 wt.% of COC have improved stiffness. The core layer usually contains less than 20 wt.%, preferably from 5 to 10 wt.%, COC based on the wt. of the polymers present in the core layer. In some embodiments, the COC in the core layer may come from the recycling of the edge trims or reclaimed film.

10 [0035] It is contemplated that the core layer may comprise other polymer(s) such as PETG, PET, polylactic acid (PLA), PVC, polystyrene (PS) or combination thereof. However these polymers are usually excluded from the core layer of the films according to the disclosure.

[0036] The core layer may contain other additives such as inorganic fillers, pigments, 15 antioxidants, acid scavengers, ultraviolet absorbers, processing aids such as zinc stearate, extrusion aids, slip additives, permeability modifiers, antistatic additives, cavitating agents such as calcium carbonate and β -nucleating agents. These additives may be introduced into the core layer in the form of master batch in a polyolefin, typically in low density polyethylene (LDPE).

20 [0037] The core layer will preferably comprise from 20 to 90%, more preferably from 30 to 90% still more preferably from 50 to 85% and even more preferably from 50 to 70 wt.% of the multilayer films of the present disclosure. For economical reasons, the core layer usually comprises from 70 to 85 wt.% of the multilayer films of the present invention.

SKIN LAYER

25 [0038] The multilayer film of the present disclosure also comprises at least one skin layer comprising preferably at least one cyclic olefin copolymer (COC). Preferably, the film comprises 2 skin layers, each comprising at least one COC.

[0039] The COC used in the present disclosure are random copolymers of ethylene or propylene and a cyclic olefin, such as, norbornene and/or its derivatives and 30 tetracyclododecene and/or its derivatives. The glass transition temperature of the COC used according to the present disclosure is usually from 60°C to 120°C, more preferably 70°C to 80°C to achieve low natural shrinkage. COC with lower glass transition temperature, for example with a glass transition temperature as low as 50°C, may be used for films which

shrink at very low temperature but those films could have higher natural shrinkage and could require transportation and/or storage under controlled conditions. The material's volume flow rate (MVR) measured at 260°C under 2.16 kg according to ISO 113 is preferably between 1 and 60 ml/10min preferably between 20 and 50 ml/10min. The density of the COC according to ISO 1183 is preferably in the range of from 1.00 to 1.06. The number average molecular wt. measured by GPC is typically from 1,000 to 1,000,000. COC useful according to the present disclosure include Topas® products available from Ticona and Zeonor® products available from Zeon Chemicals.

[0040] In an embodiment, the skin layer comprises at least 55 wt.%, preferably at least 70 wt.%, and most preferably, at least 90 wt.% of COC of the polymers present in the skin layer. In addition to the COC the skin layer(s) may also contain other film forming polymer resin(s) in a lesser amount, generally less than 45 wt.%. Amounts less than 30 wt.%, preferably less than 15 wt.% and more preferably less than 10 wt.% based on the other polymer resin(s) are suitable. Such polymeric resin(s) include propylene and ethylene homopolymers and copolymers and any combination thereof.

[0041] The use in the COC skin layer of polymer(s) with melting point lower than, or equal to, the stretching temperature, such as for example, the Exceed metallocene LLDPE or the Exact ethylene based plastomer, is preferred for the preparation of transparent films. The addition of material with higher melting point may be used when transparency is not an issue.

[0042] The skin layer(s) may also advantageously contain other additives such as pigment, antioxidants, acid scavengers, ultraviolet absorbers, processing aids such as zinc stearate, extrusion aids, antiblock, slip additives or antistatic additives.

[0043] The skin layers may comprise from 10 to 80 wt.%, preferably from 10 to 70 wt.% and more preferably from 15 to 50 wt.% and even more preferably from 30 to 50 wt.% of the multilayer films of the present disclosure. For economical reasons, the skin layer usually comprises from 30 to 15 wt.% of the multilayer films of the present invention.

[0044] The skin layers may be made of different polymer(s) or of the same polymer(s) in different or in the same ratio. More preferably the films according to the present disclosure have two skin layers of the same polymer configurations and polymer composition ratios.

[0045] The multilayer film of the disclosure may optionally comprise one or more tie layers. Tie layers can be beneficial in helping to ensure good adhesion between the skin layers and the core layer. The tie layer, if present, will preferably comprise from 5 wt.% to 15 wt.% of the entire multilayer film. Tie layers may also be used to increase the stiffness of the

films to level required by the sleeve dispensing devices. The polymer to be used preferably for the tie layer(s) are alpha-olefin polymers having a melting point from 50 to 145°C. Their tensile modulus is usually higher than 20 MPa. Secant modulus is usually higher than 50 MPa. Materials suitable for these tie layers include 8573 commercialised by Total
5 Petrochemical or JPP 7701, JPP 7510 and JPP 7790 commercialised by Japan Polypropylene Corporation.

[0046] In some embodiments, the multilayer films of the disclosure do not comprise tie layer(s).

[0047] The film has typically a thickness of from 5 to 300 µm, preferably from 10 to 150
10 µm. Films having a thickness of from 20 to 90 µm are particularly suitable according to the present disclosure.

[0048] The films of the present disclosure can be produced by any known method. The films may be obtained by extrusion or coextrusion through cast die or annular die. The films may be oriented in either the machine direction (MD), the transverse direction (TD) or in
15 both directions.

[0049] In a preferred embodiment the films are preferentially oriented at least in the transverse direction. The following method may be used. Using a plurality of extruders, the resins are melted, coextruded from the T-die, solidified by cooling with a chilled roll, roll stretched in the MD if needed, tenter-stretched in the TD, heat set, cooled, optionally
20 subjected to corona discharge treatment at least on one surface, and wound up with a winder, thus obtaining a film. While stretching in the MD does not seem essential according to that embodiment, some stretching in the MD direction is desirable to improve the easiness of splitting the film in the lateral direction. As the conditions for the MD stretching, the following ranges are preferable. The temperature is from 70 to 90°C, the stretching ratio is
25 from 1.05 to 1.35, preferably 1.2 to 1.3, and the stretching time is more preferably as short as possible specifically below 0.3 second. The conditions for the TD stretching are preferably as follows. The temperature is in the range from 80 to 120°C, the stretching ratio is from 4 to 8. The films according to the disclosure may also be taken through secondary processes. This includes, corona and/or flame plasma treatments, metallization through vacuum metallization,
30 printable topcoat applied as needed to enhance the decorative nature of the label, lamination or protecting coating such as lacquers.

[0050] In a preferred embodiment the multilayer film of the present disclosure consists in a three layers film mono-oriented in the transverse direction and comprising a core layer

comprising at least 90 wt.% of a at least one alpha-olefin polymer selected from propylene based elastomers, ethylene plastomers and metallocene catalysed linear low density polyethylene, or preferably a blend of propylene based elastomer and copolymer of propylene ethylene and optionally butene as described above, and two skin layers comprising at least 90 wt.% of a COC having a glass transition temperature of from 70 to 80°C.

[0051] The multilayer heat shrink films of the present disclosure usually have a shrinkage of 30% or more, preferably 40% or more, more preferably 50% or more in the oriented direction when placed during 7 minutes in an oven at temperature of from 60°C to 150°C, typically from 70°C to 135°C or during 10 seconds in water bath at temperature of from 60 to 100°C. Shrinkage is determined by measuring the difference of sample length before and after placing the sample, unrestrained, in an oven or in a water bath at the selected temperature (ASTM 1204). Shrinkage below 20% tends to undesirably limit the extent to which a film can conform to a container contour. While an upper limit on the extent of shrink is unknown, it will be preferably below 95%.

[0052] Clarity (especially contact clarity) and transparency are desirable in applications where a non-obscure view of the product around which the films label resides. High clarity and transparency are also desirable for "reverse" printing of labels where printing resides between the labels and the container and a consumer views the printing through the label.

[0053] Typically, films of the present disclosure have transparency values at a film thickness of 50 µm of 10 or more, preferably 15 or more, more preferably 20% or more. Transparency is determined according to ASTM method D-1746.

[0054] Haze values of the films according to the disclosure may range depending on the application. When the application requires high clarity and low haze, the haze value, determined according to ASTM method D-1003, at a film thickness of 50 µm is 20% or less, preferably less than 15%, more preferably 10% or less. Haze values lower than 5% are preferably obtained with films whose skin layers use polymer(s) with melting point lower than, or equal to, the stretching temperature.

[0055] The stiffness of the multilayer films of the present disclosure is measured by using a Handle O Meter according to the ASTM D2923-70 and is provided in g/15 mm. The stiffness in the orientation direction according to the disclosure is of at least 25 g/15 mm, preferably at least 30 g/15 mm. Values of between 35 and 45 are easily obtained. Accordingly the oriented films according to the disclosure can be used in sleeve labelling at high line speeds.

[0056] Tensile strength is measured according to ASTM D882 and is provided in N/mm².

[0057] The shrink tension of the present films is preferably lower than 10 N/mm², ideally lower than 5 N/mm², to avoid container deformation or sleeved label breakage during label shrinkage. The shrink tension is measured using a Retramat equipment. A Retramat equipment is equipped of a heated oven. The film sample is connected to a transducer capable of measuring a force. When the test starts, the heated oven moves to enclose the sample which starts to shrink. At the end of the test, the oven moves back to its original position. The transducer measures the shrink force as a function of time. The temperature around the sample is also recorded. The conditions for the test are: oven heated at 150°C, oven around the sample for 45 sec. It has been discovered that the presence of propylene-based elastomers, such as Vistamaxx, in the core layer lowers the shrink tension.

[0058] The film density as determined according to ASTM D1505 is preferably lower than 0.96 g/cm³. Values lower than 0.96 g/cm³ may be obtained according to the present disclosure and are useful for easy separation of PET bottles flakes from the labels during the recycling process.

[0059] The films according to the disclosure are useful in many shrink film applications for packaging articles including without limitations, batteries, aluminium can containers, aerosol cans, plastic liquid beverage containers, glass containers and irregular shaped containers.

[0060] The films of the present disclosure further have a particular utility as labels such as sleeve labels.

[0061] To convert a film of the present disclosure into a sleeve label, the stretched film is usually subjected to printing by a suitable method such as gravure or offset printing on the surface subjected to corona discharge treatment. To obtain a tubular label from the printed planar heat shrinkable film thus prepared, centre sealing is carried out with the use of an organic solvent as described from example in EP 1 632 343 and cut into appropriate lengths thereby obtaining labels as sleeve form. The organic solvent is not particularly limited insofar as it dissolves or swells the front back film layers of the film. Organic solvents comprising tetrahydrofuran (THF), cyclohexane or methyl ethyl ketone (MEK) are preferred and more preferably blends of these solvents.

[0062] Films and labels of the present disclosure can also advantageously possess perforations through the film or label. Perforations are most desirably carried out immediately before the sealing.

[0063] The benefits of the presence of COC in the skin layers enable the solvent seaming of the films. The films according to the disclosure have improved stiffness.

[0064] Finally it was surprising to discover that a relatively thin COC layer not only greatly increased the shrink percentage at low shrinkage temperature, but also decreased natural shrinkage during roll storage, which would create film's deformation and difficulties on printing.

[0065] The following examples serve as an illustration of the disclosure, the measured features and the units for their expressions are explained hereafter.

EXAMPLES

Examples 1 to 6

[0066] Multilayer cast films were prepared using multilayer cast film line. Each coextruded film had an A/B/A structure where the A layers were the skin layers comprising the COC and the B layer was the core layer.

[0067] The composition of the layers and properties of the oriented films are given in Table 1 below, wherein:

Topas [®]	COC commercialized by Topas. Topas 8007 has a glass transition temperature of 78°C, Topas 9506 (used at Table 5) has a Tg of 65°C,
EOD01-05	Metallocene random copolymer of propylene commercialized by Total Petrochemicals containing 4 wt.% ethylene, having a peak melting point at 122°C and a melt flow index according to ASTM D1238, 230°C, 2.16 kg of 8 g/10 min,
Exceed [™] 1018	Metallocene LLDPE comprising hexene commercialized by ExxonMobil having a Melt Index according to ASTM 1238 (2.16 kg 190°C) of 1.0 g/10 min, a peak melting point at 119°C,
Vistamaxx [™]	Propylene based elastomer commercialized by ExxonMobil. Vistamaxx 3980 has a peak melting point at 77°C,
Tospearl [™] 145	4.5 µm spherical crosslinked silicone antiblock manufactured by Toshiba Silicone Co., Ltd.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
A	Topas® 8007 + 1000 ppm Tospearl™ 145 7μm	Topas® 8007+ 1000 ppm Tospearl™ 145 7μm	Topas® 8007 + 1000 ppm Tospearl™ 145 6μm	Topas® 8007 + 1000 ppm Tospearl™ 145 6μm	Topas® 8007 + 1000 ppm Tospearl™ 145 6μm	Topas® 8007 + 1000 ppm Tospearl™ 145 6μm
B	EOD01-05	Exceed 1018	Vistamaxx	Vistamaxx + 30 wt.% exceed	Exact 8201 + 10 wt.% LLDPE	Exact 3132 + 10 wt.% LLDPE

[0068] The core layer had a thickness of about 32 to 39 μm. The average total film thickness before the orientation step was 100 - 500 μm.

[0069] The coextruded structures were cooled on a chilled roll, roll stretched in the MD, 5 tenter stretched in the lateral direction. The MD stretching conditions comprised a temperature of 90-95°C and a stretching ratio of about 1.25, the TD stretching conditions comprised a temperature of between 80°C to 110°C depending on the composition of the core and a stretching ratio of 4 to 8. The properties of these films are reported in Table 2.

Table 2

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Gauge μm		48	46	51	50	48	52
Haze %		4.9	24	12	23	11	10.6
Dim. Stab. TD (%) (7 minutes in a heated oven)	70°C	-1	-5	0	0	0	-1
	80°C	-9	-11	-5	-5	-6	-2
	90°C	-15	-15	-56	-53	-64	-7
	100°C	-24	-24	-78	-78	-77	-28
	110°C	-42	-42	-81	-81	-81	-78
	120°C	-66	-62	-81	-81	-82	-79
	135°C	-74	-76	-81	-80	-84	-81
Dim. Stab. TD (%) (7 minutes in a heated oven)	70°C	0	0	0	0	0	0
	80°C	-1	0	1	1.5	1	1
	90°C	-2	0	7	1	7	5
	100°C	-2	0	-9	-7	-10	5
	110°C	-1	-1	13	-12	-18	-7
	120°C	0	0	15	-18	-21	-7
	135°C	-18	-4	19	-21	-30	-12
MD Stiffness (g/15 cm)		27	27	31	30	26	29
TD Stiffness (g/15 cm)		30	27	38	34	33	37
Storage Stability (%)			-6.4	-1.7	-1.6	-2.5	-1.8
Weld Strength (g/25 mm)		8040	9000	2160	1875	1485	1765

[0070] Dimensional stability was measured at temperatures from 70 to 135°C on films that had been placed during 7 min in a ventilated oven at the given temperature (ASTM D 1204) or 10 sec in a water bath at the given temperature (ASTM D2732).

[0071] Storage stability in the TD dimensional stability was measured on samples stored during 7 days in a ventilated oven at 50°C.

[0072] Weld strength was measured on an Instron™ tensile tester equipment. The samples to be tested were first welded by wiping a cotton strip dipped in solvent, folding the sample and applying pressure by rolling a 2 kg weigh roll. The weld strength was measured after 1 hour. Tetrahydrofurane (THF) was the most commonly used solvent for solvent seamed shrink films, and had been used in the tests to evaluate welding properties. Other solvents (dichloromethane, carbon tetrachloride) had been tested as well and gave good weld strength.

Examples 7 and 8

[0073] These examples are given by comparison. Multilayer cast films were prepared as in examples 1 to 6.

[0074] The composition of the layers and properties of the films are as follows:

Table 3

	Example 7	Example 8
A	EOD01-05	Exceed 1018
B	EOD01-05	Exceed 1018

[0075] The coextruded film had a thickness of about 50 µm, the average total film thickness before the orientation step is about 400 µm. The properties of these films were as follows:

Table 4

		Example 7	Example 8
Gauge µm		52	50
Haze %		2.0	1.5
Dim. Stab. TD (%)	70°C	-5	-5
	80°C	-10	-8
	90°C	-18	-13
	100°C	-26	-20
	110°C	-44	-38
	120°C	-63	-81
	135°C	-69	-84
Dim. Stab. TD (%)	70°C	-1	0

	80°C	-7	0
	90°C	-1	0
	100°C	-2	0
	110°C	-4	0
	120°C	-8	-21
	135°C	-17	-20
MD Stiffness (g/15cm)		61	17
TD Stiffness (g/15cm)		95	21
Storage Stability (%)		-3.7	-6.0
Weld Strength (g/25 mm)		0	0

[0076] With samples as Examples 1-6, tubes were welded on an automatic seaming machine Seam 300D-HS from Karlville using THF as solvent produced sleeves with destructive bonds when pulled apart.

5 **[0077]** Sleeves made of film as described in Examples 3-6 were cut into individual labels and applied around a bottle requiring 60% shrink showed perfect appearance after shrinkage in a steam tunnel.

[0078] Sleeves made of film as described in Examples 2, 4 and 5 were cut into individual labels and applied around a bottle with more than 50% shrink requirements showed perfect
10 appearance after shrinkage in a hot air tunnel.

[0079] Sleeves made of films of example 1 did not give a sufficient shrink %.

[0080] Samples as described in examples 7 and 8 could not be welded to form a tube using THF as solvent.

Examples 9 to 11

15 The following multilayer films have been prepared and tested.

Table 5

		Example 9	Example 10	Example 11
Skin	5 µm	Topas 8007	Topas 8007	Topas 9506
Core	40 µm	Vistamax+Total 8375 80/20wt. %	Vistamax+Total 8375 40/60 wt. %	Vistamax+Total 8375 80/20wt. %
Skin:	5 µm	Topas 8007	Topas 8007	Topas 9506
Dim. Stab.	70°C	-1	-2	-21
(in oven)	80°C	-27	-12	-32
TD %	90°C	-47	-25	-51
	100°C	-59	-40	-65
	110°C	-68	-53	-68
	120°C	-77	-63	-79
	135°C	-80	-76	-82
Dim. Stab	70°C	0	0	5
(in oven)	80°C	8	2	7
MD %	90°C	16	2	10

	100°C	17	2	8
	110°C	12	2	5
	120°C	2	1	-4
	135°C	7	-13	-17
Dim. Stab (in water)	70°C	0	0	-10
TD %	80°C	-8	-4	-33
	90°C	-43	-22	-51
	100°C	-60	-37	-67
Dim. Stab (in water)	70°C	0	0	3
MD %	80°C	3	1	8
	90°C	13	2	10
	100°C	13	2	7
Shrink Force Retramat		3,7 N/mm ²	6 N/mm ²	3,3 N/mm ²

Wherein Total 8573 is a copolymer of propylene containing 3.5% ethylene and having a melting temperature of 135°C commercialised by Total Petrochemicals.

Film of Example 9 performs particularly well in shrink steam tunnel and does not need storage under controlled conditions, Film of Example 10 performs particularly well in shrink air tunnel and does not need storage under controlled conditions, Film of Example 11 performs particularly well in shrink steam tunnel. Having a high shrink at low temperature film of example 11 needs storage under controlled conditions (low temperature).

[0081] All patents and patent applications, test procedures (such as ASTM methods, UL methods, and the like), and other documents cited herein are fully incorporated by reference to the extent such disclosure is not inconsistent with this disclosure and for all jurisdictions in which such incorporation is permitted.

[0082] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated. While the illustrative embodiments of the disclosure have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present disclosure, including all features which would be treated as equivalents thereof by those skilled in the art to which the disclosure pertains.

CLAIMS***What is claimed is:***

1. A multilayer heat shrink film comprising:
 - a) a core layer including at least,
 - (i) from 50 to 98 wt.% of at least one polymer selected from propylene based elastomers, ethylene plastomers, metallocene catalysed linear low density polyethylenes, and blend thereof, and
 - (ii) from 50 to 2 wt.% of at least one alpha-olefin polymer having a melting point higher than polymer (i); and
 - b) at least one skin layer comprising a cyclic olefin copolymer (COC).
2. The film of claim 1, comprising two skin layers, each of the skin layers comprising a cyclic olefin copolymer.
3. The film of claim 1 or 2, wherein the alpha-olefin polymer has a peak melting point in the range of from 60°C to 125°C.
4. The film of any one of claims 1 to 3, wherein the metallocene catalysed core layer further comprises a copolymer of propylene and ethylene.
5. The film of any one of claims 1 to 4, wherein the core layer contains (i) from 50 to 95 wt.% of ethylene plastomer and 50 to 5 wt.% of metallocene linear low density polyethylene.
6. The films of any one of claims 1 to 4, wherein the core layer contains 50 to 95 wt.% of propylene-based elastomers and 50 to 5 wt.% of copolymer of propylene with ethylene and optionally butene (copolymer or terpolymer) having a melting point lower than 145°C.
7. The films of claim 4, wherein the core layer contains 5 to 50 wt.% of propylene-based elastomers and 95 to 50 wt.% of copolymer of propylene with ethylene and optionally butene (copolymer or terpolymer) having a melting point lower than 145°C.
8. The films of any one of claims 1 to 7, wherein the COC is selected from random copolymers of ethylene or propylene and a cyclic olefin comprising at least one of norbornene, norbornene derivatives, tetracyclododecene, and tetracyclododecene derivatives.
9. The film of claim 7, wherein the COC has a glass transition temperature of from 70 to 80°C.

10. The film of any one of claim 1 to 9, wherein each skin layer comprises at least 50 wt.% of COC.
11. The film according to claim 1, consisting in a three layers film monoaxially oriented in the transverse direction and comprising a core layer comprising at least 90 wt.% of one or more alpha-olefin polymer selected from propylene based elastomers, metallocene catalysed copolymer of propylene and ethylene, ethylene plastomers and metallocene catalysed linear low density polyethylene, and two skin layers comprising at least 90 wt.% of a COC having a glass transition temperature of from 70 to 80°C.
12. A process for the preparation of the film according to any one of claims 1 to 11 by co-extrusion through a cast die and monoaxial orientation in the transverse direction.
13. A process for the preparation of the film according to any one of claims 1 to 11 by co-extrusion through a cast die and biaxial orientation.
14. Use of the film according to any one of claims 1 to 11 in packaging and/or labelling.
15. Label comprising a film according to any of claims 1 to 7.
16. The label of claim 15, wherein the shrink label is a sleeve label.
17. Article comprising a film according to any one of claim 1 to 11 or a label according to claim 15 or 16.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/057762

A. CLASSIFICATION OF SUBJECT MATTER

INV. B32B27/32 C08L23/04 C08L23/06 C08L23/08 C08L23/10
C08L23/14

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)
B32B 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 practical, 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	DE 102 38 515 A1 (TICONA GMBH [DE]) 4 March 2004 (2004-03-04) paragraphs [0005], [0007], [0008], [0011], [0014], [0019], [0033], [0040]; claims 1-5,12-15	1,2,8,9, 12,14-16
X	WO 2005/097493 A (IPG TECHNOLOGIES INC [US]) 20 October 2005 (2005-10-20)	1-3,5,6, 8,9, 12-14
A	page 25, paragraphs 28,39,40,42,44,47,49,58,60,87; claims 1,2,8,11; tables 7,8	4
X	US 2005/214557 A1 (ARTHURS TREVOR [CA] ET AL) 29 September 2005 (2005-09-29)	1-3,8,9, 12-14
A	paragraphs [0034] - [0036], [0039], [0040], [0044], [0045], [0092]; claims 1,2,8,11; table 6	4
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☒ 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

29 January 2010

Date of mailing of the international search report

05/02/2010

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/057762

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 300 238 A (FLEXOPACK S A [GR]) 9 April 2003 (2003-04-09) claims 1,4,8,9,18,21,24,27,36,43	1,8
A	EP 1 632 343 A (GUNZE KK [JP]; MITSUI CHEMICALS INC [JP]) 8 March 2006 (2006-03-08) cited in the application paragraph [0095]; claim 1	1,2,9,10
X	DATABASE WPI Week 200520 Thomson Scientific, London, GB; AN 2005-187019 XP002565436 & JP 2005 047182 A (ASAHI KASEI LIFE & LIVING KK) 24 February 2005 (2005-02-24) abstract	1,2,8,9
X	& JP 2005 047182 A (ASAHI KASEI LIFE & LIVING KK) 24 February 2005 (2005-02-24) paragraph [0014]; claim 1	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2009/057762

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 10238515	A1	04-03-2004	AU 2003255450 A1 WO 2004018198 A2	11-03-2004 04-03-2004
WO 2005097493	A	20-10-2005	NONE	
US 2005214557	A1	29-09-2005	NONE	
EP 1300238	A	09-04-2003	NONE	
EP 1632343	A	08-03-2006	WO 2004110750 A1 US 2006159878 A1	23-12-2004 20-07-2006
JP 2005047182	A	24-02-2005	NONE	

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10 2009 041 841.5
18. September 2009 (18.09.2009) DE

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(81) Bestimmungsstaaten (soweit nicht anders angegeben, für jede verfügbare nationale Schutzrechtsart): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, 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, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Bestimmungsstaaten (soweit nicht anders angegeben, für jede verfügbare regionale Schutzrechtsart): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), eurasisches (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches (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, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Veröffentlicht:

— mit internationalem Recherchenbericht (Artikel 21 Absatz 3)

(54) Title: UV AND LIGHT PROTECTIVE FILM

(54) Bezeichnung : UV- UND LICHT-SCHUTZFOLIE

(57) Abstract: The present invention relates to an at least contact transparent single layer or multilayer film absorbing and/or reflecting UV radiation and short-wavelength visible light, comprising at least one layer based on at least one optionally modified thermoplastic olefin homo- or co-polymer, comprising a combination of at least one organic or inorganic colored pigment or dye absorbing and/or reflecting short-wavelength visible light, and of at least one organic or inorganic compound absorbing and/or reflecting the UV radiation, and to the use of said film as a protective film against the effects of UV radiation and short-wavelength visible light, and a sewer cleaning system comprising said multilayer film as an external hose film and an inner, multilayer plastic film, and an impregnated UV-curable carrier material present between the two hose films.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft eine zumindest kontakttransparente, UV-Strahlung und kurzwelliges, sichtbares Licht absorbierende und/oder reflektierende, einschichtige oder mehrschichtige Folie umfassend wenigstens eine Schicht basierend auf wenigstens einem gegebenenfalls modifizierten thermoplastischen Olefin-Homo-oder Copolymeren enthaltend eine Kombination aus wenigstens einem kurzwelliges, sichtbares Licht absorbierenden und/oder reflektierenden organischen oder anorganischen Farbpigment oder Farbstoff, und aus wenigstens einer die UV-Strahlung absorbierenden und/oder reflektierenden, organischen oder anorganischen Verbindung, sowie die Verwendung dieser Folie als Schutzfolie gegen die Einwirkung von UV- Strahlung und kurzwelligem, sichtbarem Licht und ein Kanalsanierungssystem umfassend diese Mehrschichtfolie als außenliegende Schlauchfolie und eine innenliegende, mehrschichtige Kunststoffolie und einem zwischen den beiden Schlauchfolien befindlichen, durch UV-Strahlung aushärtbaren, imprägnierten Trägermaterial.

UV- und Licht-Schutzfolie

Die vorliegende Erfindung betrifft eine zumindest kontakttransparente, UV-Strahlung und kurzwelliges, sichtbares Licht absorbierende und/oder reflektierende, einschichtige oder mehrschichtige Folie umfassend wenigstens eine Schicht basierend auf wenigstens einem gegebenenfalls modifizierten thermoplastischen Olefin-Homo-oder Copolymeren enthaltend eine Kombination aus wenigstens einem kurzwelliges, sichtbares Licht absorbierenden und/oder reflektierenden organischen oder anorganischen Farbpigment oder Farbstoff und aus wenigstens einer die UV-Strahlung absorbierenden und/oder reflektierenden, organischen oder anorganischen Verbindung, sowie die Verwendung dieser Folie als Schutzfolie gegen die Einwirkung von UV-Strahlung und kurzwelligem, sichtbarem Licht, vorzugsweise in Kanalsanierungssystemen, sowie ein entsprechendes Kanalsanierungssystem.

Aus dem Stand der Technik sind Schutzfolien bekannt, die zwar eine Schutzwirkung gegen UV-Strahlung aufweisen, jedoch blickdicht sind.

Aus verschiedenen Gründen ist es jedoch vorteilhaft, wenn derartige Schutzfolien transparent sind. So ist es bspw. im Fall von Lebensmittelverpackungen wünschenswert, dass die vor der Einwirkung von UV-Strahlung zu schützenden Verpackungsgüter von außen vom Käufer betrachtet werden können. In EP 1 138 479 B1 wird eine solche Schutzfolie beschrieben, die vor Einwirkung von UV-Strahlung bis zu einer Wellenlänge von < 350 nm schützt, indem sie Titandioxid als UV-Strahlung absorbierendes Pigment enthält. Das Titandioxid muss in einer bestimmten feindispersen Form vorliegen, um eine ausreichende Transparenz der Schutzfolie zu gewährleisten.

In DE 1 002 177 A1 wird eine thermoformbare, transparente Folie aus einem Thermoplasten beschrieben, bei der die UV-Strahlung bis zu einer Wellenlänge < 380 nm mit Hilfe von organischen oder metallorganischen Verbindungen vollständig absorbiert wird.

In WO 00/27914 wird eine transparente ein- oder mehrschichtige Folie beschrieben, die eine Schutzwirkung gegen UV-Strahlung in einem Wellenlängenbereich von 280-390 nm aufweist, indem sie eine UV-Strahlung absorbierende Kombination aus einer anorganischen und einer organischen Verbindung wie z. B. einer Kombination aus Zinkoxid oder Titandioxid und einem Benzotriazol aufweist.

Schutzfolien, die eine Schutzwirkung gegen UV-Strahlung aufweisen, werden u.a. bei der Sanierung von Kanälen und Kanalrohrleitungen im sogenannten Schlauchlining-Verfahren eingesetzt. Gemäß diesem Verfahren wird zunächst ein flexibler Schlauch bereitgestellt, der in das zu sanierende Rohr eingezogen wird. Dieser Schlauch umfasst zwei Schlauchfolien mit unterschiedlichem Durchmesser zwischen denen ein Trägermaterial, vorzugsweise Glasfasermaterial, eingebracht ist, das mit einem reaktiven Kunststoffharz getränkt ist. Nach dem Einbringen des Schlauches in das Kanalrohr und Aufblasen des Schlauches im Kanalrohr muss das Kunststoffharz zwischen den beiden Schlauchfolien ausgehärtet werden, um ein stabiles Rohr an der zu sanierenden Innenwand des Kanalrohres zu ergeben. Die Aushärtung kann durch Bestrahlung mit UV-Strahlung erreicht werden, wobei Photoinitiatoren in dem Kunststoffharz bei Einwirkung von UV-Strahlung den Polymerisations- bzw. Aushärtungsvorgang auslösen. Um eine ungewollte, vorzeitige Aushärtung des Kunststoffharzes vor dem Einbringen in das zu sanierende Kanalrohr zu verhindern, muss die außenliegende Schlauchfolie des Schlauches eine Schutzschicht aufweisen oder daraus bestehen, die eine vorzeitige Einwirkung von UV-Strahlung und damit eine vorzeitige Harzhärtung verhindert. Die innenliegende Schlauchfolie eines solchen Sanierungsschlauches muss dagegen UV-Strahlung durchlässig sein, um im aufgeblasenen Zustand den Aushärtungsvorgang zu ermöglichen. Schläuche aus herkömmlichen mehrschichtigen Schlauchfolien, die bei der Kanalsanierung gemäß Schlauchlining-Technik eingesetzt werden, weisen üblicherweise eine ausreichende Absorption der UV-Strahlung auf. Da jedoch die in den reaktiven Kunststoffharzen enthaltenen Photoinitiatoren auch bereits bei Einwirkung längerwelliger Strahlung wie bspw. von kurzwelligem, sichtbarem Licht aktiviert werden können, ist es notwendig, auch diese Gefahr einer vorzeitigen Aushärtung, insbesondere bei Lagerung zu unterbinden. Dies wurde u. a. durch die Verwendung undurchsichtiger Schlauchfolien versucht.

Dadurch ist jedoch keine Kontrolle einer gleichmäßigen Tränkung des Trägermaterials mit dem auszuhärtenden Kunststoffharz und damit keine Vermeidung von durch ungleichmäßige Tränkung verursachten Fehlstellen im sanierten Kanalrohr möglich.

Es besteht daher ein Bedarf an Schutzfolien, die zumindest eine Kontakttransparenz aufweisen, d.h. nicht blickdicht sind, aber trotzdem sowohl die Einwirkung von UV-Strahlung als auch von kurzwelligem, sichtbaren Licht unterbinden.

Eine Aufgabe der vorliegenden Erfindung war es daher, eine Schutzfolie zur Verfügung zu stellen, die zumindest kontakttransparent ist, aber trotzdem die Einwirkung von UV-Strahlung und von kurzwelligem, sichtbaren Licht verhindert.

Diese Aufgabe wird gelöst durch die Bereitstellung der erfindungsgemäßen, zumindest kontakttransparenten, UV-Strahlung und kurzwelliges, sichtbares Licht absorbierenden und/oder reflektierenden, einschichtigen oder mehrschichtigen Folie umfassend wenigstens eine Schicht basierend auf wenigstens einem gegebenenfalls modifizierten, thermoplastischen Olefin-Homo-oder Copolymeren enthaltend eine Kombination aus wenigstens einem kurzwelliges, sichtbares Licht absorbierenden und/oder reflektierenden organischen oder anorganischen Farbpigment oder Farbstoff und aus wenigstens einer die UV-Strahlung absorbierenden und/oder reflektierenden, organischen oder anorganischen Verbindung.

Unter dem Begriff "kontakttransparent" wird im Sinne dieser Erfindung verstanden, dass die erfindungsgemäße Folie zumindest so transparent ist, dass die Kontrolle einer gleichmäßigen Tränkung des Trägermaterials mit dem auszuhärtenden Kunststoffharz möglich ist. Dies beruht auf der Prüfung der Helligkeit des getränkten Trägermaterials. Die Bestimmung der Kontakttransparenz wird mit der nachstehend in den Beispielen beschriebenen Methode durchgeführt.

Unter dem Begriff "UV-Strahlung" wird im Sinne dieser Erfindung elektromagnetische Strahlung in einem Wellenlängenbereich von 200 bis 400 nm verstanden.

Unter dem Begriff "kurzwelliges, sichtbares Licht" wird im Sinne dieser Erfindung elektromagnetische Strahlung in einem Wellenlängenbereich von 400 bis 500 nm, vorzugsweise von 400 bis 450 nm verstanden.

Die erfindungsgemäße Folie enthält vorzugsweise wenigstens ein organisches oder anorganisches Farbpigment oder wenigstens einen organischen oder anorganischen Farbstoff ausgewählt aus der Gruppe umfassend Carbonyl-Farbstoffe, vorzugsweise Chinon-Farbstoffe, Indigo-Farbstoffe und Chinacridone, Azo-Verbindungen, Cyanin-Verbindungen, vorzugsweise Triphenylmethan-Verbindungen, Azomethine, Isoindoline, Dioxazine, Metalloxide, Übergangsmetalloxide, Metalloxidhydrate und Übergangsmetalloxidhydrate. Besonders bevorzugt werden von diesen Farbstoffgruppen oder Farbpigmenten die gelben Farbstoffgruppen oder Farbpigmente ausgewählt.

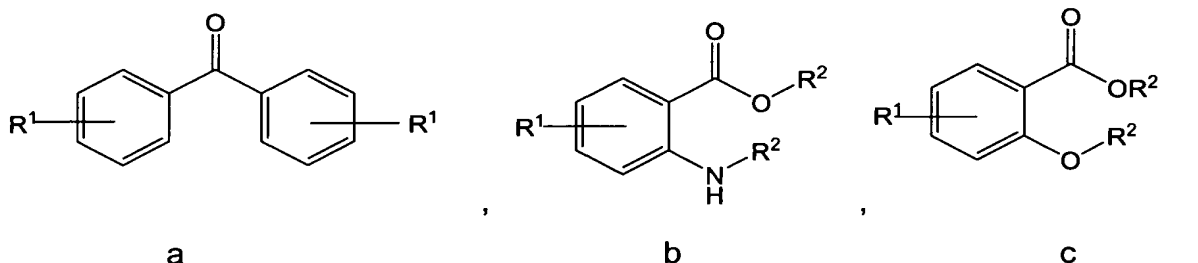
Vorzugsweise liegt ein organisches, gelbes Farbpigment oder ein organischer, gelber Farbstoff ausgewählt aus der Gruppe umfassend Benzimidazol-Derivate, Benzotriazol-Derivate, 1,4-Chinon-Derivate, 1,4-Naphthochinon-Derivate, 9,10-Anthrachinon-Derivate, Phenylazophenol-Derivate, jeweils in Form der freien Verbindungen, in Form von Tautomeren oder der Salze von Säuren oder Basen oder der Solvate, vorzugsweise der Hydrate vor. Vorzugsweise liegt ein anorganisches, gelbes Farbpigment oder ein anorganischer, gelber Farbstoff ausgewählt aus der Gruppe umfassend Übergangsmetalloxide und Übergangsmetalloxidhydrate vor. Besonders bevorzugt ist ein gelbes Farbpigment oder ein gelber Farbstoff ausgewählt aus der Gruppe umfassend 4-Phenylazophenol, 2-(2'-Methyl)phenylazo-4-methylphenol, N-(4-Phenylazo)phenyldiethanolamin, Benzotriazole, Benzimidazolon, Eisenoxid und Eisenoxidhydrat, ganz besonders bevorzugt ist Benzimidazolon.

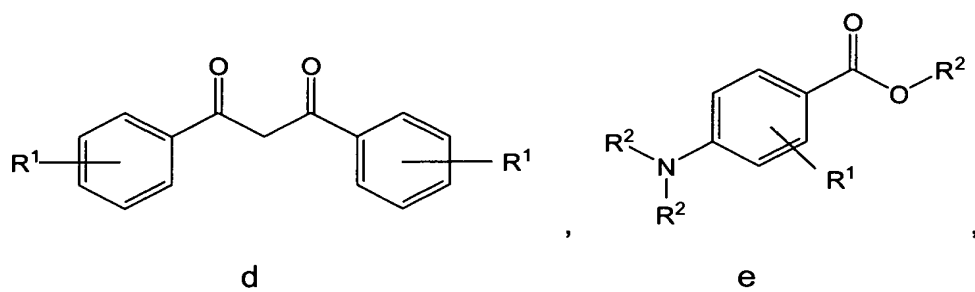
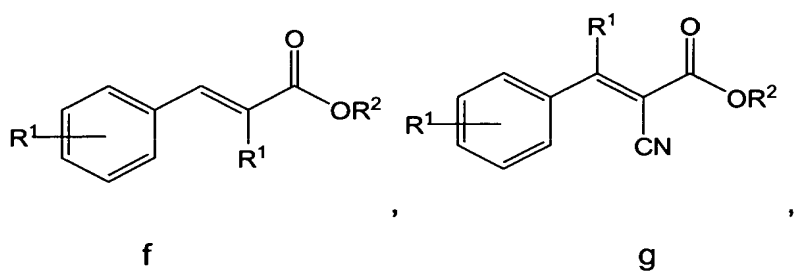
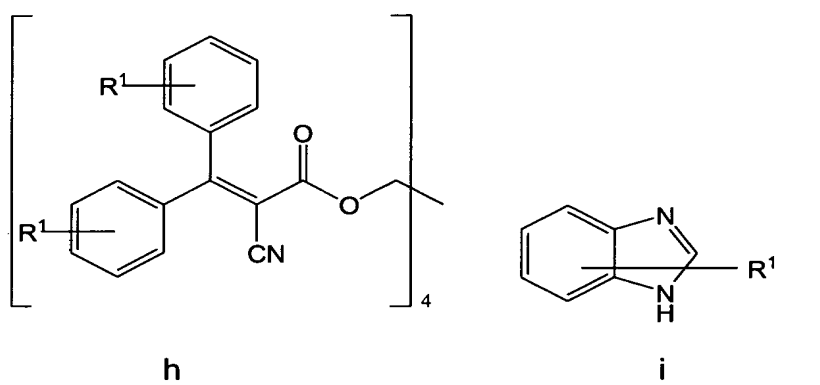
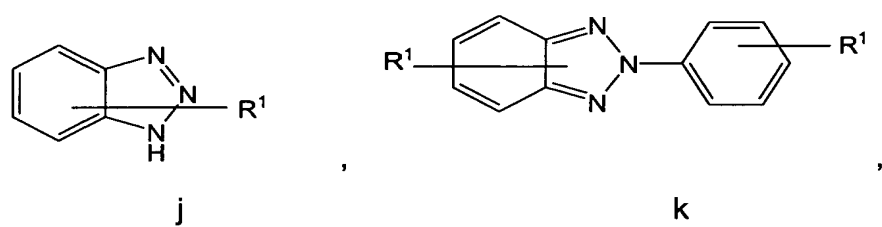
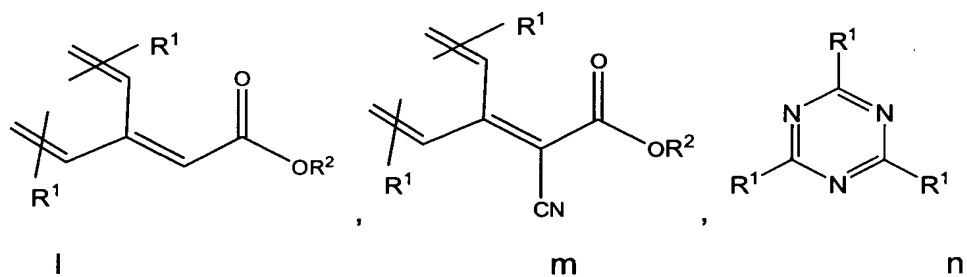
Vorzugsweise absorbiert und/oder reflektiert das organische oder anorganische Farbpigment oder der organische oder anorganische Farbstoff kurzwelliges, sichtbares Licht im Wellenbereich von 400 bis 500 nm, besonders bevorzugt im Wellenbereich von 400 bis 450 nm, vorzugsweise jeweils zu mehr als 90 %.

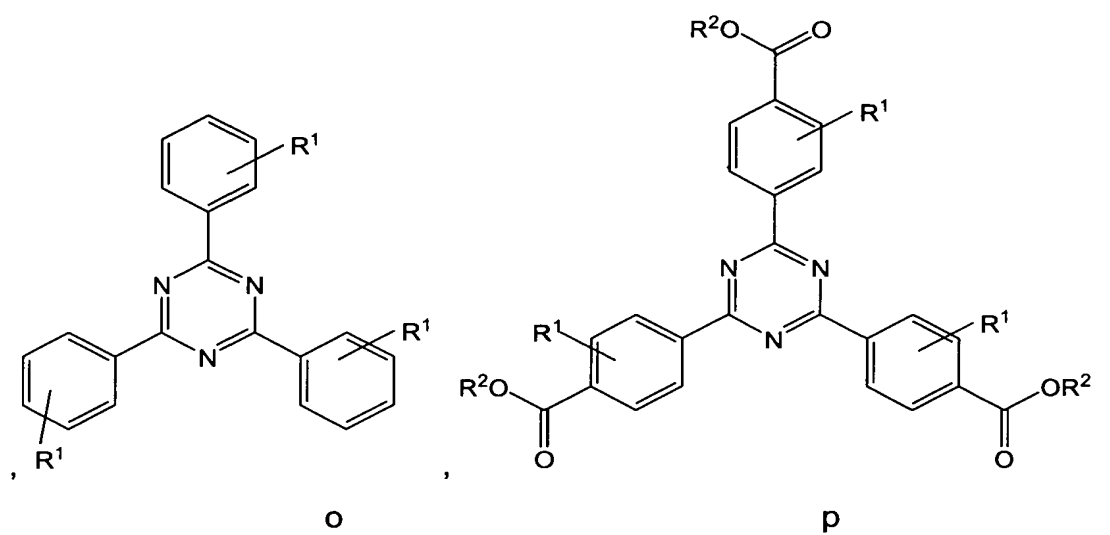
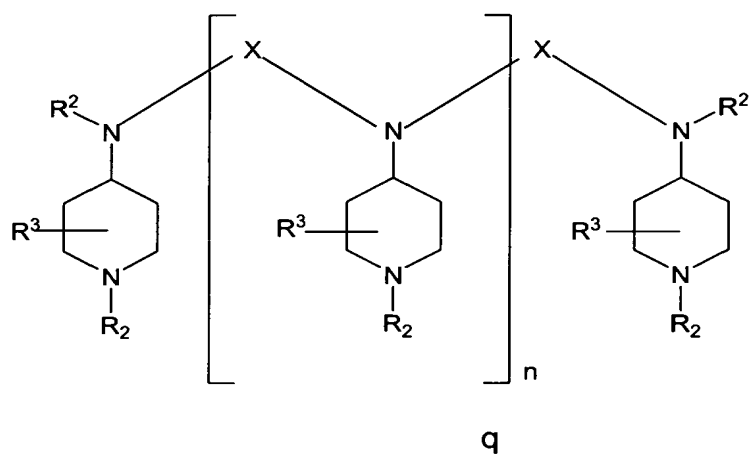
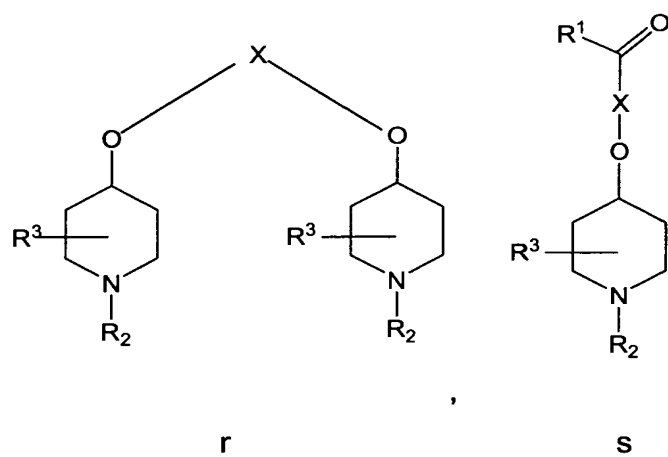
In einer bevorzugten Ausführungsform enthält die erfindungsgemäße Folie wenigstens eine organische oder anorganische Verbindung ausgewählt aus der Gruppe umfassend Metalloxide, Übergangsmetalloxide, Metalloxidhydrate, Übergangsmetalloxidhydrate, Phosphite, Benzophenone, Anthranilate, Salicylate, Dibenzoylmethane-Derivate, p-Aminobenzosäure-Derivate, Zimtsäure-Derivate (Phenylacrylsäure – Derivate), Benzimidazol-Derivate, Benzotriazol-Derivate, Cyanoacrylate, Benzotriazol-Derivate, β - β' -Divinylacrylate, Alkyl- α -cyano- β - β' -divinylacrylate, 1,3,5-Triazin-Verbindungen und sterisch gehinderte Amine, jeweils in Form der freien Verbindungen, in Form ihrer Tautomeren oder jeweils ihrer Salze von Säuren oder Basen als UV-Strahlung absorbierende und/oder reflektierende Verbindung. Derartige Verbindungen sind teilweise marktgeführte Produkte, wie z. B. Uvinule® der BASF AG.

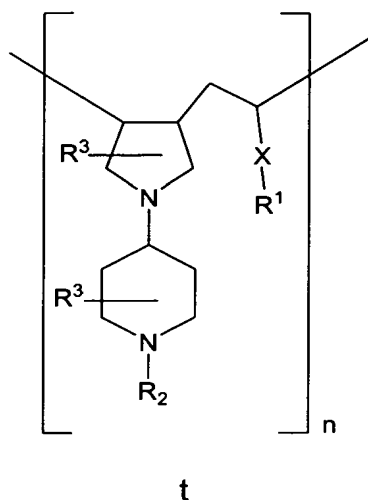
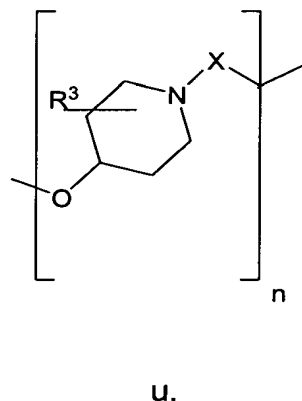
Unter dem Begriff "sterisch gehinderte Amine" werden Verbindungen verstanden, bei denen an wenigstens ein dreibindiges Stickstoffatom ein oder mehrere raumfüllende, organische Reste gebunden sind. Vorzugsweise handelt es sich um aromatische oder aliphatische, azyklische oder zyklische, sekundäre und tertiäre Amine wie N,N'-disubstituierte p-Phenylendiamine oder substituierte (Amino)-Piperidine.

Vorzugsweise liegt als UV-Strahlung absorbierende und/oder reflektierende, organische oder anorganische Verbindung wenigstens eine Verbindung ausgewählt aus der Gruppe umfassend Metall- und Übergangsmetalloxide und Verbindungen der nachstehenden allgemeinen Strukturformeln a bis u vor:









R^1 in denen jeweils für einen oder mehrere, z.B. zwei, drei oder vier Reste jeweils unabhängig voneinander ausgewählt aus der Gruppe umfassend Wasserstoff; OH; Halogen; NH_2 ; CN; $C(=O)H$; $C(=O)OH$; SO_3H ; $O-C_{1-10}-Alkyl$, $NH(C_{1-10}-Alkyl)$, $N(C_{1-10}-Alkyl)_2$, $C_{1-10}-Alkyl$, $-C_{1-10}-Alkyl-O-C_{1-10}-Alkyl-$, jeweils verzweigt oder unverzweigt, gesättigt oder ungesättigt, unsubstituiert oder einfach oder mehrfach substituiert mit OH, Halogen, $=O$, $C(=O)H$, $C(=O)OH$, Phenyl, NH_2 , $C(=O)-C_{1-10}-Alkyl$, $C(=O)-O-C_{1-10}-Alkyl$, $O-C_{1-10}-Alkyl$, $O-C(=O)-C_{1-10}-Alkyl$, jeweils verzweigt oder unverzweigt, gesättigt oder ungesättigt; Phenyl, Menthyl, Homomenthyl, Benzyl, Cyclohexyl, jeweils unsubstituiert oder einfach oder mehrfach substituiert mit OH, Halogen, $C(=O)H$, $C(=O)OH$, NH_2 , $C(=O)-C_{1-10}-Alkyl$, $C(=O)-O-C_{1-10}-Alkyl$, $O-C_{1-10}-Alkyl$, $O-C(=O)-C_{1-10}-Alkyl$ steht;

R^2 jeweils für einen oder mehrere, z.B. zwei, drei oder vier Reste jeweils unabhängig voneinander ausgewählt aus der Gruppe umfassend Wasserstoff, $C_{1-8}-Alkyl$, jeweils verzweigt oder unverzweigt, gesättigt oder ungesättigt, unsubstituiert oder einfach oder mehrfach substituiert mit OH, Halogen, $=O$, NH_2 , $C(=O)H$; $C(=O)OH$; CN; $C(=O)-C_{1-10}-Alkyl$, $C(=O)-O-C_{1-10}-Alkyl$, $O-C_{1-10}-Alkyl$, $O-C(=O)-C_{1-10}-Alkyl$, jeweils verzweigt oder unverzweigt, gesättigt oder ungesättigt; Phenyl, Menthyl, Homomenthyl, Benzyl, Cyclohexyl, jeweils unsubstituiert oder einfach oder mehrfach substituiert mit OH, Halogen, $C(=O)H$; $C(=O)OH$; NH_2 , $C(=O)-C_{1-10}-Alkyl$, $C(=O)-O-C_{1-10}-Alkyl$, $O-C_{1-10}-Alkyl$, $O-C(=O)-C_{1-10}-Alkyl$ steht;

R^3 jeweils für einen oder mehrere, z.B. zwei, drei, vier, fünf oder sechs Reste jeweils unabhängig voneinander ausgewählt aus der Gruppe umfassend Wasserstoff; OH; NH_2 ; CN; $C(=O)H$; $C(=O)OH$; $=O$; SO_3H ; $O-C_{1-10}-Alkyl$, $NH(C_{1-10}-Alkyl)$, $N(C_{1-10}-Alkyl)_2$, $C_{1-10}-Alkyl$, $-C_{1-10}-Alkyl-O-C_{1-10}-Alkyl-$, jeweils verzweigt oder unverzweigt, gesättigt oder ungesättigt, unsubstituiert oder einfach oder mehrfach substituiert mit OH, Halogen, $=O$, Epoxy, NH_2 , Phenyl, $C(=O)-C_{1-8}-Alkyl$, $C(=O)-O-C_{1-10}-Alkyl$, $O-C_{1-10}-Alkyl$, $O-C(=O)-C_{1-10}-Alkyl$, jeweils verzweigt oder unverzweigt, gesättigt oder ungesättigt; Phenyl, Menthyl, Homomenthyl, Benzyl, Cyclohexyl, jeweils unsubstituiert oder einfach oder mehrfach substituiert mit OH, Halogen, $C(=O)H$; $C(=O)OH$; NH_2 , $C(=O)-C_{1-10}-Alkyl$, $C(=O)-O-C_{1-10}-Alkyl$, $O-C_{1-10}-Alkyl$, $O-C(=O)-C_{1-10}-Alkyl$ steht;

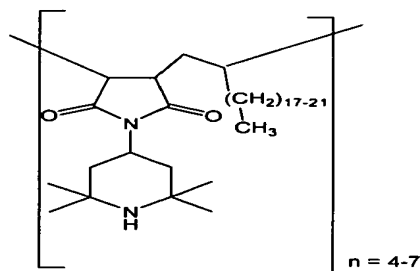
X für $C_{1-20}-Alkyl$, verzweigt oder unverzweigt, gesättigt oder ungesättigt, unsubstituiert oder einfach oder mehrfach substituiert mit Substituenten unabhängig voneinander ausgewählt aus der Gruppe umfassend H; Halogen; OH; $=O$; Epoxy; NH_2 ; $C(=O)H$; $C(=O)OH$; CN; $C(=O)-C_{1-10}-Alkyl$, $C(=O)-O-C_{1-10}-Alkyl$, $O-C_{1-10}-Alkyl$, $O-C(=O)-C_{1-10}-Alkyl$, jeweils verzweigt oder unverzweigt, gesättigt oder ungesättigt steht, wobei ein oder mehrere, z.B. ein, zwei oder drei C-Atome des $C_{1-20}-Alkyls$ ggf. durch ein oder mehrere, z.B. ein, zwei oder drei Heteroatome unabhängig voneinander ausgewählt aus der Gruppe umfassend N, O, S, NH oder $N(C_{1-8}-Alkyl)$ ersetzt sein können;

n für 0 bis 200, vorzugsweise für 0 bis 100, besonders bevorzugt für 0 bis 20, ganz besonders bevorzugt für 0 bis 10 steht;

Die Ausdrücke " $C_{1-10}-Alkyl$ " und " $C_{1-20}-Alkyl$ " umfassen im Sinne dieser Erfindung acyclische, gesättigte oder ungesättigte Kohlenwasserstoffreste, die verzweigt oder unverzweigt sowie unsubstituiert oder ein- oder mehrfach substituiert sein können, mit 1 bis 8 bzw. 1 bis 20 C-Atomen, d.h. $C_{1-10}-Alkanyle$, $C_{2-10}-Alkenyle$ und $C_{2-10}-Alkinyle$ bzw. $C_{1-20}-Alkanyle$, $C_{2-20}-Alkenyle$ und $C_{2-20}-Alkinyle$. Dabei weisen Alkenyle mindestens eine C-C-Doppelbindung und Alkinyle mindestens eine C-C-Dreifachbindung auf.

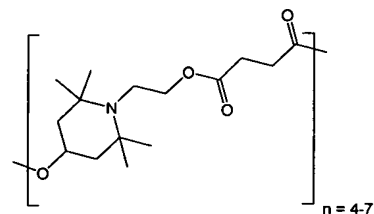
Bevorzugt ist Alkyl aus der Gruppe ausgewählt umfassend, die Methyl, Ethyl, n-Propyl, 2-Propyl, n-Butyl, iso-Butyl, sec.-Butyl, tert.-Butyl, n-Pentyl, iso-Pentyl, neo-Pentyl, n-Hexyl, n-Heptyl, n-Octyl, n-Nonyl, n-Decyl, Ethylenyl (Vinyl), Ethinyl, Propenyl ($-\text{CH}_2\text{CH}=\text{CH}_2$, $-\text{CH}=\text{CH}-\text{CH}_3$, $-\text{C}(=\text{CH}_2)-\text{CH}_3$), Propinyl ($-\text{CH}-\text{C}\equiv\text{CH}$, $-\text{C}\equiv\text{C}-\text{CH}_3$), Butenyl, Butinyl, Pentenyl, Pentinyl, Hexenyl und Hexinyl, Heptenyl, Heptinyl, Octenyl und Octinyl.

Besonders bevorzugt wird als UV-Strahlung absorbierende und/oder reflektierende, organische oder anorganische Verbindungen wenigstens eine Verbindung aus der Gruppe umfassend Zinkoxid, Titandioxid, 2-Ethoxy-ethyl-p-methoxycinnamat, Diethanolamin-p-methoxycinnamat, Octyl-p-methoxycinnamat, 2-Ethylhexyl-2-cyano-3,3-diphenylacrylat, Kaliumcinnamat, Propyl-4-methoxy-cinnamat, Amyl-4-methoxycinnamat, α -Cyano-4-methoxyzimtsäure bzw. der entsprechende Hexylester, Cyclohexyl-4-methoxycinnamat, Glyceryl-p-amino-benzoat, Amyl-p-dimethylaminobenzoat, Ethyl-4-bis(hydroxypropyl)-aminobenzoat, Octyl-p-dimethylaminobenzoat, Ethoxylierte-4-Aminobenzosäure, Octylsalicylat, Triethanolaminsalicylat, Salze der Salicylsäure, 4-Isopropylbenzylsalicylat, 2-Ethylhexyl-2-(4-phenylbenzoyl)benzoat, Homomenthylsalicylat, 2-Hydroxy-4-methoxybenzophenon, 2,4,6-Triänilino-(p-carbo-2-ethylhexyloxy)-1,3,5-triazin, 2-Phenylbenzimidazol-5-sulfonsäure, 1-(4-tert-Butylphenyl)-3-(4-methoxyphenyl)propan-1,3-dion, p-Cumenyl-3-phenylpropan-1,3-dion, 1,3-Bis(4-Methoxyphenyl)propan-1,3-dion, Menthylantranilat, Homomenthyl-N-acetylantranilat, 2-Hydroxy-4-octylbenzophenon (Uvinul® 3008, Uvinul® 3008 FL), 6-tert-Butyl-2-(5-chlor-2H-benzotriazol-2-yl)-4-methylphenol (Uvinul® 3026, Uvinul® 3026 GR), 2,4-Di-tert-butyl-6-(5-chlor-2H-benzotriazol-2-yl)-phenol (Uvinul® 3027), 2-(2H-Benzotriazol-2-yl)-4,6-di-tert-pentylphenol (Uvinul® 3028, Uvinul® 3028 GR), 2-(2H-Benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol (Uvinul® 3029, Uvinul® 3029 GR), 1,3-Bis-[(2'-cyano-3',3'-diphenylacryloyl)oxy]-2,2-bis-[(2'-cyano-3',3'-diphenylacryloyl)oxy]methylpropan (Uvinul® 3030, Uvinul® 3030 GR), 2-(2H-Benzotriazol-2-yl)-4-methylphenol (Uvinul® 3033 P), 2-(2H-Benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol (Uvinul® 3034), Ethyl-2-cyano-3,3-diphenylacrylat (Uvinul® 3035), (2-Ethylhexyl)-2-cyano-3,3-diphenylacrylat (Uvinul® 3039), N,N'-Bisformyl-N,N'-bis-(2,2,6,6-tetramethyl-4-piperidiny)-hexamethyldiamin (Uvinul® 4050 H), Bis-(2,2,6,6-tetramethyl-4-piperidyl)-sebacat (Uvinul® 4077 H, Uvinul® 4077 GR), Bis-(1,2,2,6,6-pentamethyl-4-piperidyl)-sebacat, Methyl-(1,2,2,6,6-pentamethyl-4-piperidyl)-sebacat (Uvinul® 4092 H),



(Uvinul® 5050 H)

und



(Uvinul® 5062 H, Uvinul® 5062 GR)

eingesetzt.

Vorzugsweise absorbiert und/oder reflektiert die organische oder anorganische Verbindung UV-Strahlung in einem Wellenlängenbereich von 200 bis 400 nm, besonders bevorzugt von 300 bis 400 nm, vorzugsweise jeweils zu mehr als 90 %.

Vorzugsweise enthält die erfindungsgemäße Folie 0,05 bis 20 Gew.%, besonders bevorzugt 0,1 bis 5 Gew.%, ganz besonders bevorzugt 0,1 bis 2 Gew.%, jeweils bezogen auf das Gesamtgewicht der Folie, der Kombination aus wenigstens einem organischen oder anorganischen Farbpigment oder Farbstoff und wenigstens einer organischen oder anorganischen Verbindung.

Vorzugsweise enthält die erfindungsgemäße Folie 0,05 bis 10 Gew.%, besonders bevorzugt 0,1 bis 3 Gew.%, bezogen auf das Gesamtgewicht der Folie, des organischen oder anorganischen Farbpigments oder Farbstoff.

Vorzugsweise enthält die erfindungsgemäße Folie 0,05 bis 10 Gew.%, besonders bevorzugt 0,1 bis 2 Gew.%, bezogen auf das Gesamtgewicht der Folie, der organischen oder anorganischen Verbindung.

Vorzugsweise ist jede Komponente der Kombination bei Temperaturen bis zu 300 °C stabil.

Die erfindungsgemäße Folie ist einschichtig oder mehrschichtig, vorzugsweise mehrschichtig. Vorzugsweise ist die erfindungsgemäße Folie nicht schrumpffähig.

Vorzugsweise umfasst die erfindungsgemäße Folie wenigstens eine Barrierschicht, besonders bevorzugt eine Sauerstoffbarrierschicht, Wasserdampfbarrierschicht oder eine Ölbarrierschicht.

Zur Herstellung der Barrierschicht eignet sich bevorzugt wenigstens ein Polyamid (PA), Ethylen-Vinylalkohol-Copolymer (EVOH), Polyvinylalkohol (PVOH), zyklisches Olefin-Copolymer (COC), Polyvinylidenchlorid (PVdC) oder eine Mischung aus wenigstens zwei der genannten Polymere, besonders bevorzugt wenigstens ein Polyamid.

Die zur Herstellung der Barrierschicht eingesetzten Polyamide (PA) sind vorzugsweise thermoplastische aliphatische, teilaromatische oder aromatische Polyamide. Entsprechend können die zur Herstellung dieser Polyamide eingesetzten Diamine entweder aliphatische Diamine mit 2-10 Kohlenstoffatomen wie z.B. Hexamethylen-diamin oder aromatische Diamine mit 6-10 Kohlenstoffatomen sein wie z. B. p-Phenylendiamin und die zur Herstellung dieser Polyamide eingesetzten Dicarbonsäuren aliphatische oder aromatische Dicarbonsäuren mit 6-14 Kohlenstoffatomen wie z.B. Adipinsäure, Terephthalsäure oder Isoterephthalsäure sein. Weiterhin können die Polyamide aus Lactamen mit 4-10 Kohlenstoffatomen wie z.B. ϵ -Caprolactam hergestellt werden. Erfindungsgemäß verwendete Polyamide sind z.B. PA 6, PA 12, PA 66, PA 6I, PA 6T und/oder Mischungen aus wenigstens zwei der genannten Polymere.

Die zur Herstellung der Barrierschicht eingesetzten Polyvinylalhoole werden durch vollständige oder unvollständige Hydrolyse von entsprechenden Polyvinylacetaten (PVA) gewonnen und umfassen somit sowohl teilverseifte Polyvinylacetate, die einen Verseifungsgrad von 50 bis 98 mol-% aufweisen, als auch vollverseifte Polyvinylacetate mit einem Verseifungsgrad ≥ 98 %.

Die zur Herstellung der Barrierschicht eingesetzten Ethylen-Vinylalkohol-Copolymere (EVOH) werden durch vollständige oder unvollständige Hydrolyse von entsprechenden ethylenhaltigen Polyvinylacetaten (EVAc) gewonnen und umfassen vor allem vollverseifte ethylenhaltige Polyvinylacetate mit einem Verseifungsgrad $\geq 98\%$.

Die zur Herstellung der Barrierschicht eingesetzten cyclischen Olefin-Copolymere (COC) können auch Copolymere von α,β -ungesättigten cyclischen Olefinen mit 4-10 Kohlenstoffatomen wie z.B. Norbornen und thermoplastischen α,β -ungesättigten Olefinen wie Ethylen oder Propylen sein.

Vorzugsweise basiert wenigstens eine Oberflächenschicht der erfindungsgemäßen Folie auf wenigstens einem thermoplastischen Olefin-Homo-oder Copolymeren, das vorzugsweise siegelfähig ist.

Olefin-Homo-oder Copolymere im Sinne dieser Erfindung sind thermoplastische Polymere von α,β -ungesättigten Olefinen mit 2-6 Kohlenstoffatomen wie z.B. Polyethylen (PE, insbesondere LDPE oder HDPE), Polypropylen (PP), Polybutylen (PB), Polyisobutylen (PI) oder Mischungen aus wenigstens zwei der genannten Polymere. Mit "LDPE" wird Polyethylen niedriger Dichte bezeichnet, welches eine Dichte im Bereich von $0,86-0,93\text{ g/cm}^3$ aufweist und sich durch einen hohen Verzweigungsgrad der Moleküle auszeichnet. Mit "HDPE" wird Polyethylen hoher Dichte bezeichnet, welches nur eine geringe Verzweigung der Molekülkette aufweist, wobei die Dichte im Bereich zwischen $0,94$ und $0,97\text{ g/cm}^3$ liegen kann.

Gegebenenfalls können die genannten Olefin Homo- oder Copolymere mit wenigstens einer organischen Säure oder wenigstens einem organischen Säureanhydrid, vorzugsweise mit einem cyclischen, organischen Säureanhydrid, besonders bevorzugt mit Maleinsäureanhydrid, modifiziert sein und so als Material für eine Haftvermittlerschicht in einer erfindungsgemäßen Mehrschichtfolie dienen.

So kann in einer bevorzugten Ausführungsform zwischen einer Oberflächenschicht und der Barrierschicht eine Haftvermittlerschicht, vorzugsweise enthaltend wenigstens ein modifiziertes Polyolefin, angeordnet sein.

Als modifizierte Polyolefine sind ein thermoplastische Polymere von einem α,β -ungesättigten Olefinen mit 2-6 Kohlenstoffatomen wie z.B. Polyethylen (PE, insbesondere LDPE oder HDPE), Polypropylen (PP), Polybutylen (PB), Polyisobutylen (PI) oder eine Mischung aus wenigstens zwei der genannten Polymere zu verstehen, welche(s) mit wenigstens einer organischen Säure oder wenigstens einem organischen Säureanhydrid modifiziert sind. Bevorzugt ist als ein modifiziertes Polyolefin ein mit einem zyklischen, organischen Säureanhydrid modifiziertes Polyethylen oder Polypropylen, besonders bevorzugt ein mit Maleinsäureanhydrid modifiziertes Polyethylen oder Polypropylen.

Vorzugsweise besteht die Haftvermittlerschicht aus einem modifizierten Polyolefin, das besonders bevorzugt mit Maleinsäureanhydrid gepfropft ist.

In einer bevorzugten Ausführungsform basiert jede der Oberflächenschichten der erfindungsgemäßen Mehrschichtfolie auf wenigstens einem vorzugsweise siegelfähigen Olefin-Homo oder -Copolymer und ist jeweils über eine vorstehend beschriebene Haftvermittlerschicht mit der Barrierschicht verbunden.

In einer bevorzugten Ausführungsform enthält wenigstens eine der innenliegenden Schichten einer erfindungsgemäßen Mehrschichtfolie die die schädliche Strahlung absorbierende und/oder reflektierende Kombination aus wenigstens einem organischen oder anorganischen Farbpigment oder Farbstoff und wenigstens einer organischen oder anorganischen Verbindung

Vorzugsweise liegen die Komponenten der Kombination in derselben Schicht einer erfindungsgemäßen Mehrschichtfolie, besonders bevorzugt in einer Haftvermittlerschicht vor.

Vorzugsweise kann jede der Haftvermittlerschichten der erfindungsgemäßen Mehrschichtfolie die schädliche Strahlung absorbierende und/oder reflektierende Kombination aus wenigstens einem organischen oder anorganischen Farbpigment oder Farbstoff und wenigstens einer organischen oder anorganischen Verbindung enthalten.

In einer weiteren bevorzugten Ausführungsform liegen die Komponenten der Kombination in unterschiedlichen Schichten einer erfindungsgemäßen Mehrschichtfolie vor.

Vorzugsweise liegen das Farbpigment oder der Farbstoff in wenigstens einer Oberflächenschicht und die organische oder anorganische Verbindung in wenigstens einer innenliegenden Schicht der erfindungsgemäßen Mehrschichtfolie vor.

Bevorzugt kann jede der Haftvermittlerschichten der erfindungsgemäßen Mehrschichtfolie wenigstens eine organische oder anorganische Verbindung enthalten.

In einer weiteren bevorzugten Ausführungsform kann jede der Schichten einer erfindungsgemäßen Mehrschichtfolie mit Ausnahme der Barrierschicht wenigstens ein organisches oder anorganisches Farbpigment oder Farbstoff enthalten.

Vorzugsweise kann die erfindungsgemäße Folie in Bezug auf eine zentrale Verbindungsschicht, vorzugsweise eine Klebstoffschicht symmetrisch angeordnet sein.

Vorzugsweise weist die erfindungsgemäße Folie eine Schichtdicke von 20 bis 2000 µm, besonders bevorzugt von 50 bis 1500 µm, ganz besonders bevorzugt von 100 bis 1000 µm, insbesondere von 150 bis 500 µm auf.

Die Herstellung der erfindungsgemäßen Folie kann nach beliebigen Herstellungsverfahren wie z.B. durch Laminierung, Extrusion oder vorzugsweise durch Co-Extrusion erfolgen.

Dabei können sowohl einzelne als auch sämtliche Schichten einer erfindungsgemäßen Mehrschichtfolie durch Extrusion, insbesondere durch Blasfolien-Extrusion und/oder Flachfolien-Extrusion, insbesondere Blasfolien-Co-Extrusion und/oder Flachfolien-Co-Extrusion gebildet werden.

Werden einzelne Schichten einer erfindungsgemäßen Folie nach einem der vorstehenden Verfahren separat hergestellt, so kann der Haftvermittler z.B. als Pulver, in Form einer Folie, Schmelze oder als Flüssigzubereitung, zum Beispiel als Lösung oder Dispersion, nach üblichen Methoden wie Sprühen oder Gießen auf eine der Schichten der erfindungsgemäßen Folie, wie z.B. der Barrierschicht oder eine der Oberflächenschichten aufgebracht und eine weitere Schicht oder weitere Schichten damit verbunden werden. Alternativ kann der Haftvermittler auch auf eine der Schichten, wie z.B. der Barrierschicht oder eine der Oberflächenschichten durch Extrusion laminiert werden und eine weitere Schicht oder weitere Schichten damit verbunden werden.

Diese Herstellungsverfahren und entsprechende Produktionsparameter sind dem Fachmann allgemein bekannt.

Die erfindungsgemäße Mehrschichtfolie kann vorzugsweise durch Co-Extrusion hergestellt werden, wobei ein Blasfolien-Co-Extrusionsverfahren ganz besonders bevorzugt ist.

Die erfindungsgemäße Folie kann vorzugsweise geprägt und/oder gereckt werden.

Weiterhin kann die erfindungsgemäße Folie vorzugsweise bedruckt werden.

Die erfindungsgemäße Folie, insbesondere die erfindungsgemäße Mehrschichtfolie eignet sich zur Herstellung von Schutzfolien gegen die Einwirkung von UV-Strahlung und kurzwelligem sichtbaren Licht.

Ein weiterer Gegenstand der vorliegenden Erfindung ist daher die Verwendung der erfindungsgemäßen Folie, insbesondere der erfindungsgemäßen Mehrschichtfolie zur Herstellung von Schutzfolien gegen die Einwirkung von UV-Strahlung und kurzwelligem sichtbaren Licht.

Ein weiterer Gegenstand der vorliegenden Erfindung ist die Verwendung einer erfindungsgemäßen Folie als schlauchförmige Schutzfolie, insbesondere als äußere, schlauchförmige Schutzfolie eines zwei, schlauchförmige Folien aufweisenden, d. h. doppelwandigen, Schlauches zur Vermeidung von einer durch UV-Strahlung und/oder kurzwelligem Licht ausgelöste Aushärtung eines zwischen den beiden Schlauchfolien verpackten, mit reaktivem Kunststoffharz getränkten Trägermaterials.

Besonders bevorzugt ist die Verwendung einer erfindungsgemäßen Folie als außenliegende, schlauchförmige Schutzfolie eines doppelwandigen Folienschlauches mit einem zwischen den beiden Folienschläuchen liegenden mit reaktivem Kunststoffharz getränkten Trägermaterial zur Kanalrohrsanie rung gemäß Schlauchlining-Technik.

Die Verwendung einer erfindungsgemäßen Folie als außenliegende schlauchförmige Schutzfolie des beim Schlauchlining zum Einsatz kommenden, doppelwandigen Schlauches hat den großen Vorteil, dass sie neben der Einwirkung von UV-Strahlung auch die Einwirkung von kurzwelligem, sichtbaren Licht unterbindet. Dadurch können die in den auszuhärtenden Kunststoffharzen enthaltenen Photoinitiatoren auch bei Einwirkung längerwelliger Strahlung nicht aktiviert werden, wodurch eine ungewollte vorzeitige Aushärtung verhindert wird und der Schlauch langfristig, vorzugsweise wenigstens ein Jahr lagerfähig ist. Da die erfindungsgemäße Folie zudem kontakttransparent ist, kann die Kontrolle einer gleichmäßigen Tränkung des Trägermaterials mit dem auszuhärtenden Kunststoffharz einfach erfolgen, wodurch das Auftreten von Fehlstellen im sanierten Kanalrohr verhindert wird.

Sofern die erfindungsgemäße Schutzfolie auch eine Barrierschicht aufweist, wird mit ihrem Einsatz als Schutzfolie beim Kanalsanieren durch Schlauchlining-Technik zudem eine Barrierewirkung gegen eine mögliche Austrocknung des Harzes sowie ein Eintritt von Substanzen wie Monomeren in das Kanalsystem und ins Grundwasser verhindert. Außerdem kann die siegelfähige Oberfläche der erfindungsgemäßen Schutzfolie mit dem Trägermaterial durch vorzugsweise Heißsiegelung zumindest teilweise, vorzugsweise voll umfänglich verbunden werden, was die Stabilität des Systems verstärkt.

Weiterhin kann die erfindungsgemäße Schutzfolie auch zur Bedachung, als Außenverkleidung, für Schutzanzüge, als außenliegende Abdeckungen von Gebäudeteilen, Schildern sowie Anzeigetafeln jeder Art, für Brillengläser oder Fensterscheiben, als Verpackungsmaterial verwendet werden.

Der bei der Kanalsanierung gemäß Schlauchlining-Technik zum Einsatz kommende Schlauch sollte vorteilhafterweise nicht nur eine erfindungsgemäße Schutzfolie als außenliegende Schutzfolie aufweisen, um das zur Kanalsanierung zum Einsatz kommende Trägermaterial, das mit einer auszuhärtenden Kunststoffharzmasse getränkt ist, zu schützen, sondern auch als innenliegende Schlauchfolie eine vorzugsweise transparente Kunststofffolie, die die bei der Kanalsanierung notwendigen Eigenschaften aufweist.

Dazu muss die Folie nicht nur ausreichend lagerstabile mechanische Eigenschaften aufweisen, damit sie den Belastungen bei der Handhabung des Kanalsanierungsschlauches, insbesondere beim Aufblasen im Kanalsystem, bei dem vorangegangenen Transport und der vorangegangenen Lagerung standhält, sondern auch nach der Aushärtung des Kunststoffmaterials im Trägermaterial zum Sanierungsrohr ohne ein Ab- oder Zerreißen davon abziehbar ist.

Darüber hinaus muss gewährleistet sein, dass bis zum Einsatz des zur Kanalsanierung verwendeten Schlauches auch die innenliegende Schlauchfolie eine genügende Barriere gegen das Austrocknen des Harzes, d. h. gegen den Verlust von Monomeren bzw. übrigen Tränkmaterial bietet und bei der Aushärtung im Kanalrohr genügend UV-Strahlung durchlässt.

Eine weitere Aufgabe der vorliegenden Erfindung war es daher, ein Kanalrohrsanierungssystem zur Verfügung zu stellen, dass nicht nur vor dessen Einsatz die Einwirkung von UV-Strahlen und kurzwelligen, sichtbaren Licht verhindert, sondern auch die bei dessen Handhabung während und nach der Kanalrohrsanierung auftretende Probleme vermeidet.

Durch die Bereitstellung des erfindungsgemäßen Kanalrohrsanierungssystems gelingt dies.

Dieses erfindungsgemäße Kanalsanierungssystem zeichnet sich nicht nur durch einen Schlauch aus, dessen außenliegende Schlauchfolie der vorstehend beschriebenen erfindungsgemäßen Schutzfolie entspricht, die zumindest kontakttransparent und UV-Strahlung und kurzwelliges, sichtbares Licht absorbierende und/oder reflektierende Eigenschaften aufweist, sondern auch eine innenliegende Schlauchfolie, die zumindest für UV-Strahlen durchlässig, vorzugsweise transparent ist, umfasst, die das notwendige Eigenschaftsprofil aufweist. Vorzugsweise ist die innenliegende Schlauchfolie nicht schrumpffähig.

Vorzugsweise weist der Schlauch eine außenliegende Schlauchfolie als Schutzfolie und eine innenliegende Schlauchfolie sowie das dazwischenliegende Trägermaterial auf, das mit dem auszuhärtenden Kunststoffharz getränkt ist. Aus diesem getränkten Trägermaterial wird nach der Aushärtung das sanierte Kanalrohr gebildet. Als Trägermaterial kommt vorzugsweise Glasgewebe aus Glasfasern, Vliese und/oder nonwoven Textilfabrikate in Frage, das vorzugsweise mit ungesättigten Polyestherharzen und α,β -ungesättigten Monomeren, wie z. B. Styrol getränkt ist.

Nach der Aushärtung wird die innenliegende, aufgeblasene Schlauchfolie vom sanierten, aus Kunststoff und Trägermaterial gebildeten Kanalrohr abgezogen.

Um den Anforderungen einer problemlosen Handhabung der Innenschlauchfolie bei der Kanalrohrsanierung gemäß Schlauchlining-Technik gerecht zu werden, wird erfindungsgemäß vorzugsweise wenigstens eine 3-schichtige Kunststofffolie eingesetzt, die eine Barrierschicht, vorzugsweise eine Sauerstoffbarrierschicht, Wasserdampfbarrierschicht und/oder Ölbarrierschicht umfasst, und deren an das getränkte Trägermaterial unmittelbar angrenzende Oberflächenschicht sich mit auszuhärtenden, flüssigen Tränkmaterial, d. h. mit der auszuhärtenden Kunststoffharzmasse, nicht dauerhaft z. B. durch Quellung und Aushärtung verbindet, sondern ohne Abreißen abziehbar bleibt.

Vorzugsweise basiert die Barrierschicht auf wenigstens einem der Polymeren, die auch für die Herstellung der Barrierschicht der außenliegenden, schlauchförmigen Schutzfolie des erfindungsgemäßen Kanalsanierungssystems vorstehend angegeben ist, besonders bevorzugt auf wenigstens einem Polyamid, Ethylen/vinylalkohol-Copolymer, Polyvinylalkohol, einem zyklischen Olefincopolymer, Polyvinylidenchlorid, ganz besonders bevorzugt auf wenigstens einem Polyamid.

Die Barrierschicht der innenliegenden schlauchförmigen Mehrschichtfolie des Schlauches trägt vorzugsweise auf jede ihrer Oberflächen eine weitere Kunststoffschicht, von denen die an das auszuhärtende Trägermaterial unmittelbar angrenzende Oberflächenschicht durch die Tränkflüssigkeit weder in ihren mechanischen Eigenschaften noch in ihrer Abziehbarkeit beeinflusst werden darf.

Bevorzugt eignen sich zur Herstellung dieser Oberflächenschichten Olefin-Homo oder Copolymeren. Besonders geeignete Olefin-Homo oder Copolymere sind thermoplastische Polymere von α,β ungesättigten Olefinen mit 2 bis 8 Kohlenstoff-Atomen, wie beispielsweise Polyethylen, Polypropylen, Polybutylen, Polyisobutylen oder Mischungen von wenigstens zwei der genannten Polymeren. Ganz besonders bevorzugt wird ein Polypropylen, vorzugsweise mit statistischem Aufbau, oder eine Mischung aus Polyethylen und Polypropylen, zur Herstellung einer oder beider Oberflächenschichten verwendet. Eine Mischung aus Polyethylenen, vorzugsweise aus Polyethylen mit niedriger Dichte und aus einem linearen Polyethylen niedriger Dichte, kann auch vorzugsweise zur Herstellung einer oder beider Oberflächenschichten eingesetzt werden. Vorzugsweise ist die Barrierschicht mit den genannten Oberflächenschichten über eine Haftvermittlerschicht verbunden.

Die vorstehend angegebenen Polymermaterialien für Haftvermittlerschichten können auch zur Herstellung der Haftvermittlerschichten zwischen der Barrierschicht und der jeweiligen Oberflächenschicht eingesetzt werden.

Ganz besonders bevorzugt wird als innenliegende Schlauchfolie für das erfindungsgemäße Kanalsanierungssystem eine 5-schichtige Folie mit folgendem Aufbau eingesetzt:

Schicht a) basierend auf einer Mischung aus Polypropylen vorzugsweise mit statistischem Aufbau, und Polyethylen die direkt an das auzuhärtende Trägermaterial angrenzt

Schicht b) basierend aus gepropften Polypropylen als Haftvermittlerschicht

Schicht c) basierend auf einem thermoplastischen Polyamid als Barrierschicht

Schicht d) basierend aus gepropften Polypropylen als Haftvermittlerschicht

Schicht e) basierend auf Polyethylen, vorzugsweise auf einer Mischung von LDPE und LLDPE,

Jede der Schichten des innenliegenden Folienschlauches kann auch, wenn notwendig, jeweils unabhängig voneinander mit Additiven ausgewählt aus der Gruppe umfassend Antioxidantien, Antiblockmittel, Antifogmittel, Antistatika, antimikrobielle Wirkstoffe, Hitze-Stabilisatoren, Prozess-Stabilisatoren, Prozesshilfsmittel, Flammschutzmittel, Nukleierungsmittel, Kristallisationsmittel, vorzugsweise Kristallkeimbildner, Gleitmittel, Flexibilisierungsmittel, Siegelmittel, Weichmacher, Silane, Abstandshalter, Füllstoffe, Peel-Additive, Wachse, Benetzungsmittel, oberflächenaktive Verbindungen, vorzugsweise Tenside, und Dispergiermittel ausgerüstet sein.

In dem erfindungsgemäßen Kanalsanierungssystem wird vorzugsweise die innenliegende, schlauchförmige Mehrschichtfolie so verwendet, dass an die Oberflächenschicht basierend auf der Mischung von Polypropylen und Polyethylen das auszuhärtende Trägermaterial direkt angrenzt.

Die innenliegende Schlauchfolie der erfindungsgemäßen Kanalsanierungssystems hat vorzugsweise eine Gesamtdicke von 20 – 2.000 μm , vorzugsweise von 120 – 300 μm , ganz besonders bevorzugt 150 – 250 μm und zeichnet sich durch hervorragende mechanische Werte aus.

Durch den Einsatz des erfindungsgemäßen Schlauchsanierungssystems, insbesondere durch die vorstehend beschriebenen Innenschlauchfolie, kann der in den zu sanierenden Kanal eingezogene, doppelwandige Schlauch problemlos, d. h. ohne Aufplatzen aufgeblasen werden, um eine problemlose UV-Aushärtung des im Schlauch befindlichen, mit dem flüssigen Tränkmaterial getränkten Trägermaterials zu erzielen. Außerdem kann nach der Aushärtung, wenn das gefestigte, sanierte Kanalrohr aus dem ausgehärteten Trägermaterial vorliegt, die Innenschlauchfolie ohne Abreißen bzw. Festsitzen davon abgezogen werden.

Beispiele:

Die nachfolgenden Beispiele dienen der Erläuterung der Erfindung, sind jedoch nicht einschränkend auszulegen.

Chemische Charakterisierung der eingesetzten Rohstoffe:

Batch 1:	Masterbatch (Zinkoxid und sterisch gehindertes Amin (Polypiperidinaminoderivat) (60 Gew.%), LDPE (40 Gew.%))
Batch 2:	Masterbatch (gelbes Pigment: Benzimidazolone (40 Gew.%), PE (60 Gew.%))
Admer NF 498E:	mit Maleinsäureanhydridgruppen modifiziertes LDPE der Firma Mitsui (Haftvermittler)
Durethan C 38F:	Copolyamid
Admer Q B 520 E:	Polypropylen mit Maleinsäureanhydrid geproft
Dow R 338-02N:	Statisch aufgebautes Polypropylen der Firma Dow

Die Mehrschichtfolien der Vergleichsbeispiele 1 bis 3 sowie des Beispiels 1 bestehen jeweils aus 5 Schichten, weisen eine Schichtdicke von jeweils 200 µm auf und wurden durch Blasfolien-Co-Extrusion hergestellt. Die Schichten 1-5 grenzen in nachstehender Reihenfolge jeweils unmittelbar aneinander. Alle nachfolgenden %-Angaben stellen jeweils Gew.% dar.

Vergleichsbeispiel 1 (farblose, transparente Folie):

- Schicht 1 (65 µm): 100% LDPE
- Schicht 2 (20 µm): 100% Admer NF 498E
- Schicht 3 (30 µm): 100% PA
- Schicht 4 (20 µm): 100% Admer NF 498E
- Schicht 5 (65 µm): 100% LDPE

Vergleichsbeispiel 2 (farblose Folie enthaltend wenigstens eine UV-Strahlung absorbierende und/oder reflektierende Verbindung):

Schicht 1 (65 µm): 100% LDPE

Schicht 2 (20 µm): 97% Admer NF 498E und 3% Batch 1

Schicht 3 (30 µm): 100% PA

Schicht 4 (20 µm): 97% Admer NF 498E und 3% Batch 1

Schicht 5 (65 µm): 100% LDPE

Vergleichsbeispiel 3 (gelbe Folie enthaltend wenigstens ein kurzwelliges, sichtbares Licht absorbierendes und/oder reflektierendes Farbpigment oder Farbstoff):

Schicht 1 (65 µm): 97% LDPE und 3% Batch 2

Schicht 2 (20 µm): 100% Admer NF 498E

Schicht 3 (30 µm): 100% PA

Schicht 4 (20 µm): 100% Admer NF 498E

Schicht 5 (65 µm): 97% LDPE und 3% Batch 2

Vergleichsbeispiel 4:

Die Mehrschichtfolie des Vergleichsbeispiels 4 besteht aus 5 Schichten, weist eine Schichtdicke von 230 µm auf, ist handelsüblich erhältlich und stellt eine undurchsichtige silberfarbene bis graue Folie dar. Die Schichten 1-5 grenzen in nachstehender Reihenfolge jeweils unmittelbar aneinander. Die nachfolgenden %-Angaben stellen jeweils Gew.% dar.

Schicht 1 (95 µm): LDPE und silberner Farbbatch

Schicht 2 (9 µm): 100% Admer NF 498E

Schicht 3 (26 µm): 100% PA

Schicht 4 (9 µm): 100% Admer NF 498E

Schicht 5 (93 µm): LDPE und silberner Farbbatch

Beispiel 1 (gelbe Folie enthaltend wenigstens ein kurzwelliges, sichtbares Licht absorbierendes und/oder reflektierendes Farbpigment oder Farbstoff und wenigstens eine UV-Strahlung absorbierende und/oder reflektierende Verbindung):

Schicht 1 (65 µm): 97% LDPE und 3% Batch 2

Schicht 2 (20 µm): 97% Admer NF 498E und 3% Batch 1

Schicht 3 (30 µm): 100% PA

Schicht 4 (20 µm): 97% 100% Admer NF 498E und 3% Batch 1

Schicht 5 (65 µm): 97% LDPE und 3% Batch 2

Beispiel 2 (gelbe Folie enthaltend wenigstens ein kurzwelliges, sichtbares Licht absorbierendes und/oder reflektierendes Farbpigment oder Farbstoff und wenigstens eine UV-Strahlung absorbierende und/oder reflektierende Verbindung):

Die Mehrschichtfolie des Beispiels 2 besteht aus 9 Schichten, weist eine Schichtdicke von 170 µm auf und wurde durch Blasfolien-Co-Extrusion und durch Schlauchverklebung hergestellt. Die Schichten 1-9 grenzen in nachstehender Reihenfolge jeweils unmittelbar aneinander. Die nachfolgenden %-Angaben stellen jeweils Gew.% dar.

Schicht 1 (29 µm): 97,5% LDPE und 2,5% Batch 2

Schicht 2 (6 µm): 100% Admer NF 498E

Schicht 3 (30 µm): 100% PA

Schicht 4 (6 µm): 100% Admer NF 498E

Schicht 5 (58 µm): 87,5 % Ethylen-Vinylacetat-Copolymer, 2,5 % Batch 2,
10% Batch 1

Schicht 6 (6 µm): 100% Admer NF 498E

Schicht 7 (30 µm): 100% PA

Schicht 8 (6 µm): 100% Admer NF 498E

Schicht 9 (29 µm): 97,5% LDPE und 2,5% Batch 2

Beispiel 3 Eine farblose, transparente Mehrschichtfolie gemäß der nachstehenden Angabe wurde mit einer Gesamtschichtdicke von 200 µm durch Blasfolien-Co-Extrusion hergestellt. Die angegebenen Schichten grenzen in der angegebenen Reihenfolge jeweils unmittelbar aneinander. Alle nachfolgenden Prozentangaben stellen jeweils Gew.% da.

Beispiel 3 (farblose, transparente Folie):

Schicht 1 (65 µm): Mischung aus 50 Gew.% Polypropylen (Dow R 338-02N) und 50 Gew.% LDPE

Schicht 2 (15 µm): 100 % Admer QP 520 E

Schicht 3 (40 µm): Durethan C 38 F (Copolyamid)

Schicht 4 (15 µm): Admer NF 498 E (Haftvermittler)

Schicht 5 (65 µm): Mischung aus LDPE/ LLDPE 70:30

Vergleichsbeispiel 5 (farblose/transparente Folie)

Diese Mehrschichtfolie mit der nachstehenden Schichtfolge und einer Gesamtschichtdicke von 200 µm wurde durch Blasfolien-Coextrusion hergestellt.

Schicht 1 (145 µm): LDPE

Schicht 2 (15 µm): Admer QB 520 E (Haftvermittler)

Schicht 3 (40 µm): Durethan C 38 F (Copolyamid)

Bestimmungsmethoden:

Bestimmung der Kontakttransparenz:

Zur Bestimmung der Kontakttransparenz wird die jeweilige Folie auf eine mit schwarzem Text (Schriftart: Arial, Schriftgröße 10) bedruckte weiße DIN A4-Seite gelegt und es wird die Lesbarkeit des darunter liegenden Textes mit einem Schulnotensystem beurteilt:

Note 1: sehr gut lesbar (Text klar erkennbar, es fällt nicht auf, dass eine Folie über dem Text liegt),

Note 2: sehr leichte Beeinträchtigung der Lesbarkeit des Textes unter der Folie,

Note 3: leichte Beeinträchtigung der Lesbarkeit des Textes unter der Folie,

Note 4: Merkliche Beeinträchtigung der Lesbarkeit des Textes unter der Folie. Der Text kann aber insgesamt noch gelesen werden.

Note 5: Deutliche Beeinträchtigung der Lesbarkeit des Textes unter der Folie. Die Buchstaben erscheinen sehr verschwommen und sind verdeckt und sind fast nicht mehr zu erkennen. Der Text kann praktisch nicht mehr gelesen werden.

Note 6: Der Text unter der Folie kann nicht mehr erkannt werden und ist unlesbar. Die Folie deckt den Text (nahezu) vollständig ab. Es liegt keine Kontakttransparenz mehr vor.

Die Kontakttransparenz ist von den Schichtdicken der jeweiligen Folien abhängig. Bei den Beispielen 1 und 2 und den Vergleichsbeispielen 1-3 ist die Schichtdicke der Folie kleiner oder gleich 200 µm. Bei Vergleichsbeispiel 4 beträgt die Schichtdicke der Folie 230 µm. Ein analoges Resultat wäre bei Vergleichsbeispiel 4 aber auch bei einer Schichtdicke dieser Folie kleiner als 200 µm erzielt worden, da diese undurchsichtig ist.

Bestimmung der UV/Licht-Blockerwirkung:

Verwendetes UV-VIS-Gerät: UV-3101PC von Shimadzu.

Für die Bestimmung der Schutzwirkung der Folie gegen UV-Strahlung bzw. kurzwelliges, sichtbares Licht wird aus der Folie ein kleiner Beutel (Abmessung 10 cm x 10 cm) durch entsprechendes Siegelng geformt. In diesen Beutel legt man – in einem abgedunkelten Raum - innerhalb von 1 Minute ca. 50 g einer reaktiven Harzmischung, die durch UV- oder kurzwelliges, sichtbares Licht aushärten kann. Anschließend wird der Beutel vollständig und dicht verschlossen, und dem Sonnenlicht ausgesetzt (die Versuche fanden an Sonnentagen mit mehr als 8 Stunden Sonnenstrahlung pro Tag im Juli statt).

Es wird die Zeit ermittelt, bis sich das verpackte Harz durch strahleninduzierte Aushärtung durch Sonnenlicht verfestigt hat. Bei maximaler Schutzwirkung gegen UV-Strahlung bzw. kurzwelliges, sichtbares Licht kann das Harz unendlich lange dem Sonnenlicht ausgesetzt werden, ohne auszuhärten.

Messergebnisse:

Beispiel	Transmission [%] bei den Wellenlängen 300/350/380/400/430 und 450 nm	Kontakttransparenz [Note]	Zeit der Aushärtung des Harzes in der Folie durch Sonnenlicht
Vergleichsbeispiel 1	90.3/91.2/92.2/92.7/93.7/95.6	1	kleiner 1 min
Vergleichsbeispiel 2	1.02/0.12/0.58/33.6/84.9/91.03	1	30 min
Vergleichsbeispiel 3	12.31/20.63/3.25/2.25/1.32/0.92	2	14 min
Vergleichsbeispiel 4	0.92/1.21/1.42/1.63/1.43/1.30	6	25 Tage
Beispiel 1	0.22/0.33/0.043/0.037/0.032/0.066	2	keine Härtung nach 3 Monaten
Beispiel 2	0.026/0.018/0.021/0.043/0.071/0.082	3	keine Härtung nach 3 Monaten

Vergleichsbeispiel 1 zeigt, dass eine herkömmliche, farblose, hoch transparente Folie keinerlei Blockerwirkung gegen UV- bzw. kurzwelliges sichtbares Licht (Vis) aufweist, so dass bei Einwirkung von UV-Vis-Strahlung eine sofortige Aushärtung des Harzes stattfindet. Es liegt im Wellenlängenbereich von 300 bis 450 nm eine Transmission größer als 90% vor. Zwar ist die Kontakttransparenz der Folie dabei hervorragend, jedoch erfüllt die Folie keinerlei Schutzfunktion gegenüber strahleninduzierter Harzaushärtung, wobei die Aushärtung des Harzes im Bereich 300 bis 450 nm erfolgt.

Vergleichsbeispiel 2 zeigt, dass durch Zugabe wenigstens einer UV-Strahlung absorbierenden und/oder reflektierende Verbindung gegenüber Vergleichsbeispiel 1 eine gewisse Schutzfunktion gegenüber Aushärtung des Harzes durch UV-Strahlung (bis 380 nm) erreicht werden kann, da sich die Transmission bei der Folie bis 380 nm auf unter 1,1 % beläuft. Die Aushärtung des Harzes findet aber durch kurzwelliges, sichtbares Licht mit Wellenlängen größer 380 nm dennoch statt, was durch die zunehmende Transmission bei höher werdenden Wellenlängen begründet ist.

Somit ist die Schutzfunktion der Folie gegenüber strahleninduzierter Harzaushärtung immer noch ungenügend. Die Kontakttransparenz der Folie ist dabei immer noch hervorragend.

Vergleichsbeispiel 3 beweist, dass durch Zugabe wenigstens eines gelben, kurzwelliges, sichtbares Licht absorbierendes und/oder reflektierendes Farbpigments gegenüber Vergleichsbeispiel 1 eine gewisse Schutzfunktion gegenüber Aushärtung des Harzes durch sichtbares Licht (ab ca. 400 nm) erreicht werden kann, da sich die Transmission ab 400 nm bis 450 nm auf unter 3 % beläuft. Die Aushärtung des Harzes findet aber durch UV-Licht mit Wellenlängen kleiner 380 nm dennoch statt, da hier die Transmission viel zu hoch ist. Somit ist die Schutzfunktion der Folie gegenüber strahleninduzierter Harzaushärtung immer noch ungenügend. Die Kontakttransparenz der Folie ist durch Zugabe eines Farbbatches gegenüber Vergleichsbeispiel 1 etwas reduziert worden; die Kontakttransparenz ist aber immer noch hervorragend.

Vergleichsbeispiel 4 zeigt eine Folie, die keine Kontakttransparenz mehr aufweist. Die Transparenz dieser Folie liegt unter 1 %, der Haze-Grad bei über 99 %. In diesem Fall wurde ein silbriges bis graues Pigment in hoher Konzentration in die Folie gegeben, um eine Schutzwirkung gegen UV-Vis-Strahlung zu erreichen, damit das Harz in dem kritischen Wellenlängenbereich 300 bis 450 nm nicht aushärtet. Die Folie weist eine deutlich erhöhte Schutzfunktion gegen UV-Vis-Strahlung gegenüber den vorhergehenden Vergleichsbeispielen auf. Dennoch konnte nach 25 Tagen eine Harzaushärtung festgestellt werden, nachdem das verpackte Harz dem Sonnenlicht ausgesetzt war. Wegen der mangelnden oder nicht vorhandenen Kontakttransparenz kann aber die Folie aus Vergleichsbeispiel 4 nur sehr eingeschränkt verwendet werden.

Wird mit der Folie z.B. Glasfasergewebe getränkt mit Harz eingewickelt, so kann man nicht mehr überprüfen, ob die Tränkung des Glasfasermaterials mit Harz vollständig und homogen erfolgt ist.

Die **Beispiele 1 und 2** belegen die Eignung der erfindungsgemäßen Folien als Schutzfolie zur Vermeidung der Aushärtung strahlungshärtender Harze im Bereich 300 bis 450 nm.

Nur durch die Kombination wenigstens einer UV-Strahlung absorbierenden und/oder reflektierende Verbindung und wenigstens eines kurzwelliges, sichtbares Licht absorbierendes und/oder reflektierendes Farbpigment kann die Transmission derart reduziert werden, so dass bei Lagerung in der Sonne nach 3 Monaten praktisch keine Harzaushärtung stattfindet. Die Werte für die Transmission sind im Bereich 300 bis 450 nm stets kleiner 0,5 %. Besonders hervorzuheben ist dabei die immer noch hervorragende Kontakttransparenz der erfindungsgemäßen Folien.

Eignungstest als innenliegende Schlauchfolie

Zur Feststellung wie weit eine transparente Mehrschichtfolie gemäß Beispiel 3 bzw. Vergleichsbeispiel 5 als innenliegende Schlauchfolie für das erfindungsgemäße Schlauchsanierungssystem in Frage kommt, wurden auf einer Unterlage auszuhärtendes Trägermaterial aufgebracht und jeweils mit einer Mehrschichtfolie gemäß Beispiel 3 bzw. einer Mehrschichtfolie gemäß Vergleichsbeispiel 5 abgedeckt. Dazu wurde die Mehrschichtfolie gemäß Beispiel 3 bzw. Vergleichsbeispiel 5 mit der Schicht aus PP/PE Mischung bzw. aus Polyamid mit dem auszuhärtenden Trägermaterial in Berührung gebracht und anschließend mit UV-Licht ausgehärtet.

Die Schlauchfolie gemäß Beispiel 3 konnte ohne Mühe nach der Aushärtung des Harz/Trägermaterials wieder abgezogen werden und zeigte keine mechanische Beeinträchtigung. Dagegen war die Mehrschichtfolie an einigen Stellen fest mit dem Trägermaterial verbunden, so dass an solchen Stellen ein Abriss der Folie erfolgte.

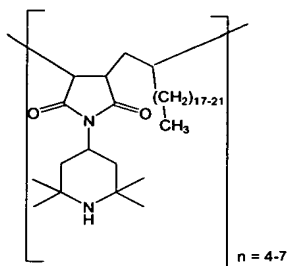
Durch diese Gefahr einer zu intensiven Verbindung der Polyamidschicht der Mehrschichtfolie gemäß Vergleichsbeispiel 5 mit dem ausgehärteten Harz ist auch eine Versprödung und damit mechanische Beeinträchtigung der innenliegenden Schlauchfolie und die Entfernung der Schlauchfolie nach der Aushärtung mit Schwierigkeiten verbunden. Beide Beeinträchtigungen sind mit der innenliegenden, schlauchförmigen Mehrschichtfolie bei einem erfindungsgemäßen Kanalsanierungssystem nicht gegeben.

Patentansprüche:

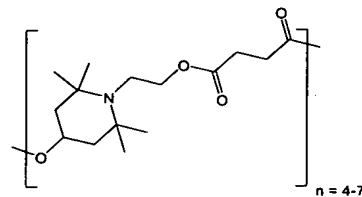
1. Eine zumindest kontakttransparente, UV-Strahlung und kurzwelliges, sichtbares Licht absorbierende und/oder reflektierende, einschichtige oder mehrschichtige Folie umfassend wenigstens eine Schicht basierend auf wenigstens einem gegebenenfalls modifizierten thermoplastischen Olefin-Homo-oder Copolymeren enthaltend eine Kombination aus wenigstens einem kurzwelliges, sichtbares Licht absorbierenden und/oder reflektierendes organischen oder anorganischen Farbpigment oder Farbstoff, und aus wenigstens einer die UV-Strahlung absorbierenden und/oder reflektierenden, organischen oder anorganischen Verbindung.
2. Eine Folie nach Anspruch 1, dadurch gekennzeichnet, dass das organische oder anorganische Farbpigment oder der Farbstoff kurzwelliges, sichtbares Licht, vorzugsweise zu mehr als 90 %, absorbiert und/oder reflektiert.
3. Eine Folie nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass das organische oder anorganische Farbpigment oder der Farbstoff Licht im Wellenbereich von 400 bis 500 nm absorbiert und/oder reflektiert.
4. Eine Folie nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, dass als organisches oder anorganisches Farbpigment wenigstens ein Farbpigment ausgewählt aus der Gruppe umfassend Carbonyl-Farbstoffe, vorzugsweise Chinone, Indigo-Farbstoffe und Chinacridone, Azo-Verbindungen, Cyanin-Verbindungen, vorzugsweise Triphenylmethan-Verbindungen, Azomethine, Isoindoline, Dioxazine, Metalloxide, Übergangsmetalloxide, Metalloxidhydrate und Übergangsmetalloxidhydrate, vorzugsweise ein gelbes Farbpigment oder ein gelber Farbstoff ausgewählt aus dieser Gruppe, vorliegt.

5. Eine Folie nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass als eine UV-Strahlung absorbierende und/oder reflektierende Verbindung wenigstens eine Verbindung vorliegt, die die UV-Strahlung in einem Wellenlängenbereich von 200 bis 400 nm, vorzugsweise zu mehr als 90 % absorbiert und/oder reflektiert.
6. Eine Folie nach Anspruch 5, dadurch gekennzeichnet, dass als UV-Strahlung absorbierende und/oder reflektierende Verbindung wenigstens eine Verbindung ausgewählt aus der Gruppe umfassend Metalloxide, Übergangsmetalloxide, Metalloxidhydrate, Übergangsmetalloxidhydrate, Benzophenone, Anthranilate, Salicylate, Dibenzoylmethane-Derivate, p-Aminobenzosäure-Derivate, Zimtsäure-Derivate (Phenylacrylsäure –Derivate), Cyanoacrylate, Benzimidazol-Derivate, Benzotriazol-Derivate, β - β' -Divinylacrylate, Alkyl- α -cyano- β - β' -divinylacrylate, 1,3,5-Triazin-Verbindungen und sterisch gehinderte Amine vorliegt.
7. Eine Folie nach Anspruch 6, dadurch gekennzeichnet, dass als eine die UV-Strahlung absorbierende Verbindung wenigstens eine Verbindung ausgewählt aus der Gruppe umfassend Zinkoxid, Titandioxid, 2-Ethoxy-ethyl-p-methoxycinnamat, Diethanolamin-p-methoxycinnamat, Octyl-p-methoxycinnamat, 2-Ethylhexyl-2-cyano-3,3-diphenylacrylat, Kaliumcinnamat, Propyl-4-methoxy-cinnamat, Amyl-4-methoxycinnamat, α -Cyano-4-methoxyzimtsäure bzw. der entsprechende Hexylester, Cyclohexyl-4-methoxycinnamat, Glyceryl-p-amino-benzoat, Amyl-p-dimethylaminobenzoat, Ethyl-4-bis(hydroxypropyl)-aminobenzoat, Octyl-p-dimethylaminobenzoat, Ethoxylierte-4-Aminobenzosäure, Octylsalicylat, Triethanolaminsalicylat, Salze der Salicylsäure, 4-Isopropylbenzylsalicylat, 2-Ethylhexyl-2-(4-phenylbenzoyl)benzoat, Homomenthylsalicylat, , 2-Hydroxy-4-methoxybenzophenon, 2,4,6-Triänilino-(p-carbo-2-ethylhexyloxy)-1,3,5-triazin, 2-Phenylbenzimidazol-5-sulfonsäure, 1-(4-tert-Butylphenyl)-3-(4-methoxyphenyl)propan-1,3-dion, p-Cumenyl-3-phenylpropan-1,3-dion, 1,3-Bis(4-Methoxyphenyl)propan-1,3-dion, Menthylanthranilat, Homomenthyl-N-acetylanthranilat, 2-Hydroxy-4-octylbenzophenon, 6-tert-Butyl-2-(5-chlor-2H-

benzotriazol-2-yl)-4-methylphenol, 2,4-Di-*tert*-butyl-6-(5-chlor-2H-benzotriazol-2-yl)-phenol, 2-(2H-Benzotriazol-2-yl)-4,6-di-*tert*-pentylphenol, 2-(2H-Benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol, 1,3-Bis-[(2'-cyano-3',3'-diphenylacryloyl)oxy]-2,2-bis-([(2'-cyano-3',3'-diphenylacryloyl)oxy]methyl)-propan, 2-(2H-Benzotriazol-2-yl)-4-methylphenol, 2-(2H-Benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol, Ethyl-2-cyano-3,3-diphenylacrylat, (2-Ethylhexyl)-2-cyano-3,3-diphenylacrylat, N,N'-Bisformyl-N,N'-bis-(2,2,6,6-tetramethyl-4-piperidiny)-hexamethyldiamin, Bis-(2,2,6,6-tetramethyl-4-piperidyl)-sebacat, Bis-(1,2,2,6,6-pentamethyl-4-piperidyl)-sebacat, Methyl-(1,2,2,6,6-pentamethyl-4-piperidyl)-sebacat,



und



eingesetzt wird.

8. Eine Folie nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, dass 0,05 bis 20, vorzugsweise 0,1 bis 5 Gew.%, besonders bevorzugt 0,1 bis 2 Gew.%, der Kombination, bezogen auf das Gesamtgewicht der Folie, vorhanden sind.
9. Eine Folie nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, dass die Folie mehrschichtig ist.
10. Eine Folie nach Anspruch 9, dadurch gekennzeichnet, dass die Komponenten der Kombination in unterschiedlichen Schichten oder in derselben Schicht vorliegen.
11. Eine Folie nach Anspruch 9 oder 10, dadurch gekennzeichnet, dass die Kombination in wenigstens einer der innenliegenden Schichten vorliegt.

12. Eine Folie nach Anspruch 9 oder 10, dadurch gekennzeichnet, dass das kurzwellige, sichtbare Licht absorbierende und/oder reflektierende Farbpigment oder der Farbstoff in wenigstens einer Oberflächenschicht der Folie und die organische oder anorganische UV-Strahlung absorbierende und/oder reflektierende Verbindung in wenigstens einer innenliegenden Schicht vorliegt.
13. Eine Folie nach Anspruch 9 bis 12, dadurch gekennzeichnet, dass sie wenigstens eine Barrierschicht, vorzugsweise eine Sauerstoffbarrierschicht, Wasserdampfbarrierschicht oder Ölbarrierschicht, umfasst.
14. Eine Folie nach Anspruch 13, dadurch gekennzeichnet, dass die Barrierschicht auf wenigstens einen Polymer ausgewählt aus der Gruppe umfassend Polyamid, EVOH, Polyvinylalkohol, COC, Polyvinylidenchlorid und einer Mischung aus wenigstens zwei der genannten Polymere basiert.
15. Eine Folie nach einem der Ansprüche 9 bis 14, dadurch gekennzeichnet, dass wenigstens eine Oberflächenschicht auf einem Olefin-Homo oder – Copolymeren basiert.
16. Eine Folie nach einem der Ansprüche 9 bis 15, dadurch gekennzeichnet, dass zwischen der Oberflächenschicht und der Barrierschicht eine Haftvermittlerschicht angeordnet ist.
17. Eine Folie nach Anspruch 16, dadurch gekennzeichnet, dass die Haftvermittlerschicht aus einem modifizierten Polyolefin besteht.
18. Eine Folie nach Anspruch 17, dadurch gekennzeichnet, dass die Kombination in der Haftvermittlerschicht vorliegt.
19. Eine Folie nach einem der Ansprüche 9 bis 18, dadurch gekennzeichnet, dass jede der Oberflächenschichten auf wenigstens einem Olefin-Homo oder Copolymeren basiert und jeweils über eine Haftvermittlerschicht mit der Barrierschicht verbunden ist.

20. Eine Folie nach Anspruch 19, dadurch gekennzeichnet, dass jede der Haftvermittlerschichten die Kombination, vorzugsweise wenigstens die UV-Strahlung absorbierende und/oder reflektierende Verbindung enthält.
21. Eine Folie nach einem der Ansprüche 1 bis 19, dadurch gekennzeichnet, dass das das kurzwellige Licht absorbierende und/oder reflektierende Farbpigment oder der entsprechende Farbstoff in jeder der Schichten mit Ausnahme der Barrierschicht der Mehrschichtfolie vorliegt.
22. Eine Folie nach einem der Ansprüche 1 bis 21, dadurch gekennzeichnet, dass sie in Bezug auf eine zentrale Verbindungsschicht, vorzugsweise eine Klebstoffschicht symmetrisch angeordnet ist.
23. Eine Folie nach einem der Ansprüche 1 bis 22, dadurch gekennzeichnet, dass jede Komponente der Kombination bei Temperaturen bis zu 300 °C stabil ist.
24. Eine Folie nach einem der Ansprüche 1 bis 23, dadurch gekennzeichnet, dass die Folie durch Coextrusion erhältlich, vorzugsweise durch Blasfolien-coextrusion erhältlich ist.
25. Eine Verwendung einer Folie nach einem der Ansprüche 1 bis 24 als Schutzfolie gegen die Einwirkung von UV-Strahlung und kurzwelligem sichtbarem Licht.
26. Eine Verwendung nach Anspruch 25 als Schutzfolie in Form einer außen liegenden Schlauchfolie eines doppelwandigen Schlauches zur Vermeidung von durch UV-Strahlung und/oder kurzwelligem Licht ausgelöster Härtung eines zwischen der äußeren und der innenliegenden Schlauchfolie verpackten, reaktiven Kunststoffharzes.
27. Eine Verwendung nach einem der Ansprüche 25 oder 26 als schlauchförmige Schutzfolie bei der Schlauchlining-Technik zur Kanalrohrsanieung.

28. Verwendung einer Folie nach einem der Ansprüche 1 bis 24 zur Bedachung, als Außenverkleidung, für Schutzanzüge, als außenliegende Abdeckungen von Gebäudeteilen, Schildern sowie Anzeigetafeln jeder Art, für Brillengläser oder Fensterscheiben, als Verpackungsmaterial.
29. Ein Kanalrohrsanierungssystem geeignet für eine Schlauchlining-Technik umfassend einen, für das Einbringen in das zu sanierende Kanalrohr vorgesehenen doppelwandigen Schlauch aus einer außenliegenden, schlauchförmigen Schutzfolie gemäß einem der Ansprüche 1 – 23 und einer innenliegenden, mehrschichtigen Kunststoffschlauchfolie und einem zwischen den beiden Schlauchfolien befindlichen, durch UV-Strahlung aushärtbaren, imprägniertem Trägermaterial, vorzugsweise einem mit einem ungesättigten Harzsystem getränkten Glasfasermaterial.
30. Ein Kanalrohrsanierungssystem nach Anspruch 29, dadurch gekennzeichnet, dass die innenliegende, mehrschichtige Schlauchfolie eine Schicht a) aus wenigstens einem Polyolefin, wenigstens einem Olefin-Copolymeren oder aus einer Mischung von Polyolefinen, die mit dem Trägermaterial direkt in Berührung kommt, eine Haftvermittlerschicht b), eine Barrierschicht c) basierend auf Polyamid, eine weitere Haftvermittlerschicht d) und eine Schicht e) basierend auf wenigstens einem Olefin-Homo oder Copolymeren umfasst.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/008845

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08J5/18 F16L55/162

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)

C08J F16L

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, 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	WO 2007/147758 A2 (CIBA SC HOLDING AG [CH]; CIBA SPEC CHEM SPA [IT]; VITALE MARCELLO [IT]) 27 December 2007 (2007-12-27) claims 1,3,5,7,9 examples 1-5	1-4,8-30
X	US 2005/005285 A1 (OLSON DANIEL ROBERT [US] ET AL) 6 January 2005 (2005-01-06) claim 1 paragraph [0020] - paragraph [0024] ----- -/--	1-4,8-30



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"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

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Authorized officer

Schambeck, Werner

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/008845

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 198045 Thomson Scientific, London, GB; AN 1980-79858C XP002571973 -& JP 55 124485 A (MITSUI TOATSU CHEM INC) 25 September 1980 (1980-09-25) abstract -----	1-4,8-30
X	DATABASE WPI Week 198324 Thomson Scientific, London, GB; AN 1983-57440K XP002571974 -& JP 58 076031 A (MITSUBISHI PETROCHEMICAL CO LTD) 9 May 1983 (1983-05-09) abstract -----	1-4,8-30
A	CH 676 029 A5 (I & C INVESTMENT AND CONTROLIN) 30 November 1990 (1990-11-30) claims 1,17 -----	1-4,8-30

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2009/008845

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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JP 55124485 A	25-09-1980	JP 1236109 C JP 58023072 B	17-10-1984 12-05-1983
JP 58076031 A	09-05-1983	JP 1588495 C JP 2006487 B	19-11-1990 09-02-1990
CH 676029 A5	30-11-1990	CH 676493 A5	31-01-1991

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES
 INV. C08J5/18 F16L55/162

Nach der Internationalen Patentklassifikation (IPC) oder nach der nationalen Klassifikation und der IPC

B. RECHERCHIERTE GEBIETE

Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)
 C08J F16L

Recherchierte, aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

EPO-Internal, WPI Data

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	WO 2007/147758 A2 (CIBA SC HOLDING AG [CH]; CIBA SPEC CHEM SPA [IT]; VITALE MARCELLO [IT]) 27. Dezember 2007 (2007-12-27) Ansprüche 1,3,5,7,9 Beispiele 1-5	1-4,8-30
X	US 2005/005285 A1 (OLSON DANIEL ROBERT [US] ET AL) 6. Januar 2005 (2005-01-06) Anspruch 1 Absatz [0020] - Absatz [0024]	1-4,8-30

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Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen



Siehe Anhang Patentfamilie

* Besondere Kategorien von angegebenen Veröffentlichungen :

"A" Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist

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"&" Veröffentlichung, die Mitglied derselben Patentfamilie ist

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Bevollmächtigter Bediensteter

Schambeck, Werner

C. (Fortsetzung) ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	<p>DATABASE WPI Week 198045 Thomson Scientific, London, GB; AN 1980-79858C XP002571973 -& JP 55 124485 A (MITSUI TOATSU CHEM INC) 25. September 1980 (1980-09-25) Zusammenfassung</p> <p>-----</p>	1-4,8-30
X	<p>DATABASE WPI Week 198324 Thomson Scientific, London, GB; AN 1983-57440K XP002571974 -& JP 58 076031 A (MITSUBISHI PETROCHEMICAL CO LTD) 9. Mai 1983 (1983-05-09) Zusammenfassung</p> <p>-----</p>	1-4,8-30
A	<p>CH 676 029 A5 (I & C INVESTMENT AND CONTROLIN) 30. November 1990 (1990-11-30) Ansprüche 1,17</p> <p>-----</p>	1-4,8-30

INTERNATIONALER RECHERCHENBERICHT

Angaben zu Veröffentlichungen, die zur selben Patentfamilie gehören

Internationales Aktenzeichen

PCT/EP2009/008845

Im Recherchenbericht angeführtes Patentdokument			Datum der Veröffentlichung		Mitglied(er) der Patentfamilie		Datum der Veröffentlichung	
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				CN	101479326	A	08-07-2009	
				EP	2038331	A2	25-03-2009	
				JP	2009540810	T	26-11-2009	
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US	2005005285	A1	06-01-2005	WO	2005007527	A1	27-01-2005	
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JP	55124485	A	25-09-1980	JP	1236109	C	17-10-1984	
				JP	58023072	B	12-05-1983	
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JP	58076031	A	09-05-1983	JP	1588495	C	19-11-1990	
				JP	2006487	B	09-02-1990	
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CH	676029	A5	30-11-1990	CH	676493	A5	31-01-1991	
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A47C 31/00 (2006.01) *B29C 73/10* (2006.01)
A61G 7/05 (2006.01) *B68G 7/12* (2006.01)

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(71) Applicant (*for all designated States except US*): **SURFACE MEDICAL INC.** [CA/CA]; #405, 1100 - 8th Avenue SW, Calgary, Alberta T2P 3T8 (CA).

(72) Inventors; and

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(74) Agent: **LEE, Brian**; Gowling Lafleur Henderson LLP, 550 Burrard Street, Suite 2300, Bentall 5, Vancouver, British Columbia V6C 2B5 (CA).

(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, 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, 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, MD, 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))

(54) Title: ADHESIVE PATCH AND METHOD OF USING THE SAME

(57) Abstract: The disclosure provides, in part, adhesive patches for repairing damaged surfaces of health care devices. In one of its aspects the disclosure provides a method of repairing the surface of health care device by applying an adhesive patch over a damaged portion of the surface, the patch comprising a film layer and an adhesive layer. In another one of its aspects, the disclosure provides an adhesive patch for repairing the surface of a health care device comprising a film layer and an adhesive layer.



ADHESIVE PATCH AND METHOD OF USING THE SAME

FIELD

[0001] The present disclosure generally relates to adhesive patches, for example, patches for repairing damaged surfaces of health care devices.

5 BACKGROUND

[0002] A typical health care device undergoes significant use and wear throughout its lifespan. Damage to the surface of the health care device, such as, tears, punctures, rips, burns, wear, cracks, and other surface damage, is unattractive, unsanitary and presents potential health risks. Increasingly, health care providers are becoming aware
10 of the role that contaminated environmental surfaces play in the transmission of pathogens. Patient care initiatives, particularly infection control efforts, are becoming more prevalent. At least 30% of health care associated infections can be prevented by following infection prevention and control strategies (Haley RW, Culver DH, White JW, Morgan WM, et al. (1985) The nationwide nosocomial infection rate: a new need
15 for vital statistics. Am J Epidemiol. Vol. 121:159-67). One challenge in cleaning or disinfecting the surfaces of health care devices is the occurrence of small tears and other damage to the surface of the device. Not only is routine cleaning of health care devices suboptimal, but damaged surfaces typically cannot be fully cleaned or disinfected thereby creating a potential reservoir for infectious agents.

20 [0003] Health care devices used in hospital environments have been found to be a source of health care associated infections. Environmental microbiological surveys have indicated that hospital devices (for example, beds, tables, stools, wheelchairs, racks, trolleys, stretchers, mattresses, catheter-bag, and other furniture, equipment and articles used in a hospital environment) can be contaminated with pathogens at a
25 higher incidence relative to other surfaces (see, for example, Rampling A, Wiseman S, Davis L., et al. (2001) Evidence that hospital hygiene is important in the control of methicillin-resistant *Staphylococcus aureus*. J Hosp Infect. Vol. 49:109-116; and Blythe D, Keenlyside D, Dawson SJ, Galloway A. (1998) Environmental contamination due to methicillin-resistant *Staphylococcus aureus*. J Hosp Infect. Vol.
30 38:67-70). In addition, there have been reports of hospital mattresses contaminated with infectious agents, including for example, *Pseudomonas aeruginosa*, methicillin-

- resistant *Staphylococcus aureus* (MRSA), vancomycin-resistant *Enterococci* (VRE), *Acinetobacter*, and other fungal and viral pathogens. Hospital mattresses damaged by extensive use, tears and sharp objects, such as needles, may create a potential reservoir for infectious agents and a portal for entry and exit of infectious agents.
- 5 Several studies have demonstrated that damaged mattresses have had a role in outbreaks, the transmission of disease to patients, and in some cases patient death (see Creamer E, Humphreys H. (2008) The contribution of beds to healthcare-associated infection: the importance of adequate decontamination, *J Hosp Infect.* Vol. 69:8-23; Sherertz RJ, Sullivan ML. (1985) An outbreak of infections with
- 10 *Acinetobacter calcoaceticus* in burn patients: contamination of patients' mattresses. *J Infect Dis.* Vol. 151:252-258; Moore EP, Williams EW. (1991) A maternity hospital outbreak of methicillin resistant *Staphylococcus aureus*. *J Hosp Infect.* Vol.19:5-16; Ndawula EM, Brown L. (1991) Mattresses as reservoirs of epidemic methicillin-resistant *Staphylococcus aureus*. *Lancet.* Vol. 337:488.; Fujita K, Lilly HA, Kidson A,
- 15 Ayliffe GA. (1981) Gentamicin resistant *Pseudomonas aeruginosa* infection from mattresses in a burns unit. *Br Med J.* Vol. 283:219-220; Robertson MH, Hoy G, Peterkin IM. (1980) Anti-static mattress as a reservoir of *pseudomonas* infection. *Br Med J.* Vol. 280:831-832; and O'Donoghue MA, Allen KD. (1992) Costs of an outbreak of wound infection in an orthopaedic ward. *J Hosp Infect.* Vol. 22:73-79).
- 20 These studies discuss that damaged hospital mattresses may harbour infectious agents and result in nosocomial infections, and intact mattresses or health care devices are preferred for appropriate cleaning, disinfection and infection prevention and control.

[0004] As a result, many health care providers have instituted policies requiring the replacement of health care devices having damaged surfaces or the replacement of

25 the damaged components of the device. However, replacement of a health care device or its damaged components can be costly, may result in equipment downtime, and the likelihood of a tear or other surface damage occurring after replacement is high. Thus many health care devices are left in a damaged state.

[0005] Prior art solutions exist to repair damaged surfaces of a variety of non-

30 medical devices. In one solution, ready-mix glue is applied to the damaged portion of the surface. However, this solution tends to be messy, leaves the surface temporarily out of service, and may create toxic fumes or be toxic through direct contact. In

another solution, duct or other types of tape are applied to the damaged portion of the surface. However, the edges of the tape tend to breakdown after extended use or following the application of liquids or body fluids. These edges can be difficult to clean properly, thereby, creating an additional potential reservoir for infectious agents.

5 SUMMARY

[0006] The disclosure provides, at least in part, adhesive patches for repairing damaged surfaces of health care devices.

[0007] In certain aspects the disclosure provides a method of repairing the surface of health care device by applying an adhesive patch over a damaged portion of the
10 surface, the patch comprising a film layer and an adhesive. In certain aspects, the disclosure provides an adhesive patch for repairing the surface of a health care device comprising a film layer and an adhesive.

[0008] The film layer may comprise one or more of the following properties: adhesion or bonding to the adhesive or interlayer, anti-decubitus, heat-resistance,
15 resistance to ultraviolet radiation, durability, flexibility, stretchable, breathability, cleanability, resistance to chemical cleaning products; anti-microbial properties, hypoallergenic and non-cytotoxic properties.

[0009] The adhesive may comprise one or more of the following properties: adhesion to film layer or interlayer and device surface, heat-resistance, pressure-
20 resistance, resistance to ultraviolet radiation, durability, flexibility, cleanability, resistance to chemical cleaning products; plasticizer resistant, anti-microbial, hypoallergenic and non-cytotoxic properties.

[0010] As used herein, the term ‘patch’ refers to articles having a size and adhesion characteristics suitable for affecting a durable repair to health care devices
25 such as, for example, mattresses used in hospital beds. In certain embodiments, the patches are generally planar in shape with a film layer and an adhesive layer.

[0011] As used herein, “a” or “an” means “at least one” or “one or more”.

[0012] This summary does not necessarily describe all features of the invention. Other aspects, features and advantages of the invention will be apparent to

those of ordinary skill in the art upon review of the following description of specific embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Figure 1A is a top plan view of a health care device having a damaged
5 surface.

[0014] Figure 1B is a side elevation view of the health care device shown in Figure 1B.

[0015] Figure 2A is a top plan view of the health care device shown in Figures 1A and 1B having an adhesive patch applied to the damaged portion of the surface of the
10 health care device.

[0016] Figure 2B is a side elevation view of the health care device shown in Figures 1A and 1B having an adhesive patch applied to the damaged portion of the surface of the health care device.

[0017] Figure 3A is top plan view of the patch shown in Figures 2A and 2B.

15 [0018] Figure 3B is side elevation view of the patch shown in Figures 2A and 2B.

DETAILED DESCRIPTION

[0019] The present adhesive patches comprise a film layer and an adhesive.

[0020] The film layer may be any suitable substance. For example, the film layer may comprise a thermoplastic or thermosetting polymer or a combination of
20 polymers. Examples of thermoplastic polymers include, but are not limited to, polyacetals, polyolefins, polyacrylics, polycarbonates, polystyrenes, polyesters, polyamides, polyvinyl, polysulfonates, polysulfides, polythioesters, polysulfones, polysulfonamides, polyureas, polyurethane, or the like, and combinations thereof. The present film layer may comprise a polyethylene, polyurethane, polypropylene, nylon,
25 silicone, polyamide, polyester, polyvinyl, or the like, or combinations thereof. Preferably the film layer comprises a polyvinyl, polyurethane, or the like. Such films are available commercially from a variety of sources, such as, for example Dartex Coatings Inc. (Nottingham, UK), DermaMed Coatings Company LLC. (Ohio, USA),

Argotec Inc. (Massachusetts, USA), Flexcon Inc. (Massachusetts, USA), ETC Technologies Inc. (Massachusetts, USA), and Medical Adhesive Tape Technologies Inc. (New York, USA). Films available from Dartex Coatings may include, but not limited to, DartexTC84. Films available from DermaMed Coatings Company may include, but not limited to, DermaMed4mil PU. Films available from Argotec may include, but not limited to, Argotec2mil PU. Films available from Flexcon may include, but not limited to, FlexconV400 and V600. Films available from ETC Technologies may include, but not limited to, ETC 2 mil, 3 mil, 4 mil, and 6 mil. Films available from Medical Adhesive Tape Technologies may include, but not limited to, M.A.T.T. 2.5GA PU, M.A.T.T. 3.0GA Vinyl, and M.A.T.T. 3.5GA vinyl. The film layer may be non-cytotoxic, hypoallergenic, resistant to bacterial growth, or a combination thereof. The film layer may have a dyne level of 36 dynes/cm or greater, 37 dynes/cm or greater, 38 dynes/cm or greater, 39 dynes/cm or greater, 40 dynes/cm or greater, for the side that will come into contact with the adhesive in the final construction.

[0021] Any suitable adhesive may be used herein. For example, pressure-sensitive adhesives (PSA), permanent adhesives, adhesives that cure with time, light-activated adhesives that cure with electromagnetic energy such as UV or visible light, or heat-activated adhesives may be used. The adhesive may be non-cytotoxic, hypoallergenic, resistant to bacterial growth, or a combination thereof. The adhesive may be in the form of an adhesive layer.

[0022] A pressure-sensitive adhesive may comprise polyurethane, silicone polymer, or other synthetic polymer based adhesive, and may or may not be cross-linked. Adhesives are available commercially from, for example, Adchem Inc. (New York, USA), 3M Canada Inc. (Ontario, Canada), Flexcon Inc. (Massachusetts, USA), and Medical Adhesive Tape Technologies Inc. (New York, USA). Adhesives from Adchem may include, but not limited to, Adchem 7833, Adchem 653, Adchem 7603, Adchem 7854, Adchem 7333 and Adchem 730. Adhesives from 3M may include, but not limited to, 3M9465. Adhesives from Flexcon may include, but not limited to, Flexmark TT200. Adhesives from Medical Adhesive Tape Technologies may include, but not limited to, COL-RZ002, COL-ACR003 and COL-ACR007.

[0023] In certain aspects, the present patches preferably are able to elongate at least 30%. For example, 31% or more, 32% or more, 33% or more, 34% or more, 35% or more, 36% or more, 37% or more, 38% or more, 39% or more, 40% or more. While not wishing to be bound by theory it is believed that the ability to elongation
5 reduces the risk of peeling or separation from the surface of the medical device while in use. Peeling or separation could reduce the efficacy of cleaning and/or disinfection procedures thus creating a potential reservoir for pathogens. The average of elongation may be measured by any suitable method such as, for example, ASTM D882.

10 [0024] In certain aspects, the present patches preferably have an average edge thickness of 10 mil or less, such as 9 mil or less, 8 mil or less, 7 mil or less, 6 mil or less. While not wishing to be bound by theory it is believed that thicker patches can present a risk of peeling or separation from the surface occurring. Peeling or separation could reduce the efficacy of cleaning and/or disinfection procedures thus
15 creating a potential reservoir for pathogens. The edge thickness may be measured by any suitable method such as, for example, using thickness gauges available from Mitutoyo or Mahr.

[0025] In certain aspects, the present patches preferably have an adhesion value of at least about 2.5 lbs/inch for at least 7 days after application wherein the temperature
20 is 16-21°C and the relative humidity is 15-50%. For example, the adhesion value may be 2.6 lbs/inch, 2.7 lbs/inch, 2.8 lbs/inch, 2.9 lbs/inch, 3.0 lbs/inch. While not wishing to be bound by theory it is believed that patches with lower adhesion values can present a risk of peeling or separation from the surface occurring. Peeling or separation could reduce the efficacy of cleaning and/or disinfection procedures thus
25 creating a potential reservoir for pathogens. The adhesion value may be measured by any suitable method such as, for example, ASTM D3330 or PSTC-101.

[0026] Health care devices may be subjected to cleaning and disinfection via a number of methods. For example, mattresses on hospital beds may be cleaned with compositions comprising hydrogen peroxide, sodium hypochlorite, ammonium-based
30 cleaning compositions, isopropanol, or the like. In certain embodiments, the present patches are resistant to one or more of such compositions. That is, the performance of

the patches *in situ* is not significantly affected by transitory but repeated exposure to the cleaning solution.

[0027] The present patches may be provided in any suitable shape such as, for example, square, rectangle, circle, oval, rhomboid, cross, or the like. The present patches may be provided in a roll or sheet form. In certain embodiments the patch may be trimmed to the desired size before application. The present patches may be provided in any suitable size. For example, the maximum diameter of the present patches may be 1 cm or more, 2 cm or more, 3 cm or more, 4 cm or more, 5 cm or more, 6 cm or more, 7 cm or more, 8 cm or more, 9 cm or more, 10 cm or more, 11 cm or more, 12 cm or more, 13 cm or more, 14 cm or more, 15 cm or more. The maximum diameter of the present patches may be 100 cm or less, 95 cm or less, 90 cm or less, 85 cm or less, 80 cm or less, 75 cm or less.

[0028] The present patches may comprise an anti-microbial agent. As used herein, the term “anti-microbial” means the reduction or inhibition of microbial bioburden, colonization, or attachment by microbial organisms. Antimicrobial agents include but not limited to, antibiotics, antiseptics, biocides, or other antimicrobial compounds, such as, for example, silver, silver nanoparticles, ionic silver, combinations of one or more silver compounds, other metals such as zinc, copper, gold, platinum, and their salts or complexes, for example, zinc undecylenate, quaternary ammonium salts, isoniazid, ethambutol, pyrazinamide, streptomycin, clofazimine, rifabutin, fluoroquinolones, ofloxacin, sparfloxacin, rifampin, azithromycin, clarithromycin, dapson, tetracycline, erythromycin, ciprofloxacin, doxycycline, ampicillin, amphotericin B, ketoconazole, fluconazole, pyrimethamine, sulfadiazine, clindamycin, lincomycin, pentamidine, atovaquone, paromomycin, diclazaril, acyclovir, trifluorouridine, foscarnet, penicillin, gentamicin, ganciclovir, iatroconazole, miconazole, Zn-pyrithione, chlorohexidine, polyhexamethylenebiguanides, polyhexamethylenebiguanides, triclosan, iodine, iodinepolyvinylpyrrolidone complex, urea-peroxide complex, benzalkonium salts, quaternary ammonium compounds based on saccharinate, algacides, carbamates, cyanates, turmeric extract, other natural anti-infective compounds and combinations thereof. Anti-microbial agents may be effective against one or more bacteria from the genus *Bordetella*, *Borrelia*, *Brucella*, *Campylobacter*, *Chlamydia*, *Chlamydomydia*,

Clostridium, Corynebacterium, Enterococcus, Escherichia, Francisella, Haemophilus, Helicobacter, Legionella, Leptospira, Listeria, Mycobacterium, Mycoplasma, Neisseria, Pseudomonas, Rickettsia, Salmonella, Shigella, Staphylococcus, Streptococcus, Treponema, Vibrio, and/or Yersinia. For example, Bordetella
 5 pertussis, Borrelia burgdorferi, Brucella abortus, Brucella canis, Brucella melitensis, Brucella suis, Campylobacter jejuni, Chlamydia pneumoniae, Chlamydia trachomatis, Chlamydophila psittaci, Clostridium botulinum, Clostridium difficile, Clostridium perfringens, Clostridium tetani, Corynebacterium diphtheriae, Enterococcus faecalis, Enterococcus faecium, Escherichia coli, Francisella tularensis, Haemophilus
 10 influenzae, Helicobacter pylori, Legionella pneumophila, Leptospira interrogans, Listeria monocytogenes, Mycobacterium leprae, Mycobacterium tuberculosis, Mycobacterium ulcerans, Mycoplasma pneumoniae, Pseudomonas aeruginosa, Rickettsia rickettsii, Salmonella typhi, Salmonella typhimurium, Shigella sonnei, Staphylococcus aureus, Staphylococcus epidermidis, Staphylococcus saprophyticus,
 15 Streptococcus agalactiae, Streptococcus pneumoniae, Streptococcus pyogenes, Treponema pallidum, Vibrio cholerae, Yersinia pestis, and the like. It is preferred that the present anti-microbial agent be efficacious against Escherichia coli, Legionella pneumophila, Streptococcus pneumoniae, Streptococcus pyogenes, and the like.

[0029] The present patches may contain an interlayer film to enhance the rigidity
 20 and handling of the invention. This interlayer can be, but not limited to, polyurethane, polyvinyl, polyester, kraft paper, or the like. Such films are available commercially from Adhesive Films, Inc. (New Jersey, USA). Examples from Adhesive films may include, but not limited to, UAF-472 1 mil, UAF-472 2 mil, and PAF-110 2 mil.

[0030] The present patches may comprise a release liner and/or a transfer liner on
 25 the film layer and/or adhesive layer to protect the patch before use. Such liners may also improve the ease of handling of the patch prior to application to device.

[0031] Referring to Figures 1A and 1B, an embodiment of a health care device 10
 30 is shown. The health care device 10 may be any device used in a health care environment, such as, for example, beds, tables, stools, wheel chairs, racks, trolleys, stretchers, mattresses, catheter-bags, and other furniture, equipment and articles used in a health care environment. The device 10 generally comprises a surface layer 12 and a supporting layer 14. The surface layer 12 defines at least a portion of the outer

surface of the device 10 that may be subject to contact with a person during the use of the device 10. The surface layer 12 may be comprised of any material suitable for a health care environment, such as, for example, while not limited to, nylon, silicone, polyurethane, polyvinyl, polyethylene, polyamides and polyesters. The supporting layer 14 supports the surface layer 12 and may be comprised of any material suitable to provide structural support to the surface layer 12, such as, for example, while not limited to, foam, wood, cotton, plastics, and metals. In the alternative, the device 10 may not comprise a supporting layer 14.

[0032] Figures 1A and 1B depict a damaged portion 20 of the surface layer 12. The damaged portion 20 may comprise one or more tears, punctures, rips, burns, wear, cracks, and other damage to the surface layer 12. As discussed above, damaged portions 20 of surface layers 12 in health care devices 10 are unattractive, unsanitary and present potential health risks by creating a host or reservoir for infectious agents.

[0033] Referring to Figures 2A and 2B, one embodiment of an adhesive patch 30 for repairing damaged surfaces of a health care device 10 is shown. The patch 30 is applied to the surface layer 12 of the device 10 to cover the damaged portion 20 and adhere to the surface layer 12. The patch 30 is configured to be suitable for application in health care environments. In particular, amongst other suitable properties for a health care environment, the patch 30 may comprise one or more of the following properties: physical properties, including, adhesion, anti-decubitus, heat-resistance, resistance to ultraviolet radiation, durability, flexibility, stretchable, breathability, cleanability, resistance to chemical cleaning products; anti-microbial properties, hypoallergenic and non-cytotoxic properties. The patch 30 comprises an adhesive layer 34 and a film layer 32.

[0034] Referring to Figures 3A and 3B, the patch 30 generally comprises a film layer 32, a peel-off layer 36, and an adhesive layer 34 disposed in between the film layer 32 and peel-off layer 36. Prior to application of the patch 30 to a health care device 10, the adhesive layer 34 functions to adhere the film layer 32 and peel-off layer 36 into a unitary patch 30. The film layer 32 and peel-off layer 36 protect the adhesive layer 34 and prevent the adhesive layer 34 from adhering to other objects. During application of the patch 30 to the device 10, the peel-off layer 36 is removed from the patch 30 and the adhesive layer 34 functions to adhere the film layer 32 to

the surface layer 12 of the device 10. The adhesive layer 34 may be comprised of any suitable adhesive suitable for a health care environment, such as, for example, acrylic, silicone. In particular, amongst other suitable properties for a health care environment, the adhesive layer 34 may comprise one or more of the following properties: physical
5 properties, including, adhesion to film layer and device surface, heat-resistance, pressure-resistance, resistance to ultraviolet radiation, durability, flexibility, cleanability, resistance to cleaning products, plasticizer resistant, anti-microbial properties, hypoallergenic and non-cytotoxic properties.

[0035] The film layer 32 comprises a top surface 42 and a bottom surface 44. The
10 top surface 42 is an externally facing surface that may be subject to contact with a person during use of the device 10; while the bottom surface 44 is an interior surface that is adhered by the adhesive layer 34, adhesive layer 34, adhesive layer 34 is also adhered to the top layer 46 of the peel-off layer 36, which prior to application of the patch 30 to the device 10 the peel-off-layer 36 is removed from the adhesive layer 34,
15 and is adhered by the adhesive layer 34 to the surface layer 12 of the device 10 during application of the patch 30 to the device 10. The film layer 32 may be comprised of any material suitable for a health care environment, such as, for example, nylon, silicone, polyurethane, polyvinyl, polyethylene, polyamides and polyesters. In particular, amongst other suitable properties for a health care environment, the film
20 layer 32 may comprise one or more of the following properties: physical properties, including, adhesion or bonding to the adhesive, anti-decubitus, heat-resistance, resistance to ultraviolet radiation, durability, flexibility, stretchable, breathability, cleanability, resistance to chemical cleaning products; anti-microbial properties, hypoallergenic and non-cytotoxic properties.

[0036] The peel-off layer 36 comprises a top surface 46 and a bottom surface 48. The top surface 46 is an internal surface that is adhered by the adhesive layer 34 to the bottom surface 44 of the film layer 32, prior to application of the patch 30 to the device 10 and peel-off layer 36 is removed from top surface 46 during application of the patch 30 to the device 10. The peel-off layer 36 may be comprised of any material
30 suitable to be removably adhered to the film layer 32 by the adhesive layer 34, such as, for example, kraft paper or polyester.

[0037] The present disclosure provides health care devices comprising a patch according to the present invention. The present disclosure provides a mattress comprising a patch according to the present invention.

[0038] The present disclosure provides the use of a patch as described herein for repairing the surface of a health care device such as a mattress. Said use comprises applying the patch over the damaged portion of the surface of the health care device.

[0039] The present disclosure provides a method of repairing the surface of health care device by applying a patch according to the present invention over a damaged portion of the surface. The patch may comprising a film layer and an adhesive layer. The patch may comprise an anti-microbial agent. The patch may comprise one or more of the following properties: adhesion, heat-resistance, pressure-resistance, resistance to ultraviolet radiation, durability, flexibility, cleanability, resistance to cleaning products; anti-microbial, wound healing, hypoallergenic and non-cytotoxic properties. The film layer may comprise a polyvinyl, polyurethane, or the like. The adhesive layer may comprise an acrylic, silicone, or the like. The patch may comprise a peel-off layer removably adhered to the film layer by the adhesive layer.

[0040] It is contemplated that the different parts of the present description may be combined in any suitable manner. For instance, the present examples, methods, aspects, embodiments or the like may be suitably implemented or combined with any other embodiment, method, example or aspect of the invention.

[0041] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as is commonly understood by one of ordinary skill in the art to which this invention belongs. Unless otherwise specified, all patents, applications, published applications and other publications referred to herein are incorporated by reference in their entirety. If a definition set forth in this section is contrary to or otherwise inconsistent with a definition set forth in the patents, applications, published applications and other publications that are herein incorporated by reference, the definition set forth in this section prevails over the definition that is incorporated herein by reference. Citation of references herein is not to be construed nor considered as an admission that such references are prior art to the present invention.

[0042] Use of examples in the specification, including examples of terms, is for illustrative purposes only and is not intended to limit the scope and meaning of the embodiments of the invention herein. Numeric ranges are inclusive of the numbers defining the range. In the specification, the word “comprising” is used as an open-ended term, substantially equivalent to the phrase “including, but not limited to,” and the word “comprises” has a corresponding meaning.

[0043] The invention includes all embodiments, modifications and variations substantially as hereinbefore described and with reference to the examples and figures. It will be apparent to persons skilled in the art that a number of variations and modifications can be made without departing from the scope of the invention as defined in the claims. Examples of such modifications include the substitution of known equivalents for any aspect of the invention in order to achieve the same result in substantially the same way.

[0044] The present invention will be further illustrated in the following examples. However it is to be understood that these examples are for illustrative purposes only, and should not be used to limit the scope of the present invention in any manner.

EXAMPLES

[0045] 28 different prototypes were developed based on a combination of 13 commercially available film layers and 9 commercially available adhesives layers. These prototypes were evaluated for their suitability in repairing damaged portions of the surfaces of health care devices. The film and adhesive layers were combined using standard manufacturing techniques.

[0046] Patches were evaluated for their ability to withstand standard hospital cleaning products.

[0047] Table 1 compares patch (Dartex + acrylic PSA, 3M and Adchem) relative to other tested compositions and that which is commercially available (Tear-Aid). Physical damages (cracking, shrinking, wrinkling) was observed for the material tested after 1 hour of immersion in the four chemicals (5.5% Sodium Hypochlorite, 7% Hydrogen Peroxide, 70% Isopropanol, Ammonium Chloride)

TABLE 1

Film	Adhesive	Surface	Adhesion Failure before 60 mins			
			Sodium Hypochlorite (5.5%)	Hydrogen Peroxide (7%)	Isopropanol (70%)	Ammonium Chloride
Argotex PU 2 mil	Flexmark TT200	Mattress Cover	Yes	n/a	Yes	n/a
Flexcon V400	3M 9465U	Mattress Cover	n/a	n/a	Yes	n/a
Flexon V400	Flexmark TT200	Mattress Cover	No	Yes	Yes	n/a
ETC 3mil PU	Flexmark TT200	Mattress Cover	Yes	Yes	Yes	n/a
Argotex PU 2 mil	3M 9465U	Mattress Cover	n/a	n/a	Yes	n/a
ETC 3mil PU	3M 9465U	Mattress Cover	No	No	Yes	No
M.A.T.T. 2.5 GA PU	COL-RZ002	Mattress Cover	n/a	n/a	Yes	n/a
M.A.T.T. 3.0GA Vinyl	COL-ACR003	Mattress Cover	n/a	n/a	Yes	n/a
M.A.T.T. 3.5GA Vinyl	COL-RZ002	Mattress Cover	n/a	n/a	Yes	n/a
ETC 3mil PU	AdChem 730	Mattress Cover	No	Yes	Yes	No
ETC 4mil PU	AdChem 730	Mattress Cover	No	Yes	Yes	No
DermaMed 4mil	3M9465U	Mattress Cover	No	No	No	No
Dartex TC84	3M9465U	Mattress Cover	No	No	No	No
Dartex TC84	AdChem 7833	Mattress Cover	No	No	No	No
Tear-Aid		Mattress Cover	No	Yes	Yes	No
Masta Plasta		Mattress Cover	Yes	Yes	Yes	Yes
Duct Tape		Mattress Cover	n/a	n/a	Yes	n/a

The patch may comprise an antimicrobial additive. Table 2 summarizes the presence or absence of an additive for a sample of patches.

5 TABLE 2

Composition	Additive (film / adhesive)
Dartex TC84 / Adchem 7833	Yes / Yes
DartexTC84 / 3M 9465U	Yes / No
Tear-Aid	No / No
MastaPlasta	No / No
Duct Tape	No / No

The patch may have a thickness of 10 mil or less after application to the health care device. Table 3 summarizes the thickness of a sample of patches.

TABLE 3

Composition	Thickness
Dartex TC84 / Adchem 7833	(5mil)
DartexTC84/ 3M 9465U	(7mil)
Tear-Aid	(12mil)
MastaPlasta	(>20 mil)

Duct Tape	(8 mil)
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The adhesive is preferably non-cytotoxic, hypoallergenic, and/or resistant to microbial growth. Table 4 summarizes these characteristics for certain adhesives.

TABLE 4

Composition		Non-Cytotoxicity	
Adchem 7833		Yes	
3M 9465U		No	
Tear-Aid		No	
MastaPlasta		No	
FlexconTT200		No	
Adchem 730		No	
ACR007		Yes	
ACR003		Yes	
RZ002		Yes	
Composition		Hypoallergenic	
Adchem 7833		Yes	
3M 9465U		No	
Tear-Aid		No	
MastaPlasta		No	
FlexconTT200		No	
Adchem 730		No	
ACR007		Yes	
ACR003		Yes	
RZ002		Yes	
Sample	Microbial Growth		
	S. aureus	P. aeruginosa	A. brasiliensis
Control	Heavy Growth	Heavy Growth	Heavy Growth
3M9465U	No Growth	No Growth	No Growth
Tear-Aid Adhesive	Minimal Growth	Minimal Growth	Minimal Growth

5

The film layer is preferably non-cytotoxic, hypoallergenic, and/or resistant to microbial growth. Table 5 summarizes these characteristics for certain films.

TABLE 5

Composition	Non-Cytotoxic
Dartex	Yes
Tear-Aid	No
MastaPlasta	No
ETC PU (3mil, 4 mil, 6mil)	Yes
3M7931	No
DermaMed4mil	Yes
Argotex2mil	No
FlexconV400 / V600	No
Composition	Hypoallergenic
Dartex	Yes
Tear-Aid	No
MastaPlasta	No
ETC PU (3mil, 4 mil, 6mil)	Yes
3M7931	No
DermaMed4mil	Yes

Argotex2mil		No	
FlexconV400 / V600		No	
Sample	Microbial Growth*		
	S aureus	P aeruginosa	Abrasiliensis
Control	Heavy Growth	Heavy Growth	Heavy Growth
DartextTC84	No Growth	No Growth	Minimal Growth
Tear-Aid	No Growth	No Growth	Minimal Growth

* microbial growth rate of less than 10% based on test standard ASTM G21

The adhesion value of the patch to the device is preferably 2.5 lbs / inch or greater 7 days after application at 16-21°C and relative humidity of 15-50% relative humidity.

5 Table 6 summarizes the performance of certain patches.

TABLE 6

Condition	Test Surface	180 degree Peel (lbs/in)			
		Adchem 730	Adcem 7833	3M9465U	Tear-Aid
1 day @RT	Stainless Steel	5.9	3.9	3.3	5.2
1 day @RT	Mattress Surface	3.0	2.0	2.4	n/a
7 day @RT	Stainless Steel	9.1	4.9	4.4	n/a
7 day @RT	Mattress Surface	6.5	2.7	3.2	n/a
7 day @ 150	Stainless Steel	9.1	6.9	7.7	n/a
7 day @ 150	Mattress Surface	3.6	3.8	4.6	n/a

In summary, 2 samples made from the film Dartex TC84 and the adhesive Adchem 7833 or 3M9465 were found to perform best against a variety of criteria required to be a function patch for the repair and regeneration of surface integrity on mattresses or other planar surfaces in a health care environment.

10

Claims:

1. A repair patch for health care devices, said patch comprising a film layer and an adhesive wherein the patch has an average edge thickness of 10 mil or less.
2. A repair patch for health care devices, said patch comprising a film layer and an adhesive wherein the patch has an average of elongation of 30% or greater.
3. A repair patch for health care devices, said patch comprising a film layer and an adhesive wherein the patch has an adhesion value of at least about 2.5 lbs/inch.
4. A patch according to any of claims 1 to 3, comprising an antimicrobial agent.
5. A patch according to any of claims 1 to 4, wherein the film layer comprises polyethylene, polyurethane, polypropylene, nylon, silicone, polyamide, polyester, polyvinyl, or a combination thereof.
6. A patch according to any of claims 1 to 5, wherein the film layer comprises polyvinyl, polyurethane, or a combination thereof.
7. A patch according to any of claims 1 to 6, wherein the adhesive is a pressure-sensitive adhesive.
8. A patch according to any of claims 1 to 7, wherein the adhesive is comprised within an adhesive layer.
9. A patch according to any of claims 1 to 7, wherein the adhesive is comprised within an adhesive layer and the layer comprises acrylic.
10. A patch according to any of claims 1 to 9, wherein the patch comprises a film layer and an adhesive layer, each layer having an average thickness of from 1 to 9 mils, wherein the average thickness of the two layers does not exceed 10 mils.
11. A patch according to any of claim 1 to 10, wherein the health care device is a mattress.

12. Use of a patch according to any of claims 1 to 11 for the repair of a health care device.
13. A health care device comprising a patch according to any of claims 1-11.
14. A method of repairing a health care device, said method comprising providing a patch according to any of claims 1 to 10 and adhering said patch to said health care device.
15. The method of claim 14 wherein the health care device is a mattress.

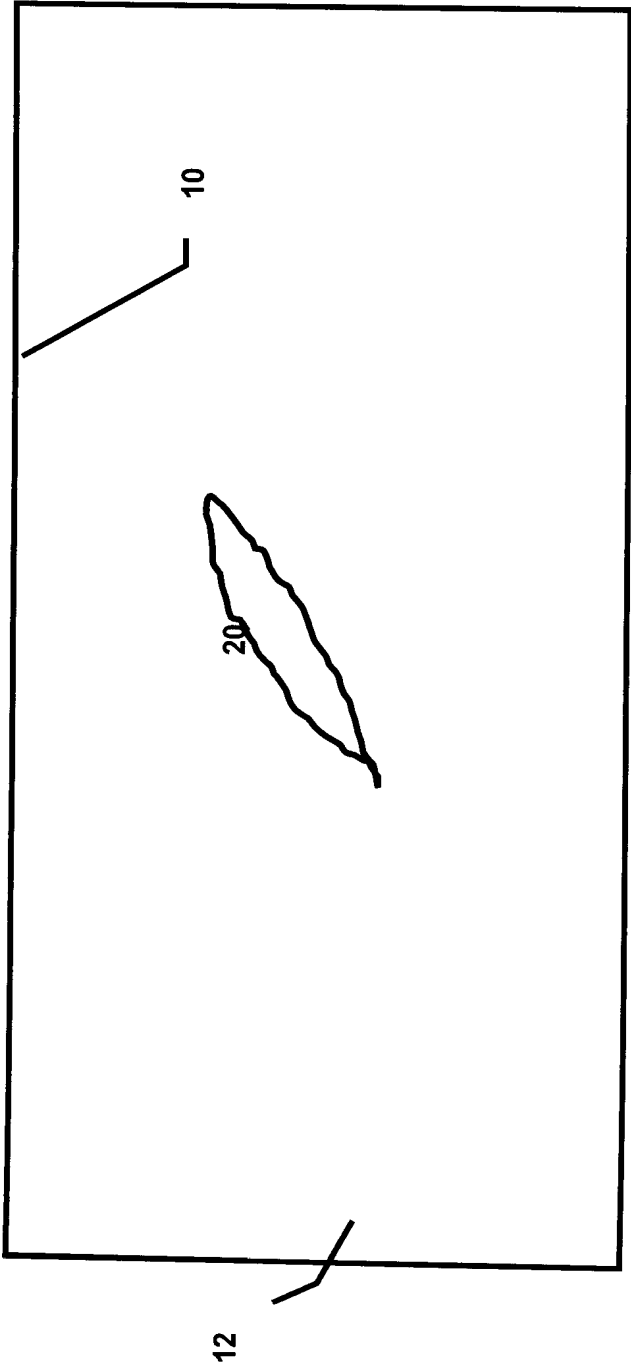


Fig 1A

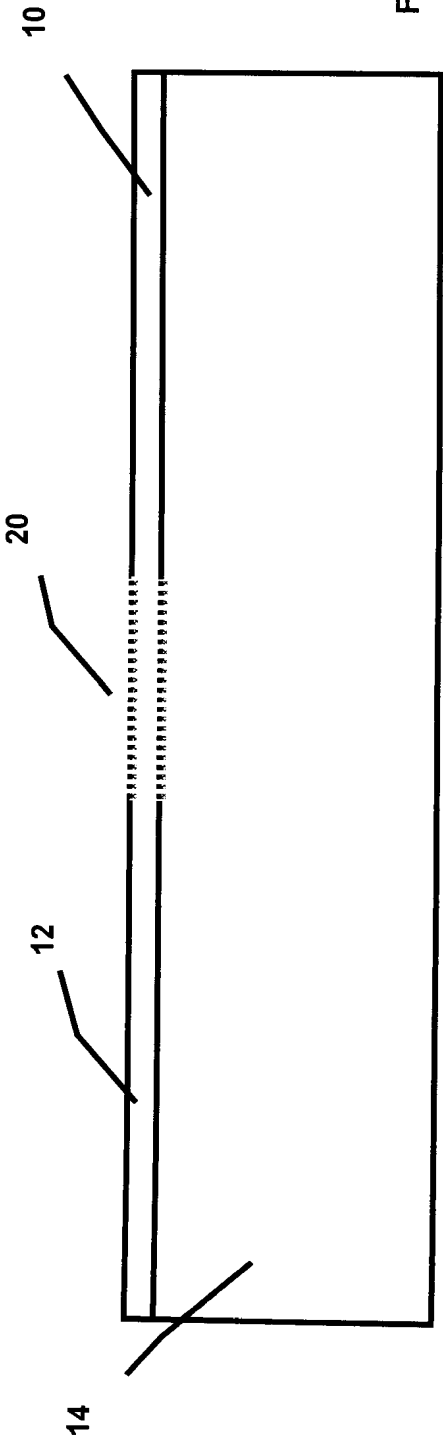


Fig 1B

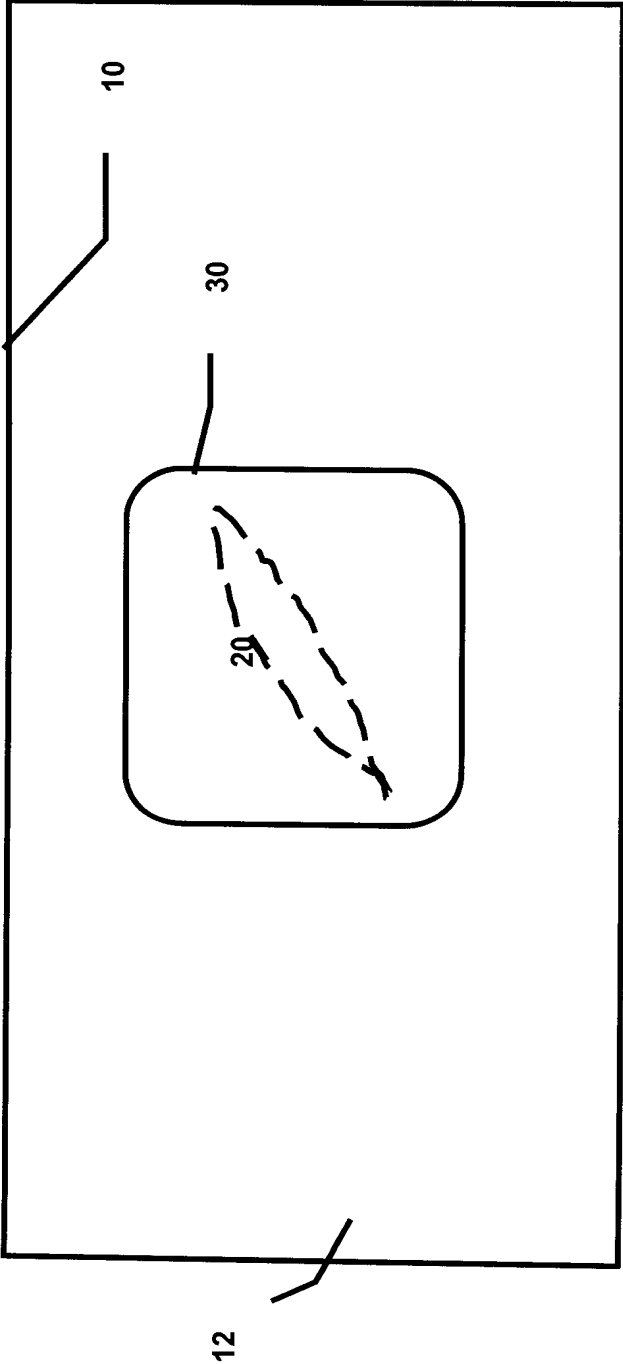


Fig 2A

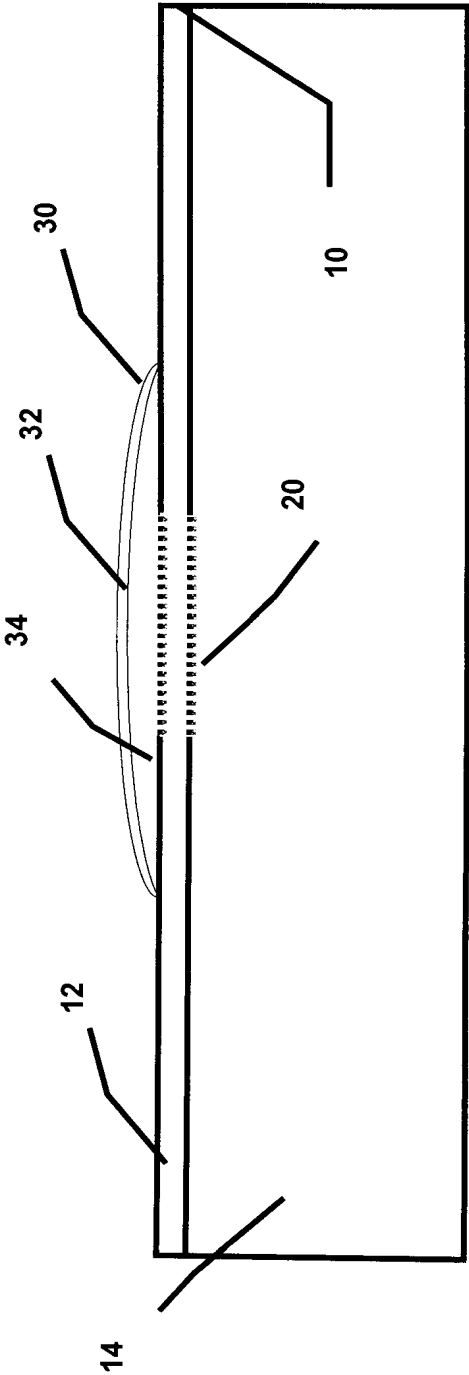


Fig 2B

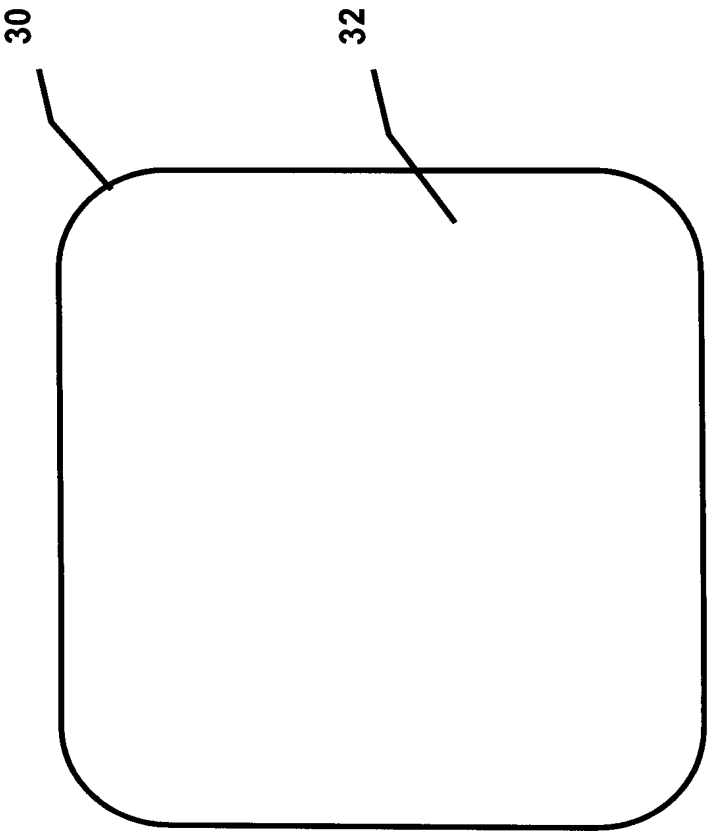


Fig 3A

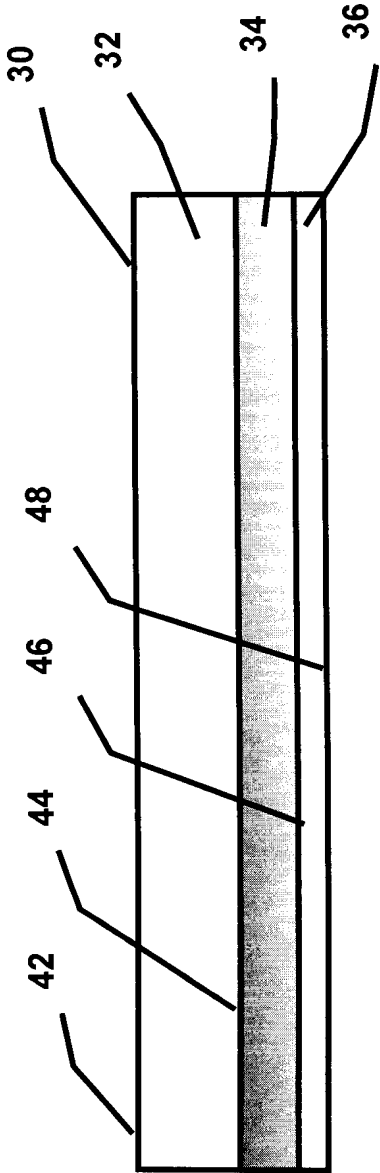


Fig 3B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2012/000195

<p>A. CLASSIFICATION OF SUBJECT MATTER</p> <p>IPC: <i>C09J 7/02</i> (2006.01) , <i>A47C 31/00</i> (2006.01) , <i>A61G 7/05</i> (2006.01) , <i>A61L 2/16</i> (2006.01) , <i>B29C 73/10</i> (2006.01) , <i>B68G 7/12</i> (2006.01)</p> <p>According to International Patent Classification (IPC) or to both national classification and IPC</p>																							
<p>B. FIELDS SEARCHED</p> <p>Minimum documentation searched (classification system followed by classification symbols) C09J (2006.01)</p> <p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched</p> <p>Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) Canadian Patent Database, esp@cenet, TotalPatent, (repair, patch, adhesive, tape, antimicrobial/antibacterial)</p>																							
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>US 2010/0104791 A1 (Baudrion et al.) 29 April 2010 (29-04-2010)</td> <td>1-10</td> </tr> <tr> <td>Y</td> <td>*abstract*, *paragraphs [0028], [0037], [0040], [0062], [0064], [0098]*</td> <td>11-15</td> </tr> <tr> <td>X</td> <td>US 2004/0001948 A1 (Mussig et al.) 01 January 2004 (01-01-2004)</td> <td>1-3, 5, 6, 8-10</td> </tr> <tr> <td>Y</td> <td>*abstract*, paragraph [0021], claims 1, 9, 19*</td> <td>4, 7, 11-15</td> </tr> <tr> <td>Y</td> <td>US 2003/0031687 A1 (Falder et al.) 13 February 2003 (13-02-2003) *paragraphs [0090], [0095]</td> <td>4, 7, 11-15</td> </tr> <tr> <td>A</td> <td>US 4,310,509 (Berglund et al.) 12 January 1982 (12-01-1982) *abstract*, *column 4, lines 32-43*, *claim 1*</td> <td>1-15</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	US 2010/0104791 A1 (Baudrion et al.) 29 April 2010 (29-04-2010)	1-10	Y	*abstract*, *paragraphs [0028], [0037], [0040], [0062], [0064], [0098]*	11-15	X	US 2004/0001948 A1 (Mussig et al.) 01 January 2004 (01-01-2004)	1-3, 5, 6, 8-10	Y	*abstract*, paragraph [0021], claims 1, 9, 19*	4, 7, 11-15	Y	US 2003/0031687 A1 (Falder et al.) 13 February 2003 (13-02-2003) *paragraphs [0090], [0095]	4, 7, 11-15	A	US 4,310,509 (Berglund et al.) 12 January 1982 (12-01-1982) *abstract*, *column 4, lines 32-43*, *claim 1*	1-15
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<p>[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.</p>																							
<table border="0"> <tr> <td style="vertical-align: top;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="vertical-align: top;"> <p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p> </td> </tr> </table>			<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p>																			
<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p>																						
<p>Date of the actual completion of the international search 18 May 2012 (18-05-2012)</p>		<p>Date of mailing of the international search report 18 June 2012 (18-06-2012)</p>																					
<p>Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476</p>		<p>Authorized officer Orysia Zaporozan (819) 994-3359</p>																					

INTERNATIONAL SEARCH REPORTInternational application No.
PCT/CA2012/000195**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the 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. ☐ Claim Nos. :
 because they relate to subject matter not required to be searched by this Authority, namely :

2. ☐ Claim 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. ☐ Claim 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 separate 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 claim 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 claim Nos. :

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.

From Box III:

The claims are directed to a plurality of inventive concepts as follows:

Group A - Claims 1, 4-15 (in part) are directed to a repair patch for health care devices comprising a film layer and an adhesive, wherein the patch has an average edge thickness of 10 mil or less.

Group B - Claims 2, 4-15 (in part) are directed to a repair patch for health care devices comprising a film layer and an adhesive, wherein the patch has an average elongation of 30% or greater.

Group C - Claims 3, 4-15 (in part) are directed to a repair patch for health care devices comprising a film layer and an adhesive, wherein the patch has an adhesion value of at least about 2.5 lbs/inch.

D1: US 2010/0104791 A1

The international application is not considered to comply with the requirement of unity of invention, since the identified groups are all related to distinct repair patches for health care devices, wherein each repair patch has a different characteristic and thus are not unified *a posteriori*. Repair patches for health care devices comprising a film layer and an adhesive are known from the prior art (c.f. D1). Consequently, the differing features of the repair patches do not constitute a special technical feature that would make a contribution over the prior art, and therefore, the identified groups are not linked as to form a single inventive concept.

The claims must be limited to one inventive concept as set out in Rule 13 of the PCT.

INTERNATIONAL SEARCH REPORTInternational application No.
PCT/CA2012/000195

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 094 945 B1 (McKnight et al.) 02 May 2001, (02-05-2001) *claims 1, 6*, *paragraph [0001] - [0003], [0007], [0012], [0030]*	1-15

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2012/000195

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US2010104791A1	29 April 2010 (29-04-2010)	CA2674759A1 EP2115085A2 FR2912417A1 JP2010518055A WO2008099111A2 WO2008099111A3 WO2008099111A4	21 August 2008 (21-08-2008) 11 November 2009 (11-11-2009) 15 August 2008 (15-08-2008) 27 May 2010 (27-05-2010) 21 August 2008 (21-08-2008) 24 December 2008 (24-12-2008) 26 February 2009 (26-02-2009)
US2004001948A1	01 January 2004 (01-01-2004)	DE10218686A1 DE50303643D1 EP1362881A2 EP1362881A3 EP1362881B1 ES2264741T3 JP2003335911A JP2010007082A	27 November 2003 (27-11-2003) 20 July 2006 (20-07-2006) 19 November 2003 (19-11-2003) 31 March 2004 (31-03-2004) 07 June 2006 (07-06-2006) 16 January 2007 (16-01-2007) 28 November 2003 (28-11-2003) 14 January 2010 (14-01-2010)
US2003031687A1	13 February 2003 (13-02-2003)	AT396614T AU2002216292B2 CA2433767A1 CA2433767C CN1491079A CN1302707C CN1961666A CN1961666B DE60226840D1 EP1347684A1 EP1347684B1 ES2310595T3 GB0100155D0 GB2374011A GB2374011B GB2374011C US7674473B2 US2002137631A1 WO02062142A1 ZA200305185A	15 June 2008 (15-06-2008) 30 August 2007 (30-08-2007) 15 August 2002 (15-08-2002) 15 September 2009 (15-09-2009) 21 April 2004 (21-04-2004) 07 March 2007 (07-03-2007) 16 May 2007 (16-05-2007) 22 June 2011 (22-06-2011) 10 July 2008 (10-07-2008) 01 October 2003 (01-10-2003) 28 May 2008 (28-05-2008) 16 January 2009 (16-01-2009) 14 February 2001 (14-02-2001) 09 October 2002 (09-10-2002) 23 March 2005 (23-03-2005) 06 February 2008 (06-02-2008) 09 March 2010 (09-03-2010) 26 September 2002 (26-09-2002) 15 August 2002 (15-08-2002) 13 July 2004 (13-07-2004)
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EP1094945A1	02 May 2001 (02-05-2001)	AU4276499A DE69917031D1 EP1094945B1 GB9812026D0 WO9964238A1	30 December 1999 (30-12-1999) 09 June 2004 (09-06-2004) 06 May 2004 (06-05-2004) 29 July 1998 (29-07-1998) 16 December 1999 (16-12-1999)



(51) International Patent Classification:

B32B 7/02 (2006.01) *B32B* 27/12 (2006.01)
B32B 9/02 (2006.01) *B32B* 27/18 (2006.01)
B32B 25/00 (2006.01) *B32B* 27/32 (2006.01)
B32B 27/00 (2006.01) *B32B* 27/30 (2006.01)
B32B 27/06 (2006.01) *B32B* 5/02 (2006.01)
B32B 27/08 (2006.01)

(21) International Application Number:

PCT/US2012/050720

(22) International Filing Date:

14 August 2012 (14.08.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/525,439 19 August 2011 (19.08.2011) US

(71) Applicant (*for all designated States except US*): **AVERY DENNISON CORPORATION** [US/US]; 150 N. Orange Grove Blvd., Pasadena, CA 91103 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **PHAM, Hoang, T.** [US/US]; c/o Avery Dennison Corporation, 150 N. Orange Grove Blvd., Pasadena, CA 91103 (US). **LANEY, Thomas** [US/US]; c/o Avery Dennison Corporation, 150 N. Orange Grove Blvd., Pasadena, CA 91103 (US). **GHIAM, Farid, F.** [US/US]; c/o Avery Dennison Corporation, 150 N. Orange Grove Blvd., Pasadena, CA 91103 (US). **HENDERSON, Kevin, O.** [US/US]; c/o Avery Dennison Corporation, 150 N. Orange Grove Blvd., Pasadena, CA 91103 (US).

(74) Agents: **BEMBENICK, Brian, G.** et al.; Avery Dennison Corporation, 8080 Norton Parkway, 22-D, Mentor, OH 44060 (US).

[Continued on next page]

(54) Title: BARRIER FILMS

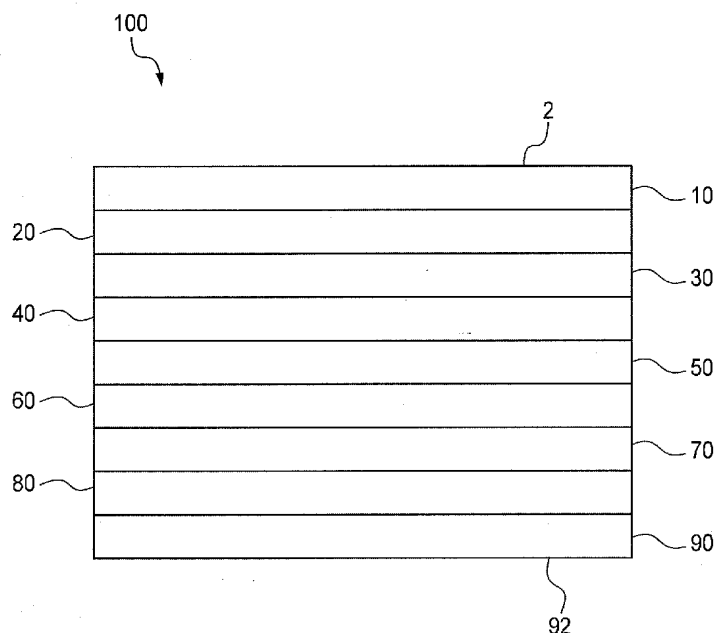


FIG. 1

[Continued on next page]



WO 2013/028398 A1



(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, 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).

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))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(57) **Abstract:** Various polymeric barrier compositions are described which when formed into films, are useful in reducing transmission of odors. The films can be incorporated into a wide range of products such as multilayer barrier films used in medical applications and particularly in ostomy appliances. In certain versions, the films include semi-crystalline cyclic olefin copolymers.

BARRIER FILMS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present application claims the benefit of U.S. Provisional Patent Application No. 61/525,439 filed August 19, 2011, which is incorporated herein by reference in its entirety.

FIELD

[0002] The present subject matter relates to polymeric barrier films for reducing transmission of odors. The subject matter also relates to articles comprising such films. The subject matter additionally relates to methods for reducing transmission of odors by use of the polymeric barrier films. The films, articles, and methods associated therewith are useful in various fields such as medical and health care applications, and find particular application in ostomy appliances and devices.

BACKGROUND

[0003] Barrier films in medical applications and particularly as used in ostomy applications, typically contain halogens. An example of a material used in such applications is polyvinylidene chloride (PVDC). Although use of that material is satisfactory in many regards, films containing halogens such as chloride and bromide are difficult and costly to recycle. In fact, with increasing environmental awareness, many regulations prohibit the disposal of halogens, thereby further increasing the inconvenience and/or cost of handling used medical products containing halogens.

[0004] Many currently known barrier films and particularly those used in certain medical applications, employ one or more layers that contain amorphous cyclic olefin copolymers (COCs). These materials provide an effective barrier to odor producing compounds such as skatole or 3-methylindole.

However, incorporating COCs into a thin multilayer film presents a formidable technical challenge, particularly if other characteristics of the film are to be maintained such as flexibility, strength, and ability to be joined with other material(s) to form articles or goods. Accordingly, a need remains for a barrier film that provides comparable or superior odor blocking properties as currently known barrier films, without compromising flexibility, strength, and other characteristics.

SUMMARY

[0005] The difficulties and drawbacks associated with previously known barrier films and products using such films are addressed in the present compositions, films, and methods.

[0006] In one aspect, the subject matter provides a barrier film comprising a semi-crystalline cyclic olefin copolymer (COC) having a melting temperature (T_m) of from about 70°C to about 100°C, and a glass transition temperature (T_g) of from about -20°C to about 32°C. The cyclic olefin copolymer has a norbornene content of from about 5 mole % to about 25 mole %.

[0007] In another aspect, the subject matter provides a multilayer barrier film comprising at least one layer including a semi-crystalline cyclic olefin copolymer (COC) having a melting temperature (T_m) of from about 70°C to about 100°C, and a glass transition temperature (T_g) of from about -20°C to about 32°C. The cyclic olefin copolymer has a norbornene content of from about 5 mole % to about 25 mole %.

[0008] In yet another aspect, the subject matter provides a multilayer barrier film comprising a barrier layer including ethylene vinyl alcohol (EVOH), at least one flexible support layer including one or more polyolefins, an antimicrobial layer including at least one antimicrobial agent, and at least one layer including a semi-crystalline cyclic olefin copolymer (COC).

[0009] In still another aspect, the present subject matter provides a method for reducing transmission of odorous species. The method comprises providing a semi-crystalline cyclic olefin

copolymer (COC), forming a film including the semi-crystalline COC, and positioning the film between a source of odorous species and a user.

[0010] As will be realized, the subject matter is capable of other and different embodiments and its several details are capable of modifications in various respects, all without departing from the subject matter. Accordingly, the drawings and description are to be regarded as illustrative and not restrictive.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Figure 1 is a schematic perspective view of a preferred embodiment multilayer polymeric film according to the present subject matter.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0012] Generally, in accordance with the present subject matter, various preferred embodiment single and multilayer films have been identified that can be used in a wide range of applications and particularly ostomy applications.

[0013] The preferred embodiment barrier films and/or multilayer barrier assemblies are preferably halogen-free and are particularly well suited for medical applications such as forming ostomy pouches. Since the films and multilayer assemblies are halogen-free and particularly free of chlorine, they can be recycled and/or subjected to a wide array of material reclamation operations. In addition, the unique barrier materials and combination of barrier layers and/or other functional layers as described herein are particularly well suited for use in ostomy applications. These aspects and others are all described in greater detail as follows.

Polymeric Barrier Film

[0014] In one aspect, the present subject matter provides a unique barrier film that can be utilized in a wide range of applications in which it is desired to block the transmission of odor-producing molecules, water, and/or oxygen across the thickness of a layer. Typical barrier films use water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) to characterize their barrier properties. Materials known to have good barrier properties against water and oxygen permeation have a high modulus, and thereby are “noisy”. A goal of the present subject matter is to prevent the passage of hydrogen sulfide and other malodorous molecules and/or species. The solution may not require the same approach needed for achieving low WVTR and OTR.

[0015] In a preferred embodiment of the present subject matter, a polymeric barrier film is provided which comprises at least one layer comprising a semi-crystalline cyclic olefin copolymer (COC). Cyclic olefin copolymers are also known as cyclo ethylene copolymer, COC, cyclo olefin copolymer, cyclic olefin polymer, and ethylene-norbornene copolymer. The terms “cyclic olefin copolymer” or “COC” are used interchangeably herein and include these various terms of art. It is contemplated that in certain embodiments, various norbornene-based materials may be used instead of or in addition to the COC’s, as described in greater detail herein. And, in particular embodiments, an elastomeric COC is used. In other embodiments, it is preferred to utilize blends of one or more of these COCs and optionally with other materials such as polyolefins, tie components, and/or amorphous COCs as described in greater detail herein.

[0016] Presently, there exist numerous grades of commercially available cyclic olefin copolymers based on different types of cyclic monomers and polymerization methods. Cyclic olefin copolymers are typically produced by chain copolymerization of cyclic monomers such as 8,9,10-trinorborn-2-ene (norbornene) or 1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethanonaphthalene (tetracyclododecene) with ethene. Non-limiting examples of commercially available cyclic olefin copolymers include those

available from TOPAS Advanced Polymers under the designation TOPAS, Mitsui Chemical's APEL, or those formed by ring-opening metathesis polymerization of various cyclic monomers followed by hydrogenation, which are available from Japan Synthetic Rubber under the designation ARTON, and Zeon Chemical's ZEONEX and ZEONOR.

[0017] In accordance with the present subject matter, a barrier layer comprising a semi-crystalline COC is provided. In other preferred embodiments, a combination of COCs is used in one or more barrier layers. Most preferably, the combination of COCs includes a semi-crystalline COC and one or more amorphous COCs. However, the subject matter includes a combination of two or more semi-crystalline COCs and optionally further combined with one or more amorphous COCs.

[0018] Preferably, the semi-crystalline COC has a melting temperature (T_m) of from about 70°C to about 100°C, more preferably from about 80°C to about 90°C, and most preferably from about 82°C to about 86°C. Preferably, the semi-crystalline COC has a glass transition temperature (T_g) of from about -20°C to about 32°C, more preferably from about -8°C to about 20°C, and most preferably from about 0°C to about 12°C. In certain embodiments, it may be preferred to use a semi-crystalline COC having a glass transition temperature of from about 3°C to about 9°C. Preferably, the semi-crystalline COC has a norbornene content of from about 5 mole % to about 25 mole %, more preferably from about 10 mole % to about 20 mole %, and most preferably from about 12 mole % to about 18 mole %. In certain embodiments it is preferred to utilize a semi-crystalline COC having a norbornene content of less than 20 mole %. In certain embodiments, it is preferred to utilize a semi-crystalline COC having a particular degree of crystallinity. For example, in certain applications it is preferred to use a semi-crystalline COC having a crystallinity of 5% or more by weight. In other applications, it is preferred to utilize a semi-crystalline COC having a crystallinity of 10% or more by weight. And in still other embodiments, it is preferred to use a semi-crystalline COC having a crystallinity of 20% or more by weight.

[0019] A most preferred semi-crystalline COC is commercially available under the designation E-140 from TOPAS. The melting temperature of the E-140 grade is about 84°C and has a Vicat softening temperature of about 64°C. The glass transition temperature of the E-140 grade is about 6°C. The norbornene comonomer content of the E-140 grade is believed to be about 12 mole % to about 18 mole %. Details and property information regarding the E-140 grade are set forth below in Table 1.

Table 1 – Grade E-140 Cyclic Olefin Copolymer From TOPAS

Property	Value	Unit	Test Standard
Physical Properties			
Density	0.940	g/cm ³	ISO 1183
Melt volume rate (MVR) at 190°C and 2.16 kg	3.0	cm ³ /10 min	ISO 1133
Melt volume rate (MVR) at 260°C and 2.16 kg	12.0	cm ³ /10 min	ISO 1133
Hardness, shore A	89	-	ISO 868
WVTR (23°C / 85% RH)	1.0	g*100µm/m ² *day	ISO 15106-3
WVTR (38°C / 90% RH)	4.6	g*100µm/m ² *day	ISO 15106-3
OTR (23°C / 50% RH)	1060	cc*100µm/m ² *day	ISO 15105-2
Mechanical Properties			
Tensile stress at break (50mm/min)	>19	MPa	ISO 527-T2/1A
Tensile modulus (1mm/min)	44	MPa	ISO 527-T2/1A
Tensile strain at break (50mm/min)	>450	%	ISO 527-T2/1A
Compression set (24hr / 23°C)	35	%	ISO 815
Compression set (72hr / 23°C)	32	%	ISO 815
Compression set (24hr / 60°C)	90	%	ISO 815
Tear strength	47	kN/m	ISO 34-1
Puncture resistance	44	J	ASTM D3786-08
Film Properties - 50 µm / 2 mil cast film			
Tensile stress at break (machine direction)	8.8	Ksi	ASTM D882
Tensile modulus (MD)	5.26	Ksi	ASTM D882
Elongation at break (MD)	640	%	ASTM D882
Tensile stress at break (transverse direction)	7.31	Ksi	ASTM D882
Tensile modulus (TD)	4.93	Ksi	ASTM D882
Elongation at break (TD)	620	%	ASTM D882
Elmendorf tear (MD, 3200 grams)	1103	Grams	ASTM D1922
Elmendorf tear (TD, 3200 grams)	1221	Grams	ASTM D1922
Haze	1.5	%	ASTM D1003
Gloss (60 °C)	94	%	ASTM D2457

Electrical Properties			
Relative permittivity at 1 GHz	2.24	-	ASTM D2520 / B
Dissipation factor at 1 GHz	2.6E-04	-	ASTM D2520 / B
Dielectric strength	4000	V/mil	ASTM D149-97a
Thermal Properties			
Glass transition temperature 10°C/min	6	°C	Internal method
Ductile-brittle temperature	<-90	°C	ISO 974
Tm - melt temperature	84	°C	Internal method
Vicat softening temperature, VST/A50	64	°C	ISO 306

[0020] As noted, in certain embodiments, it may be preferred to combine one or more semi-crystalline COCs with one or more amorphous COCs. The preferred amorphous COCs have a Tg of from about 33° C to about 180° C, more preferably from about 45° C to about 130° C, and most preferably from about 60° C to about 80° C. Preferred amorphous COCs which are commercially available include grades 9506 and 8007, and particularly grade 8007F-04 from TOPAS. Details and property information for these materials are set forth below in Tables 2 and 3.

Table 2 - Grade 9506 Cyclic Olefin Copolymer From TOPAS

Property	Value	Unit	Test Standard
Physical Properties			
Density	1020	kg/m ³	ISO 1183
Melt volume rate (MVR)	6.0	cm ³ /10 min	ISO 1133
MVR test temperature	230	°C	ISO 1133
MVR test load	2.16	Kg	ISO 1133
Melt volume rate (MVR) - 2nd value	1.0	cm ³ /10 min	ISO 1133
MVR test temperature - 2nd value	190	°C	ISO 1133
MVR test load - 2nd value	2.16	Kg	ISO 1133
Water absorption (23°C-sat)	0.01	%	ISO 62
Thermal Properties			
Glass transition temperature 10°C/min	65	°C	ISO 11357-1,-2,-3
Mechanical Properties (Film)			
Tensile modulus (machine direction)	1700	MPa	ISO 527-3
Tensile modulus (transverse direction)	2000	MPa	ISO 527-3
Tensile strength @ break (machine direction)	55	MPa	ISO 527-3
Tensile strength @ break (transverse direction)	55	MPa	ISO 527-3
Elongation at break (machine direction)	2.9	%	ISO 527-3

Elongation at break (transverse direction)	3.6	%	ISO 527-3
Elmendorf tear strength (machine direction)	230	G	ISO 6383-2
Elmendorf tear strength (transverse direction)	240	G	ISO 6383-2
Dart Drop Impact Strength, F50	<36	G	ISO 7765-1
Optical Properties (Film)			
Gloss, 60°	>100	%	ISO 2813
Haze	<1	%	ISO 14782
Barrier Properties (Film)			
Water vapor permeability @ 38°C, 90% RH	0.8	$\text{g}\cdot 100\mu\text{m}/(\text{m}^2\cdot\text{day})$	ISO 15106-3
Oxygen Permeability @ 23°C, 50% RH	170.0	$\text{cm}^3\cdot 100\mu\text{m}/(\text{m}^2\cdot\text{day}\cdot\text{bar})$	ASTM D3985

Table 3 - Grade 8007F-04 Cyclic Olefin Copolymer From TOPAS

Property	Value	Unit	Test Standard
Physical Properties			
Density	1020	kg/m^3	ISO 1183
Melt volume rate (MVR)	12.0	$\text{cm}^3/10 \text{ min}$	ISO 1133
MVR test temperature	230	°C	ISO 1133
MVR test load	2.16	Kg	ISO 1133
Melt volume rate (MVR) - 2nd value	2.0	$\text{cm}^3/10 \text{ min}$	ISO 1133
MVR test temperature - 2nd value	190	°C	ISO 1133
MVR test load - 2nd value	2.16	Kg	ISO 1133
Water absorption (23°C-sat)	0.01	%	ISO 62
Thermal Properties			
Glass transition temperature 10°C/min	78	°C	ISO 11357-1,-2,-3
Mechanical Properties (Film)			
Tensile modulus (machine direction)	2200	MPa	ISO 527-3
Tensile modulus (transverse direction)	1800	MPa	ISO 527-3
Tensile strength @ break (machine direction)	57	MPa	ISO 527-3
Tensile strength @ break (transverse direction)	50	MPa	ISO 527-3
Elongation at break (machine direction)	2.9	%	ISO 527-3
Elongation at break (transverse direction)	3.0	%	ISO 527-3
Elmendorf tear strength (machine direction)	225	G	ISO 6383-2
Elmendorf tear strength (transverse direction)	230	G	ISO 6383-2
Dart Drop Impact Strength, F50	<36	G	ISO 7765-1
Optical Properties (Film)			
Gloss, 60°	>100	%	ISO 2813
Haze	<1	%	ISO 14782
Barrier Properties (Film)			
Water vapor permeability @ 38°C, 90% RH	0.8	$\text{g}\cdot 100\mu\text{m}/(\text{m}^2\cdot\text{day})$	ISO 15106-3
Oxygen Permeability @ 23°C, 50% RH	200.0	$\text{cm}^3\cdot 100\mu\text{m}/(\text{m}^2\cdot\text{day}\cdot\text{bar})$	ASTM D3985

[0021] If one or more amorphous COCs are used in combination with the semi-crystalline COC, it is preferred that the weight proportion of the semi-crystalline COC range from about 1% to about 99%, more preferably from about 5% to about 75%, and most preferably from about 10% to about 50%, based upon the total weight amount of COC's in the barrier layer. However, it will be appreciated that the subject matter includes barrier layers with less than 1% semi-crystalline COC, and greater than 99% semi-crystalline COC.

[0022] For certain applications, it may be preferred to utilize a COC having elastomeric properties. As will be appreciated, elastomers exhibit a property of viscoelasticity or as commonly referred, elasticity. Elastomers typically have a relatively low Young's modulus and a high yield strain as compared to most other materials. It is contemplated that an elastomeric COC could be used in the various embodiments described herein. Reported information for an elastomeric COC from TOPAS indicates that the COC elastomers have a tensile modulus of about 4,412 N/cm² and elongation at break greater than 450 %. In addition, the elastomeric COC exhibits relatively low dielectric properties comparable to certain fluoroelastomers, thereby providing excellent electrical insulation performance. Furthermore, the material is reported to maintain ductility at temperatures below 80°C. The noted elastomeric COC also reportedly exhibits a Shore A hardness of 89.

[0023] In certain other embodiments, it is preferred to utilize ethylene vinyl alcohol (EVOH) in the polymeric barrier film. Specifically, the EVOH may be incorporated in the layer(s) comprising COC, and/or be provided in one or more separate layers proximate the COC-containing layer(s) in the barrier film. Ethylene vinyl alcohol, commonly abbreviated EVOH, is a formal copolymer of ethylene and vinyl alcohol. Because the latter monomer mainly exists as its tautomer acetaldehyde, the copolymer is prepared by polymerization of ethylene and vinyl acetate to produce the ethylene vinyl acetate (EVA) copolymer followed by hydrolysis. EVOH is typically used to provide barrier properties, primarily as an oxygen barrier for improved food packaging shelf life and as a hydrocarbon barrier for fuel tanks. EVOH

is typically coextruded or laminated as a thin layer between cardboard, foil, or other plastics. EVOH copolymer is traditionally defined by the mole percent ethylene content. Lower ethylene content grades have higher barrier properties, and higher ethylene content grades have lower temperatures for extrusion. Additional information as to preferred aspects of EVOH used in the films of the subject matter are described in greater detail herein.

Multilayer Barrier

[0024] The present subject matter also provides multilayer films for use in medical applications and in particular, for ostomy applications. As will be appreciated, an important characteristic for such films is preventing or at least significantly reducing transmission of odors through the film, and particularly reducing transmission of skatole or 3-methylindole through the film. Another important characteristic for such films is that the films be relatively quiet and not emit excessive noise upon deflecting or movement of the film. A preferred multilayer barrier construction uses one or more barrier layers that include a semi-crystalline cyclic olefin copolymer (COC) and in combination with one or more flexible support layers. Another preferred multilayer barrier construction includes one or more barrier layers that include ethylene vinyl alcohol in conjunction with one or more layers which include a semi-crystalline COC. In other embodiments, the preferred multilayer barrier construction includes one or more of the previously noted aspects in further combination with an inner layer containing one or more antimicrobial agents.

[0025] Figure 1 is a schematic illustration of a preferred embodiment multilayer barrier assembly 100 in accordance with the present subject matter. The multilayer assembly 100 comprises an outer layer 10 defining an outer face 2, a first flexible support layer 20, a second flexible support layer 30, a first moisture and odor barrier layer 40, a secondary barrier layer 50 for reducing transmission of oxygen, a second moisture and odor barrier layer 60, a third flexible support layer 70, a fourth flexible

support layer 80, and an inner antimicrobial layer 90 defining an inner face 92 for contacting a microbe containing medium. Table 4 set forth below describes a preferred embodiment multilayer film and properties and materials for each of the layers 10, 20, 30, 40, 50, 60, 70, 80, and 90.

Table 4 - Preferred Multilayer Film

Layer	Layer Thickness %	Material	Weight %	Density	Weight %
10	10.00%	18% VA EVA Slip/AB	80.00% 20.00%	0.940 1.010	
		Total:	100.00%	0.953	10.31%
20	14.00%	Plastomer	100.00%	0.870	
		Total:	100.00%	0.870	13.18%
30	14.00%	Plastomer	100.00%	0.870	
		Total:	100.00%	0.870	13.18%
40	8.00%	COC Elastic Tie resin	80.00% 20.00%	0.940 0.910	
		Total:	100.00%	0.934	8.08%
50	7.00%	44 mol EVOH	100.00%	1.130	
		Total:	100.00%	1.130	8.56%
60	8.00%	COC Elastic Tie resin	80.00% 20.00%	0.940 0.910	
		Total:	100.00%	0.934	8.08%
70	9.00%	Plastomer	100.00%	0.870	
		Total:	100.00%	0.870	8.47%
80	20.00%	30% BA EBA Plastomer Tie resin	60.00% 20.00% 20.00%	0.930 0.870 0.910	
		Total:	100.00%	0.913	19.79%
90	10.00%	30% BA EBA Slip/AB Antimicrobial	70.00% 20.00% 10.00%	0.930 1.010 1.068	
		Total:	100.00%	0.958	10.35%
	100.00%			0.924	100%

[0026] Layer 10 is the outermost layer and preferably comprises ethylene vinyl acetate (EVA) having a vinyl acetate content of preferably about 18%. Layer 10 also optionally contains a masterbatch of slip and anti block (AB) agents. The masterbatch is preferably SAB1220 NG masterbatch available from A. Schulman, added at about 20% by weight. The masterbatch contains 8% slip and 12% antiblock agents. The slip agent is preferably Erucamide and the antiblock agent is preferably SiO₂. It will be appreciated, however, that a wide array of other slip agents and/or antiblock agents could be used. Non-limiting examples of other slip agents include primary and secondary amide slip agents, polydimethyl siloxane and its copolymers, polywax slip agents, and other like agents. Non-limiting examples of other antiblock agents include inorganic fillers such as talc, calcium carbonate, clay and the like; and polymeric agents such as low density polyethylene (LDPE), highly branched low density polyethylene, and other comparable components. In certain embodiments, effective amounts of ethylene butyl acrylate (EBA) can be included in layer 10. Optionally, an effective amount of a tie component can be used in this layer. If a tie component is used in layer 10, the material is preferably anhydride (M.A.) modified. An example of such a material is BYNEL E418, available from DuPont. That material is described as anhydride-modified EVA, and is believed to be maleic anhydride grafted EVA polymer. Another example is PLEXAR from Equistar which may include grafted M.A. HDPE, LLDPE, PS, or PP.

[0027] Layers 20, 30, 70 and 80 are each a flexible support layer. The preferred embodiment multilayer film preferably includes multiple flexible support layers. The support layers provide bulk, strength, softness, and cohesiveness to the resulting multilayer assembly. In certain multilayer configurations, the one or more flexible support layers serve to dampen noise that might otherwise be emitted upon deformation or movement of the film. These layers preferably comprise one or more polyolefins, plastomers, styrene elastomers, and/or combinations thereof. Preferably, the flexible

support layers such as layers 20, 30, 70, and 80 comprise one or more polymers having a relatively low density of from about 0.75 to about 1.10 g/cm³, more preferably from about 0.85 to about 1.01 g/cm³, and more preferably from about 0.865 to about 0.91 g/cm³. Preferably, the polyolefins in the support layers such as layers 20, 30, 70 and 80 have a melt flow index (MI) of from about 0.1 to about 1000 g/10 min, and more preferably from about 0.5 to about 10 g/10 min. Preferably, the polyolefins used in the support layer(s) such as layers 20, 30, 70, and 80, include an ethylene based polymer with one or more alkyl comonomer(s) selected from the family of propylene, butylene, hexene, octene, and the like. The polyolefin can be a random copolymer or a block copolymer. In certain embodiments, it may be preferred to utilize one or more plastomer(s) in the support layer(s) such as layers 20, 30, 70, and 80. A plastomer is a polyolefin elastomer. A preferred plastomer is a propylene based plastomer having an alkyl comonomer in the family of ethylene, butylene, hexene, octene and the like. The noted plastomer can be a random copolymer or a block copolymer.

[0028] As noted, the flexible supports in the preferred multilayer constructions utilize a low density polyolefin and preferably, a polyolefin elastomer. A wide array of commercially available polyolefin elastomers can be used for one or more of the flexible support layers. Representative preferred examples of such materials include KRATON™ D1164P and G2832 available from Kraton Polymers US, LLC of Houston, TX; DOW AFFINITY™ DG8200 and EG8100; DOW VERSIFY™ 3200 and 3000; and DOW INFUSE™ such as INFUSE 9000 from Dow Chemical Corp. of Midland, MI; DYNAFLEX™ G2755 from GLS Corp. of McHenry, IL; SEPTON™ 2063 from Kuraray of Tokyo, Japan; and VISTAMAXX™ VM1100 from ExxonMobil Chemical Co. of Houston, TX. Another preferred commercially available material for any of layers 20, 30, 70 and/or 80 is an elastomer material available from Mitsui Chemicals under the designation NOTIO™. A preferred grade is NOTIO™ PN 2070. Table 5 set forth below presents representative modulus, tear strength, and density values for films made using various specific grades of these materials.

Table 5 - Summary of Modulus, Tear Strength and Density

Core Resin Name	Modulus [MPa]		Tear Strength [g]		Density [g/cm ³]
	MD	TD	MD	TD	
KRATON™ D1164P	40.3	9.6	95	776	0.96
KRATON™ G2832	5.0	1.7	179	207	1.01
DOW AFFINITY™ DG8200	8.8	8.1	150	188	0.93
DOW AFFINITY™ EG8100G	-	-	-	-	-
DYNAFLEX™ G2755	9.8	3.2	175	186	0.89
DOW VERSIFY™ 3200	52.8	59.3	368	1026	0.93
DOW VERSIFY™ 3000	128.9	138.4	554	1205	0.87
DOW INFUSE™ 9000	-	-	-	-	0.88
Kuraray SEPTON™ 2063	8.0	8.1	83	56	1.00
Exxon VISTAMAXX™ VM1100	7.1	7.6	108	111	0.98
Mitsui NOTIO™ PN2070	-	-	-	-	-

[0029] Generally, a particular combination of properties is desired for the film material forming the flexible support(s) in the preferred ostomy multilayer film summarized in Table 4. A relatively low modulus should contribute to lower noise. Tear strength should be relatively high. Density may also be important. Typically, preferred films exhibit a modulus of less than about 9.5 MPa for MD and less than about 9 MPa for TD; a tear strength of at least about 100 g for MD and at least about 108 for TD; and a density of less than 1.1 g/cm³. Preferably, preferred films exhibit a modulus of less than or equal to about 9.3 MPa for MD and less than or equal to about 8.8 MPa for TD; a tear strength of at least or about 108 g for MD and at least or about 110 g for TD; and a density of less than or equal to 1.0 g/cm³. These combinations of properties for the materials forming the flexible supports, e.g. layers 20, 30, 70, and 80 in the preferred multilayer construction, have been found to provide a favorable combination of properties and promote ease of processing. However, the subject matter includes the use of suitable materials exhibiting only some of these properties. It will also be understood that the subject matter includes films exhibiting different properties. For example, it is contemplated that fully formed films would exhibit modulus values less than these values, and/or tear strength values that are greater than

these values. The preferred materials of the group of commercially available materials listed in Table 5 are Exxon VISTAMAXX™ and Dow AFFINITY™, VERSIFY™ and INFUSE™. It will be appreciated that the present subject matter multilayer barrier constructions are not limited to the use of these particular elastomers.

[0030] In certain versions of the subject matter, it is preferred to utilize one or more styrenic elastomers in one or more of the support layers, such as layers 20, 30, 70, and 80. The one or more styrenic elastomers can be used exclusively or in combination with one or more polyolefins and/or polyolefin elastomers. An example of a commercially available styrenic elastomer is the previously noted SEPTON™ material. In certain embodiments, it may be preferred to incorporate acrylonitrile butadiene styrene (ABS) in one or more of the support layers.

[0031] One or more of layers 20, 30, 70 and 80 may also comprise ethylene butyl acrylate (EBA). A variety of different grades of EBA can be used, however, a commercially available grade under the designation LOTRYL 30 BA 02 from Arkema has been identified as providing desired characteristics. It is also contemplated that effective amounts of ethylene vinyl acetate (EVA) for example having a vinyl acetate content of about 18% or higher, can also be included in one or more of the layers 20, 30, 70, and 80. Although EBA or other acrylate, or EVA can be incorporated in any of the layers 20, 30, 70 and/or 80, it is preferred to incorporate EBA in layer 80. If EBA or EVA is incorporated in one or more layers such as layer 80, it is preferred to incorporate the EVA or EBA at a weight ratio of about 99% to about 50% with from about 1% to about 50% of polyolefin elastomer(s), i.e. elastomer(s). Most preferably, if EBA or EVA is used in layer 80, it is preferred to utilize about 60% of that material based upon the total weight of components in that layer.

[0032] In addition, one or more of layers 20, 30, 70, and 80 may also comprise a tie component. The tie component may be as previously described, and is preferably BYNEL CXA 410E710 from DuPont. Although the subject matter is not limited to any particular concentration of the tie component in any of

the noted layers, a proportion of up to about 20% based upon the total weight of the respective layer is useful. As noted in Table 4, in certain embodiments it is particularly preferred to include about 20% of a tie component in layer 80.

[0033] The barrier layer 50 is primarily for reducing transmission of oxygen and/or water, preferably comprises EVOH. The EVOH is incorporated at nearly any effective concentration, however typical concentrations range from about 40 % to about 100 %, preferably from about 50% to about 80%, and most preferably from about 60% to about 70%. In the preferred embodiment multilayer assembly of Table 4, layer 50 includes 100% of EVOH. Layer 50 preferably comprises ethylene vinyl alcohol (EVOH) SP292, E171, and/or G176 available from Eval Americas. The EVOH used in layer 50 preferably has an ethylene content of from about 25 mole % to about 50 mole %, more preferably from about 32 mole % to about 48 mole %, and most preferably from about 35 mole % to about 48 mole %. In the embodiment detailed in Table 4, the EVOH used in layer 50 has an ethylene content of 44 mole %. As will be understood, these values are molar percents, i.e., the molar proportion of ethylene in the ethylene vinyl alcohol material used.

[0034] It is also contemplated that the barrier layer 50 may comprise one or more cyclic olefin copolymers instead of or in addition to EVOH. In certain embodiments, it may be preferred to provide an odor blocking layer that comprises one or more cyclic olefin copolymers. Although not wishing to be bound to any particular theory, it is believed that upon incorporation of a cyclic olefin copolymer, the shape of the norbornene rings in the polymeric matrix tend to trap or block odor producing molecules and/or chemical species. The use of one or more cyclic olefin copolymers in a barrier layer may be particularly desirable if water vapor transmission rate (WVTR) is not a concern for that layer.

[0035] Each of layers 40 and 60 comprises one or more semi-crystalline cyclic olefin copolymer (COC). These layers primarily function as odor barrier layers and are as previously described herein. As noted, the preferred COC is from TOPAS under the designation E-140 and has a density of 0.94 g/cc and

a comonomer content of about 12 mole % to about 18 mole % norbornene. As previously noted, the E-140 COC is a semi-crystalline material and has a melting temperature of about 84°C, a Vicat softening point of about 64°C, and a glass transition temperature of about 6°C. It is also contemplated that two grades of amorphous COC from TOPAS, grade 9506F and/or grade 8007, may be blended with the E-140 grade. A non-limiting representative blend ratio of semi-crystalline COC to amorphous COC is about 50/50 by weight. The Tg of grade 8007 is 78°C. The Tg of grade 9506F is 65°C. The one or more COCs can be used in the moisture or odor barrier layer in nearly any concentration, such as from about 10% to about 100%, more preferably from about 50% to about 99%, more preferably from about 65% to about 95%, more preferably from about 70% to about 90%, and most preferably about 80%. The COCs used in layers 40 and 60 may be same as one another. Alternatively, the COCs used in these layers may be different from one another.

[0036] One or both of layers 40 and 60 preferably also comprise a tie component. Preferably, the tie component is a polymeric resin. The tie component can be used at any effective concentration, such as from about 1% to about 40% by weight, preferably from about 10% to about 30% by weight, and most preferably about 20% by weight, based upon the total weight of the respective layer, such as layer 40 or layer 60. In layers 40 and 60, the tie component is preferably BYNEL CX410E710. It is believed that this is an anhydride modified olefin.

[0037] Layer 90 is an inner layer and preferably includes one or more antimicrobial agents. In the preferred embodiment layer film listed in Table 4, layer 90 comprises 70% EBA 30, 20% of a slip and antiblock masterbatch, and an effective amount of a silver ion anti-microbial masterbatch. In certain versions, the amount of the antimicrobial masterbatch is from about 8% to about 15%, and more preferably from about 10% to about 12%. As previously described with respect to layer 80; in layer 90, one or both of ethylene vinyl acetate (EVA) and/or ethylene butyl acrylate (EBA) can be used. If EVA is used, EVA having a vinyl acetate content of about 18% or higher is preferably utilized. For the

embodiment shown in Table 4, layer 90 preferably comprises 70% EBA having a butyl acrylate content of about 30%. In layer 90, 20% by weight of the SAB1220 NG masterbatch is preferably used. The SAB1220 NG masterbatch comprises slip agent(s) and antiblock agent(s) as previously described herein. In layer 90, the anti-microbial masterbatch is ABACT 422VA from A. Schulmann. However, it is also contemplated that such anti-microbial masterbatch may be substituted with BACTIBLOCK from Nanobiomatters. The Nanobiomatters antimicrobial is a silver ion on a modified organoclay. If the BACTIBLOCK masterbatch is used, in certain embodiments it is preferred to incorporate the masterbatch in the layer at a concentration of about 12%. In certain embodiments, the antimicrobial layer also preferably comprises one or more sealable polymers such as metallocene-catalyzed linear low density polyethylene (LLDPE).

[0038] The preferred embodiment multilayer barrier film described in Table 4 and schematically depicted in Figure 1, preferably utilizes each of layers 10, 20, 30, 40, 50, 60, 70, 80, and 90 at certain thicknesses. That is, by appropriate selection of thickness for each layer, the overall thickness of the resulting multilayer barrier is still relatively thin, yet the film exhibits excellent barrier properties. In certain embodiments, a preferred ratio of thickness for layers 10, 20, 30, 40, 50, 60, 70, 80, and 90 is 10/14/14/8/7/8/9/20/10, respectively. Other slight variations in thickness are contemplated. The total thickness of the three middle layers, i.e. layers 40, 50, and 60, is preferably about 30% or less of the total thickness of the multilayer film. Preferred film thickness for an ostomy application is about 70 to about 100 microns, but could be thinner or thicker.

[0039] In certain embodiments, the total layer thickness of layers 80 and 90 will be from about 25% to about 30% of the total thickness of the multilayer film. In certain embodiments, the layer containing EVOH, e.g. layer 50, has a thickness of from about 3% to about 10%, more preferably from about 5% to about 9%, and most preferably from about 6% to about 8% of the total thickness of the multilayer film. In certain embodiments, the total or combined thickness of layer(s) containing COC, e.g. layers 40 and

60, is from about 10% to about 40%, more preferably from about 12% to about 36%, and most preferably from about 14% to about 30% of the total thickness of the multilayer film.

[0040] Preferably, layers 80 and 90 impart heat sealability characteristics to the resulting multilayer barrier film. Preferably, at least the materials selected for these layers render the resulting multilayer barrier film weldable and most preferably thermally weldable. Accordingly, at least a portion of the materials used in layers 80 and/or 90 are polar. This enables RF welding of the multilayer assembly. One or more polar materials such as EVA or EBA are provided in the outer layer to facilitate RF welding. However, if heat sealing or other thermal means, polar compounds may not be necessary. Instead, agents such as octene-based PE's, ULDPE (non-polar), and the like can be used.

[0041] It is also contemplated that one or more ionomers and preferably zinc ionomers can be incorporated in any of the layers of the multilayer barrier film. For the embodiment depicted in Table 4, one or more ionomers can be incorporated in any of the support layers 20, 30, 70 and/or 80. Preferably and in certain embodiments, one or more ionomers are included in layer 80. It is also contemplated that one or more ionomers could be included in the secondary barrier layer 50 containing EVOH. The one or more ionomers can be used at any effective concentration. However, typically such concentrations range from about 5% to about 40%, preferably from about 10% to about 30%, and most preferably from about 15% to about 20%.

[0042] The present subject matter includes a wide array of multilayer barrier assemblies and in no way is limited to the embodiment depicted in Table 4. For example, in another preferred embodiment, a multilayer barrier film is provided in which one or more support layer(s) are disposed between a COC-containing layer and a layer containing EVOH. Representative sequences of layers in accordance with preferred embodiments of the subject matter may include:

- (i) COC/Support/EVOH/Support/COC,
- (ii) COC/Support/EVOH/Support,
- (iii) Support/EVOH/Support/COC,
- (iv) COC/EVOH/Support/COC,
- (v) COC/Support/EVOH/COC,
- (vi) COC/Support/EVOH,
- (vii) Support/EVOH/COC,
- (viii) COC/EVOH/Support, and
- (ix) Support/COC/EVOH.

Again, it is to be understood that in no way is the subject matter limited to any of the particular layer sequences noted herein. Moreover, it will also be appreciated that the subject matter includes one or more additional layers included or otherwise incorporated in the representative examples (i) – (ix) such as for instance, outer face layers and/or inner layers which may optionally include antimicrobial agents.

[0043] As stated previously, in addition to barrier properties, it is often desirable that a polymeric barrier film not emit noise when deflected, crumpled or otherwise moved. For example, in ostomy or incontinence applications, it is desirable that the ostomy or incontinence bag not emit noise. As will be appreciated, such articles are typically worn under a user's clothing so as to hide the article from view. Films or polymeric layers that are not quiet tend to emit undesirable noise when the user undergoes motion such as when walking or sitting. In the case of the preferred embodiment multilayer barrier films, the films are significantly quieter than comparable ostomy films.

[0044] The present subject matter also provides various methods. In one aspect, the subject matter provides a method for forming a polymeric barrier film with excellent barrier properties. The method generally includes providing a polymeric barrier composition. Examples of such compositions include those previously described herein. The method also includes forming a film from the polymeric

barrier composition. Extrusion techniques are preferred, however other known methods can be used for forming films. As explained herein, in certain embodiments, it is preferred that the at least one polymeric barrier composition includes a semi-crystalline cyclic olefin copolymer. In other embodiments, it is preferred that the at least one polymeric barrier composition includes ethylene vinyl alcohol (EVOH). In many of the embodiments, it is preferred that the polymeric barrier composition is free of halogens.

[0045] The various layers and films can be extruded, coated, or otherwise formed by techniques known in the art. Co-extrusion techniques can also be utilized. For certain applications in which increased toughness and/or durability are desired, films can be blown.

[0046] The subject matter further provides methods of using the various compositions, films, and multilayer assemblies described herein. For example, a method for reducing transmission of odorous species is provided. The term "odorous species" as used herein refers to molecules or chemical species which are generally perceived by a user as unpleasant. A non-limiting example of odorous species is skatole or 3-methylindole. Another non-limiting example of an odorous species is hydrogen sulfide. Still another example of odorous species is 1-propanethiol. Combinations of these odorous species and potentially with other species are contemplated. The method comprises providing a semi-crystalline cyclic olefin copolymer, preferably as described herein. The method also comprises forming a film which includes the semi-crystalline cyclic olefin copolymer. And, the method also comprises positioning or placing the film between a source of the odorous species and a user. This latter operation typically involves forming the film into a container or pouch, or incorporating the film into such, and then using the container or pouch to hold, store, or collect material containing the odorous species.

[0047] The preferred embodiment barrier film constructions are believed to exhibit several advantages over currently known ostomy films. The preferred films are halogen-free and avoid the use of polyvinylidene chloride (PVDC). The preferred films are relatively quiet and exhibit significantly less "rustle". And, the preferred films exhibit superior odor blocking characteristics. Furthermore, the preferred films exhibit a combination of some and preferably all of these features. The film construction may be transparent or contain coloring agents.

[0048] The present subject matter also provides a wide array of articles using the barrier film(s) described herein. A non-limiting example of an article using the barriers described herein is an ostomy pouch. The barrier film(s) and preferably the multilayer barrier film(s) described herein can be joined with one or more other components. For example, in forming an ostomy pouch, a flexible wall container or pouch is formed from the multilayer film of Table 4. Sealed regions are formed by thermal welding contacting face regions of the film so as to form a pouch with an enclosed interior. One or more outer external protective layers may be applied along the outer face such as face 2 of the assembly depicted in Figure 1. The external layer(s) can be fabric, nonwoven, or other materials.

[0049] Many other benefits will no doubt become apparent from future application and development of this technology.

[0050] All patents, applications, and articles noted herein are hereby incorporated by reference in their entirety.

[0051] It will be understood that any one or more feature or component of one embodiment described herein can be combined with one or more other features or components of another embodiment. Thus, the present subject matter includes any and all combinations of components or features of the embodiments described herein.

[0052] As described hereinabove, the present subject matter solves many problems associated with previously known compositions, films, multilayer assemblies, and related methods. However, it will be appreciated that various changes in the details, materials and arrangements of components and operations, which have been herein described and illustrated in order to explain the nature of the subject matter, may be made by those skilled in the art without departing from the principle and scope of the subject matter, as expressed in the appended claims.

WHAT IS CLAIMED IS:

1. A barrier film comprising:
a semi-crystalline cyclic olefin copolymer (COC) having a melting temperature (T_m) of from about 70°C to about 100°C, a glass transition temperature (T_g) of from about -20°C to about 32°C, and a norbornene content of from about 5 mole % to about 25 mole %.
2. The barrier film of claim 1 wherein the semi-crystalline COC has a melting temperature of from about 80°C to about 90°C.
3. The barrier film of claim 2 wherein the semi-crystalline COC has a melting temperature of from about 82°C to about 86°C.
4. The barrier film of any one of claims 1-3 wherein the semi-crystalline COC has a glass transition temperature of from about -8°C to about 20°C.
5. The barrier film of claim 4 wherein the semi-crystalline COC has a glass transition temperature of from about 0°C to about 12°C.
6. The barrier film of any one of claims 1-5 wherein the semi-crystalline COC has a norbornene content of from about 10 mole % to about 20 mole %.
7. The barrier film of claim 6 wherein the semi-crystalline COC has a norbornene content of from about 12 mole % to about 18 mole %.

8. The barrier film of any one of claims 1-7 further comprising at least one amorphous COC.

9. The barrier film of claim 8 wherein the amorphous COC has a glass transition temperature of from about 33°C to about 180°C.

10. The barrier film of claim 9 wherein the amorphous COC has a glass transition temperature of from about 45°C to about 130°C.

11. The barrier film of claim 10 wherein the amorphous COC has a glass transition temperature from about 60°C to about 80°C.

12. The barrier film of any one of claims 8-11 wherein the weight percent of the semi-crystalline COC is in a range of from about 1% to about 99% based upon the total weight of COCs in the film.

13. The barrier film of claim 12 wherein the weight percent of the semi-crystalline COC is in the range of from about 5% to about 75%.

14. The barrier film of claim 13 wherein the weight percent of the semi-crystalline COC is in the range of from about 10% to about 50%.

15. A multilayer barrier film comprising:
- at least one layer including a semi-crystalline cyclic olefin copolymer (COC) having a melting temperature (T_m) of from about 70°C to about 100°C, a glass transition temperature (T_g) of from about -20°C to about 32°C, and a norbornene content of from about 5 mole % to about 25 mole %.
16. The multilayer barrier film of claim 15 wherein the at least one layer includes (i) a first layer including a semi-crystalline cyclic olefin copolymer (COC), and (ii) a second layer including a semi-crystalline cyclic olefin copolymer.
17. The multilayer barrier film of claim 16 wherein the semi-crystalline cyclic olefin copolymer in the first layer is the same as the semi-crystalline cyclic olefin copolymer in the second layer.
18. The multilayer barrier film of any one of claims 15-17 further comprising:
- a secondary barrier layer including ethylene vinyl alcohol (EVOH).
19. The multilayer barrier film of claim 18 wherein the ethylene vinyl alcohol has an ethylene content of from about 25 mole % to about 50 mole %.
20. The multilayer barrier film of claim 19 wherein the ethylene vinyl alcohol has an ethylene content of from about 32 mole % to about 48 mole %.

21. The multilayer barrier film of claim 20 wherein the ethylene vinyl alcohol has an ethylene content of from about 35 mole % to about 48 mole %.

22. The multilayer barrier film of any one of claims 15-21 wherein the at least one layer including the semi-crystalline cyclic olefin copolymer also includes at least one amorphous cyclic olefin copolymer.

23. The multilayer barrier film of any one of claims 15-22 further comprising:
at least one flexible support layer including one or more polymers selected from the group consisting of styrenic elastomers, polyolefins, and polyolefin elastomers and combinations thereof.

24. The multilayer barrier film of claim 23 wherein the one or more polymers has a density of from about 0.75 to about 1.10 g/cm³.

25. The multilayer barrier film of claim 24 wherein the one or more polymers has a density of from about 0.85 to about 1.01 g/cm³.

26. The multilayer barrier film of claim 25 wherein the density is from about 0.865 to about 0.91 g/cm³.

27. The multilayer barrier film of any one of claims 23-26 wherein the one or more polymers has a melt flow index of from about 0.1 to about 1,000 g/10 min.

28. The multilayer barrier film of claim 27 wherein the melt flow index is from about 0.5 to about 10 g/10 min.

29. The multilayer barrier film of any one of claims 15-28 further comprising:
an inner antimicrobial layer including at least one antimicrobial agent.

30. A multilayer barrier film comprising:
a barrier layer including ethylene vinyl alcohol (EVOH);
at least one flexible support layer including one or more polyolefins;
an antimicrobial layer including at least one antimicrobial agent; and
at least one layer including a semi-crystalline cyclic olefin copolymer (COC).

31. The multilayer barrier film of claim 30 wherein the semi-crystalline cyclic olefin copolymer (COC) has a melting temperature (T_m) of from about 70° to about 100° C, a glass transition temperature (T_g) of from about -20° C to about 32°C, and a norbornene content of from about 5 mole % to about 25 mole %.

32. The multilayer barrier film of any one of claims 30-31 wherein the at least one layer including a semi-crystalline cyclic olefin copolymer (COC) includes a first layer having a semi-crystalline COC and a second layer having a semi-crystalline COC.

33. The multilayer barrier film of claim 32 wherein the barrier layer including EVOH is disposed between the first layer having a semi-crystalline COC and the second layer having a semi-crystalline COC.

34. The multilayer barrier film of any one of claims 30-33 wherein the at least one flexible support layer includes a first support layer, a second support layer, a third support layer, and a fourth support layer.

35. The multilayer barrier film of any one of claims 30-34 further comprising:
an outer layer including ethylene vinyl acetate (EVA).

36. The multilayer barrier film of claim 35 wherein the outer layer defines an outer face, the multilayer barrier film further comprising:

a protective cover layer disposed along the outer face, the protective cover layer including at least one of fabric and nonwoven material.

37. The multilayer barrier film of any one of claims 30-36 wherein the at least one flexible support layer is disposed between the at least one layer including a semi-crystalline COC and the barrier layer including EVOH.

38. A method for reducing transmission of odorous species, the method comprising:
providing a semi-crystalline cyclic olefin copolymer (COC);
forming a film including the semi-crystalline COC; and
positioning the film between a source of odorous species and a user.

39. The method of claim 38 wherein the semi-crystalline COC has a melting temperature (T_m) of from about 70°C to about 100°C, a glass transition temperature (T_g) of from about -20°C to about 32°C, and a norbornene content of from about 5 mole % to about 25 mole %.

40. The method of any one of claims 38-39 wherein the odorous species is selected from the group consisting of skatole, hydrogen sulfide, 1-propanethiol, and combinations thereof.

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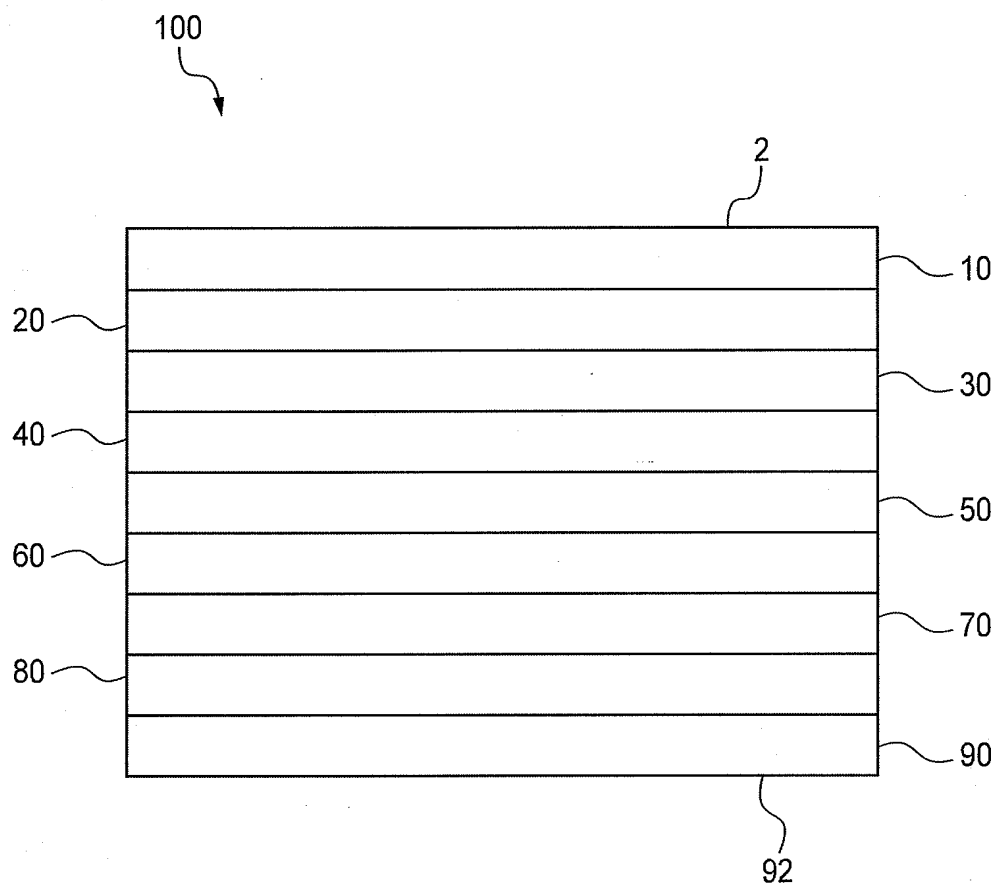


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/050720

A. CLASSIFICATION OF SUBJECT MATTER

INV. B32B7/02 B32B9/02 B32B25/00 B32B27/00 B32B27/06
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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B32B C08L C08J

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, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	EP0DOC abstract WPI abstract	15, 18-28
X	----- US 2007/110853 A1 (BEKELE SOLOMON [US]) 17 May 2007 (2007-05-17) abstract paragraphs 41-42 "Tg 30 degrees C" paragraph [0047] claims 1, 4, 5, 6, 11, 14-17, 19 paragraph [0020] - paragraph [0021] paragraph [0048] - paragraph [0050] paragraph [0008] - paragraph [0039] ----- -/-	1-39



Further documents are listed in the continuation of Box C.



See patent family annex.

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

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"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

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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(54) Title: KIT COMPRISING A PACKAGING MATERIAL AND A SOLID PHARMACEUTICAL OR NUTRACEUTICAL
PRODUCT CONTAINED IN THE PACKAGING MATERIAL

(57) Abstract: The present invention refers to a kit comprising a packaging material and a solid pharmaceutical or nutraceutical product, and in particular for a solid, opioid-based pharmaceutical product. The packaging material has an inner surface and an outer surface that avoids contamination of the product. At least that part of the inner surface, which is exposed to the pharmaceutical or nutraceutical product, is made of or covered with an inert material selected from the group consisting of polyamide, epoxy resin, polyethylene terephthalate, aluminium and mixtures thereof. The solid pharmaceutical or nutraceutical product is either a solid, opioid-based pharmaceutical product or is selected from the group consisting of acemetacin, amitriptyline, amobarbital, butalbital, carbachol, citric acid, dexamethylphenidate, fluoxetine, mephobarbital, metamizole, methadone, methylphenidate, methylphenobarbital, nicotine, nifedipine, oxprenolol, oxyconazole, pentobarbital, phenobarbital, phentermine, primidone, proparacaine, propoxyphene, secobarbital, selegiline, tetrahydropapaverine, trimethobenzamide, and mixtures thereof.



- 1 -

**Kit comprising a Packaging Material and a Solid
Pharmaceutical or Nutraceutical Product Contained in the
Packaging Material**

The present invention relates to a kit comprising a
5 packaging material and a solid pharmaceutical or
nutraceutical product contained in the packaging material.

The term "pharmaceutical product", as used throughout this
application, refers to any chemical substance intended for
use in medical diagnosis, cure, treatment or prevention of
10 disease, both in humans and animals. It includes both the
active agent (i.e. the chemical substance) in pure form,
as well as in combination with any other active agent(s)
and/or excipient(s).

Furthermore, the term "active agent", as used throughout
15 this application, includes all forms of a pharmaceutically
or nutraceutically active substance, including salts and
complexes thereof.

The term "nutraceutical product", as used throughout this
application, refers to a food or food product that
20 provides health benefits. Examples of nutraceutical
products are, for instance, dietary supplements,
functional foods or medical foods. Again, these products
may be intended for humans or animals. Furthermore,
"nutraceutical products" includes both the active agent in
25 pure form, as well as in combination with any other active
agent(s), food and/or excipient(s).