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(54) Bezeichnung: **UV- und lichtundurchlässige Folie mit hoher Reflexion**

(57) Zusammenfassung: Die Erfindung betrifft eine Folie, vorzugsweise mehrschichtig, die sich dadurch auszeichnet, dass einerseits in ein oder mehreren Schichten der Folie silb- rigfarbene Pigmente eingebracht sind und/oder eine Metalli- sierung auf mindestens einer Außenschicht der Folie aufge- bracht ist, und dass andererseits in mindestens einer oder mehreren Schichten der Folie mindestens ein UV-Absorber eingebracht ist, so dass in Abstimmung mit der bzw. den Schichtdicken und der Gesamtdicke der Folie die gesamte Folie für UV- und sichtbares Licht in einem Wellenlängen- bereich von 200 bis 800 nm zu weniger als 0,1% durchläs- sig ist und für einen Betrachter als opak, undurchsichtig und blickdicht wahrgenommen wird, und die UV- und sichtbare Strahlung in einem Wellenlängenbereich von 200 bis 800 nm zu mehr als 20% reflektiert wird. Weiterhin werden Verwen- dungen für eine derartige Folie vorgeschlagen, beispielswei- se zur Verwendung einer solchen Folie in einem Einlege- schlauch für den Rohrsanierungsbereich.

Beschreibung

[0001] Die Erfindung betrifft eine vorzugsweise mehrschichtige Folie. Insbesondere betrifft die Erfindung eine mehrschichtige schlauchförmige Außenfolie für einen Einlegeschlauch eines Rohrsanierungssystems.

[0002] Derartige schlauchförmige Außenfolien, auch Schlauchaußenfolien oder Außenschlauchfolien genannt, sind seit einigen Jahren als Teil von Einlegeschläuchen bei der Rohrsanierung, wie beispielsweise der grabenlosen Kanalrohrsanieung, im praktischen Einsatz. Diese Art von Kanalreparatur bietet aufgrund ihrer umweltschonenden und mit geringem Aufwand durchzuführenden Methodik große Vorteile. Es wird hierbei ein flexibler Einlegeschlauch (auch Schlauchliner oder lediglich Liner genannt) in das zu sanierende Rohr eingezogen (Einzugsverfahren), wobei der Einlegeschlauch über eine zuvor in dem Kanalrohr verlegte Gleitfolie bzw. einen sog. Preliner gleitet.

[0003] Ein derartiger Einlegeschlauch (Schlauchliner) weist beim System Glasfaser-Schlauchliner mit UV- oder Dampfhärtung üblicherweise einen inneren und einen äußeren Schlauch (Innen- bzw. Außenschlauch) auf, zwischen denen ein Trägermaterial aus beispielsweise Glasfasern eingebracht ist, welches mit reaktivem Kunststoffharz getränkt ist. Die Schlauchform des Außenschlauches wird hierbei durch entsprechendes Formen und Verschweißen von Flachfolien erhalten. Als reaktives Kunststoffharz kommen zum Beispiel handelsübliche UP-Harze (Polyester- bzw. ungesättigte Polyesterharze), VE-Harze (Vinylesterharze) oder EP-Harze (Epoxid-Harze) zum Einsatz. Die Härtung der Harze erfolgt bei UP- oder VE-Harzen zum Beispiel mit Hilfe von Photoinitiatoren (als Radikalbildner). Die Härtung kann aber auch thermisch erfolgen. Der Einlegeschlauch wird im Rohr solange aufgeblasen, bis er an der Rohrwand bzw. der Gleitfolie bzw. dem Preliner anliegt, um anschließend das Harz – beispielsweise mittels UV-Licht aus einer langsam durch das Rohr gezogenen UV-Lichtquelle – auszuhärten. Zum Schluss wird die innere Schlauchfolie des Einlegeschlauches meist abgezogen und entfernt. Die Schicht mit dem Trägermaterial und dem gehärteten Harz ist dann den durch das Rohr zu leitenden Substanzen exponiert.

[0004] Damit das Harz im Einlegeschlauch bei der Lagerung, d.h. vor dem Verbauen im Rohr, durch die UV-Strahlung des Sonnenlichts nicht vorzeitig aushärtet, ist es aus der WO 2013/026568 A1 bekannt, eine UV-Strahlung und ggf. kurzwelliges Licht absorbierende und/oder reflektierende Substanz in eine Außenschicht bzw. eine der Außenseite nahe Schicht einzubringen, wobei zu diesem Zweck nicht-silbrige Metalloxide, Übergangsmetalloxide und andere anorganische und organische Verbindungen eingesetzt werden können. In einer Schicht, die auf der zum Harz gewandten anderen Außenseite der Außenfolie angeordnet ist, ist eine UV-Strahlung reflektierende anorganische Verbindung eingebracht, vorzugsweise ein Weißpigment oder ein Metall oder eine Metalllegierung in multipartikulärer Form. Diese Maßnahme dient zum Reflektieren von UV-Strahlung, welche von einer durch das Rohr zu ziehenden UV-Quelle ausgeht und das Harz schon einmal durchdrungen hat, um die Effizienz und Geschwindigkeit des Aushärtungsprozesses zu steigern. Es hat sich allerdings herausgestellt, dass sowohl die Dichtheit und blockende Wirkung gegen UV-Licht und sichtbares Licht (dort nur für einen eingeschränkten Wellenlängenbereich genannt) als auch die Reflexionsausbeute dieser bekannten schlauchförmigen Außenfolie noch verbesserungswürdig sind.

[0005] Eine Alternative ist in der DE 297 00 236 U1 beschrieben, bei der eine außenliegende Hülle metallisch beschichtet ist oder aus einer schraubenförmig um das Trägersystem gewickelten Metallfolie besteht. Diese Anordnung ist allerdings zum Erreichen einer lückenlosen Reflexion kompliziert zu handhaben und aufwändig.

[0006] Es ist allgemein Aufgabe der vorliegenden Erfindung, eine Folie mit verbesserten optischen Eigenschaften hinsichtlich des Abblockens von UV- und sichtbarem Licht zur Verfügung zu stellen.

[0007] In Bezug auf eine schlauchförmige Außenfolie oder eine zu einem Schlauch formbaren Flachfolie für einen Einlegeschlauch eines Rohrsanierungssystems ist es die Aufgabe, bei einfacher Handhabung einen optimierten Schutz gegen UV-Strahlung von außen mit einer guten Rückstrahlung von UV-Strahlung, die von einer durch das Rohr zu ziehenden UV-Quelle ausgeht, zu kombinieren.

[0008] Diese Aufgabe wird durch die Merkmale des Anspruchs 1 gelöst.

[0009] Die Vorteile der Erfindung sind insbesondere darin zu sehen, dass durch den erfindungsgemäßen kombinatorischen Einsatz von silbrigfarbenen Pigmenten und UV-Absorbern in derselben oder – was in vielen Ausführungsformen bevorzugt ist – verschiedenen Schichten der erfindungsgemäßen Folie hervorragende optischen Eigenschaften hinsichtlich der Transmissionsunterbindung von äußerem UV-Licht und sichtbarem Licht (d.h. nicht von der durch das Rohr zu ziehenden UV-Quelle), z.B. Sonnenlicht, erzielt werden. Die Mes-

sungen an erfindungsgemäßen Folien ergaben, dass die Transmissionswerte um einen Faktor von bis ca. 60 gegenüber bisher bekannten Folien, eingesetzt als Außenfolien von Schlauchlinern, reduziert werden konnten.

[0010] Im Wellenlängenbereich von 200 bis 800 nm ist durch die erfindungsgemäße Kombination des Einsatzes von silbrigfarbenen Pigmenten einerseits und UV-Absorbern andererseits eine Transmission von weniger als 0,1% erzielbar. Da die Transmission auch durch die Schichtdicken bzw. die Foliendicke bestimmt wird (Lambert-Beersches Gesetz, s.u.) ist eine entsprechende – dem Fachmann ohne Weiteres geläufige – Abstimmung mit dem mindestens einen zugesetzten UV-Absorber notwendig, um die besagte Transmissionsobergrenze von 0,1% zu erzielen. Bekanntermaßen gibt der negative Zehnerlogarithmus der Transmission die Extinktion (auch optische Dichte genannt) an, welche ein Wellenlängen-abhängiges Maß für die Opazität, d.h. die Abschwächung einer Strahlung (wie z.B. Licht) nach Durchqueren eines Mediums darstellt. Die Extinktion ist hierbei als $E_\lambda = -\log_{10} (I/I_0) = -\log_{10} T$ definiert, mit E_λ = Extinktion, I = austretende Strahlung, I_0 = einfallende Strahlung, T = Transmission. An der Extinktion sind i.a. die Prozesse Absorption, Streuung, Beugung und Reflexion beteiligt, wobei die Reflexionsverluste in der obigen Formel schon in der einfallenden Strahlung I_0 berücksichtigt sind. Streuung und Beugung sind zumeist vernachlässigbar, so auch bei den erfindungsgemäßen Folien. Die obige Formel lässt sich auch in Form des Lambert-Beerschen Gesetzes schreiben: $E_\lambda = -\log_{10} (I/I_0) = \epsilon_\lambda \cdot c \cdot d$, wobei ϵ_λ den dekadischen Extinktionskoeffizienten bei der Wellenlänge λ angibt, c die Absorberkonzentration in der betreffenden Schicht und d die Schichtdicke ist. Das Lambert-Beersche Gesetz beschreibt also die Intensitätsabschwächung der in die Folie eindringenden Strahlung in Abhängigkeit von der UV-Absorberkonzentration und der Foliendicke. Gemäß der Erfindung werden die Foliendicke und insbesondere die Dicke der Schicht bzw. der Schichten mit den zugesetzten UV-Absorbern und deren Konzentrationen sowie die silbrigfarbenen Pigmenten in einer oder mehreren Schichten derart aufeinander abgestimmt, dass eine Transmission der Folie in einem Wellenlängenbereich von 200 bis 800 nm geringer ist als 0,1% und die UV- und kurzwellige sichtbare Strahlung in einem Wellenlängenbereich von 200 bis 800 nm zu mehr als 20% reflektiert wird.

[0011] Insbesondere im Falle einer Ausbildung der erfindungsgemäßen Folie als Außenschlauchfolie sind in dem Wellenlängenbereich von 200 bis 500 nm, in dem die meisten verwendeten Photoinitiatoren zur Harzhärtung aktiviert werden (also Radikale bilden), sehr niedrige Transmissionswerte von großem Vorteil, da ansonsten eine vorzeitige Harzhärtung bei der Lagerung, beim Einbringen in einen Kanal etc. stattfindet.

[0012] Unter dem Begriff „silbrigfarben“ wird im Sinne der vorliegenden Erfindung der von einem Betrachter wahrgenommene optische Sinneseindruck einer silbrigen Farbe verstanden.

[0013] Unter dem Begriff „Pigmente“ werden im Sinne der vorliegenden Erfindung farbgebende Substanzen verstanden, die im Gegensatz zu Farbstoffen im Anwendungsbereich unlöslich sind.

[0014] Unter den Begriffen „opak“, „undurchsichtig“ und „blickdicht“ wird im Sinne der vorliegenden Erfindung der von einem Betrachter wahrgenommene optische Sinneseindruck der vollständigen Opazität für sichtbares Licht verstanden. Mit anderen Worten kann ein Betrachter nicht durch die Schicht hindurchsehen, d.h. es gelangt kein sichtbares Licht durch die Schicht bzw. die Außenfolie. Der Wellenlängenbereich des sichtbaren Lichts wird vorliegend als von 380 nm bis 780 nm reichend verstanden. Eine erfindungsgemäße Transmission von weniger als 0,1% in einem Wellenlängenbereich von 200 bis 800 nm entspricht hierbei einer vollkommenen Blickdichtigkeit. Es kann hierzu auch ein entsprechender Test dergestalt durchgeführt werden, dass die jeweilige Folie auf eine mit schwarzem Text (Schriftart Arial, Schriftgröße 10) bedruckte weiße DIN A4-Seite gelegt und die Lesbarkeit des darunter liegenden Textes mit einem Schulnotensystem beurteilt wird. Die Note 6 entspricht hierbei dem Befund, dass nicht mehr erkennbar ist, dass ein Text unter der Folie vorhanden ist. Diese Situation kann auch als Kriterium für die genannte Opazität bzw. Blickdichtigkeit bzw. Undurchsichtigkeit der erfindungsgemäßen Folie herangezogen werden.

[0015] Der Begriff „schlauchförmig“ umfasst vorliegend sowohl schon als Schlauch hergestellte, beispielsweise extrudierte, Folien als auch zu einem Schlauch geformte Flachfolien, was zum Beispiel durch Siegeln, Verschweißen oder Verkleben gelingt.

[0016] Vorzugsweise ist zum einen die Art und Menge (in Gew.-%) an silbrigfarbenen Pigmenten in der mindestens einen Schicht bzw. die besagte Metallisierung und zum anderen die Art und Menge (in Gew.-%) des mindestens einen UV-Absorbers – in Abstimmung mit der Gesamtdicke der Folie und der Dicke der Schicht(en) mit silbrigfarbenen Pigmenten und insbesondere der Dicke der Schicht(en) mit zugesetztem UV-Absorber – derart gewählt, dass die gesamte Außenfolie Strahlung im Wellenlängenbereich von 200 nm bis 800 nm (also

sogar geringfügig über den wie oben definierten sichtbaren Bereich hinaus) zu weniger als 0,075% hindurchlässt, vorzugsweise zu weniger als 0,05% und besonders bevorzugt zu weniger als 0,025%.

[0017] Sichtbare Strahlung im Wellenlängenbereich von 200 nm bis 800 nm wird durch den Zusatz von silbrigfarbenen Pigmenten und/oder durch die Metallisierung vorzugsweise zu mehr als 20%, vorzugsweise mehr als 30%, am meisten bevorzugt zu mehr als 40%, reflektiert.

[0018] Im Falle einer Metallisierung ist die optische Dichte der erfindungsgemäßen Folie vorzugsweise größer als 1, besonders bevorzugt größer als 2.

[0019] Im Falle einer Ausbildung der erfindungsgemäßen Folie als Außenschlauchfolie für einen Schlauchliner ist die mindestens eine Schicht mit den silbrigfarbenen Pigmenten gemäß einer bevorzugten Ausführungsform diejenige Außenschicht, die zum Schlauchinneren, d.h. zum Harz und zur Schlauchinnenfolie, gerichtet ist. Die besagte Außenschicht dient in der Hauptsache zum Zurückwerfen der von einer UV- oder Licht-Quelle ausgesandten UV- oder Licht-Strahlung, die durch den im Kanalrohr aufgeblasenen Einlegeschlauch hindurchgezogen wird. Hierdurch wird die UV- oder Licht-Strahlung, die durch das auszuhärtende Harz unerwünschtermaßen hindurchgelangt, ohne die Photoinitiation des Photoinitiators auszulösen, an den silbrigfarbenen Pigmenten reflektiert und wieder zum Harz gerichtet. Damit erhöht sich die Geschwindigkeit und Gleichmäßigkeit der Harzaushärtung; zudem wird die Energie der UV- und Licht-Strahlen effizient ausgenutzt.

[0020] Alternativ oder zusätzlich, letzteres bevorzugt, ist die mindestens eine silbrigfarbene Pigmente enthaltende Schicht die Harz-abgewandte Außenschicht, ist also zum sanierenden Rohr gerichtet. Diese Außenschicht verhindert, dass UV- und sichtbares Licht (Tageslicht) zum Harz gelangt und dieses vorzeitig bei insbesondere der Lagerung aushärtet.

[0021] Gemäß einer vorteilhaften Variante der erfindungsgemäßen Folie als Schlauchaußenfolie sind in mindestens zwei Schichten silbrigfarbene Pigmente eingebracht und hierbei vorzugsweise in den beiden Außenschichten. Die näher zum Harz befindliche diesbezügliche Schicht ist dafür vorgesehen, Licht von der durch den aufgeblasenen Einlegeschlauch gezogenen UV-Quelle zum Harz zurück zu reflektieren (s.o.), während die weiter außen gelegene diesbezügliche Schicht insbesondere zum Reflektieren von Tageslicht dient. Hierbei unterstützt auch jede der beiden Schichten die Wirkungsweise der anderen Schicht. Lichtanteile, die beispielsweise trotz der silbrigfarbenen Pigmente durch die entsprechende äußere Schicht dringen, werden dann mit großer Wahrscheinlichkeit zumindest an den silbrigen Pigmenten der weiter innen liegenden Schicht reflektiert.

[0022] Bei einer Alternative sind beide Außenschichten der erfindungsgemäßen Außenfolie metallisiert, wobei die gleichen Wirkungen wie bei der Pigmentzumischung in die zwei Außenschichten erzielbar sind.

[0023] Die silbrigfarbenen Pigmente sind vorzugsweise aus einer Gruppe ausgewählt, die umfasst:

- Metallische Pigmente, vorzugsweise vom Leafing-Typ;
- Metalleffektpigmente, basierend auf z.B. Aluminium;
- Perlglanzpigmente; und
- Metallisierte Träger, z.B. metallisierte Perlglanzpigmente (Glimmerpigmente), beispielsweise durch Aluminium Bedampfung.

[0024] Die metallischen Pigmente und Effektpigmente können insbesondere sein: Aluminium, Titan, Chrom, Nickel, Amalgam (Quecksilber-Legierung) oder Silber oder eine Silberlegierung.

[0025] Kombinationen der obigen Substanzen sind hierbei ohne weiteres möglich. So kann insbesondere durch eine Mischung von Aluminium-Pigmenten und Perlglanzpigmenten eine sehr hohe Reflexion realisiert werden.

[0026] Es hat sich als vorteilhaft erwiesen, wenn die Pigmentgrößen der silbrigfarbenen Pigmente im Bereich von 0,1 µm bis 100 µm liegen, vorzugsweise im Bereich von 1 µm bis 75 µm, besonders bevorzugt im Bereich von 5 µm bis 50 µm. Die Konzentration der Pigmente in der silbrigfarbenen Schicht beträgt vorzugsweise 0,1 bis 50 Gew.-%, besonders bevorzugt 1 bis 30 Gew.-%.

[0027] Wird mindestens eine der Außenschichten der erfindungsgemäßen Folie metallisiert, ist das Material dieser Metallisierung vorzugsweise Aluminium, Titan, Chrom, Nickel, Amalgam (Quecksilber-Legierung) oder Silber oder eine Silberlegierung.

[0028] Insbesondere wenn die Folie als Außenschlauchfolie ausgebildet ist, sind gemäß einer bevorzugten Ausführungsform in der zum Schlauchhäußen gerichteten Außenschicht – zusätzlich zu den silbrigfarbenen Farbstoffen oder Farbpigmenten – auch andersfarbige Farbstoffe oder Pigmente eingebracht. Hierdurch kann eine firmenspezifische Kennung des Schlauchliners oder des sanierten Rohres erfolgen. Bei einer entsprechenden Ausführungsform können in einer oder mehreren weiter innenliegenden Schichten silbrigfarbene Pigmente vorhanden sein, welche für die Reflexion des Lichts sorgen. Der farbliche Eindruck von außen kann dann auch in einer Überlagerung der andersfarbigen mit den silbrigfarbenen Pigmenten bestehen.

[0029] Vorzugsweise enthält – vorteilhafterweise zu mehr als 50 Gew.-% – die mindestens eine Schicht, in welcher silbrigfarbene Pigmente eingebracht sind oder auf welche eine Metallisierung aufgebracht ist, mindestens ein thermoplastischen Olefin-Homo- oder Copolymer, wobei dieses gegebenenfalls modifiziert ist. Diese Verbindungen haben sich als Außenschichten für Schlauchaußenfolien bewährt. Sie bieten gute mechanische Eigenschaften und sind auch bei der Herstellung der Folien einfach zu handhaben.

[0030] Alternativ enthalten – vorteilhafterweise zu mehr als 50 Gew.-% – eine oder beide der Außenschichten der erfindungsgemäßen Schlauchaußenfolie mindestens ein Polyamid, gegebenenfalls modifiziert.

[0031] Alternativ enthalten – vorteilhafterweise zu mehr als 50 Gew.-% – eine oder beide der Außenschichten der erfindungsgemäßen Schlauchaußenfolie mindestens ein Thermoplastisches Elastomer (TPE), insbesondere TPU, gegebenenfalls modifiziert.

[0032] Vorzugsweise ist die Art und Menge (in Gew.-%) an dem zugesetzten mindestens einen UV-Absorber in der mindestens einen Schicht derart gewählt, dass Strahlung in dieser Schicht (und damit auch in der gesamten Folie) in einem Wellenlängenbereich von 200 nm bis 450 nm, vorzugsweise im Wellenlängenbereich der UV-Strahlung von 250 bis 400 nm, zu mehr als 95%, vorzugsweise zu mehr als 98%, besonders bevorzugt zu mehr als 99,5% absorbiert wird. Alternativ kann der mindestens eine UV-Absorber auch in mehreren Schichten in derartiger Art und Menge enthalten sein, dass in der gesamten erfindungsgemäßen Folie Strahlung von 200 nm bis 450 nm zu mehr als 95%, vorzugsweise zu mehr als 98%, besonders bevorzugt zu mehr als 99,5% absorbiert wird.

[0033] Der Begriff „UV-Licht“ wird vorliegend als von 200 nm bis 400 nm reichend verstanden. Da es keinen allgemein akzeptierten unteren oder oberen Grenzwert der UV-Strahlung gibt, wird vorliegend davon ausgegangen, dass es einen Überlappungsbereich von UV- und sichtbarer Strahlung gibt, der von ca. 380 nm bis ca. 400 nm reicht.

[0034] UV-Absorber absorbieren häufig auch über den UV-Bereich hinaus, beispielsweise etwa bis 450 nm. Der Grund liegt darin, dass UV-Absorber auch eine Eigenfarbe haben, die meist gelblich ist. Die Absorption findet dann auch im Ultravioletten bis Blauen statt.

[0035] Der besagte mindestens eine UV-Absorber kann anorganischer oder organischer Natur sein. Im Falle eines anorganischen UV-Absorbers kann dieser z.B. ein Metalloxid sein, wobei unter dem Begriff Metalloxide auch Übergangsmetalloxide fallen. Zu den geeigneten Metalloxiden zählen beispielsweise Titandioxid, Eisenoxid und Zinkoxid. Ein vorteilhaftes Beispiel für ein Zinkoxid ist Zincox®, das von der IBU-tec advanced materials AG, Weimar, entwickelt wurde; Zincox® ist ein nanoskaliges ZnO mit einer mittleren Partikelgröße von 10 nm, welches im technischen Maßstab als Pulver oder als desagglomerierte, stabilisierte und sehr leicht verarbeitbare Suspension erhältlich ist. Auch als UV-Absorber geeignete Metalloxidhydrate, welche auch Übergangsmetalloxidhydrate umfassen, sind einsetzbar. Als organische Verbindungen sind z.B. Benzotriazole, Triazine, Benzophenone und Cyanoacrylate verwendbar. Auch Derivate der vorgenannten Verbindungen können eingesetzt werden, Mischungen aus den vorgenannten Verbindungen ebenfalls. Bevorzugt sind anorganische UV-Absorber.

[0036] Es hat sich als vorteilhaft erwiesen, wenn der mindestens eine UV-Absorber in der besagten Schicht in einer Konzentration von 0,01 bis 20 Gew.-% enthalten ist, bevorzugt von 0,1 bis 10 Gew.-% und am meisten bevorzugt von 0,5 bis 5 Gew.-%.

[0037] Mit Vorteil ist der mindestens eine UV-Absorber in eine Haftvermittlerschicht (HV) eingebracht. Dies vermeidet etwa eine Migration des UV-Absorbers aus der Folie und sichert so seine dauerhafte Wirkungsweise. Beispielsweise im Falle eines Aufbaus der Außenfolie als 5-Schicht-Folie in der Form PE (Polyethylen) / HV / PA (Polyamid) / HV / PE kann in einer oder – was bevorzugt ist – beiden Haftvermittlerschichten der mindestens eine UV-Absorber eingebracht sein. In einer oder beide PE-Außenschichten können bei derartigen Ausführungs-

rungsformen, in denen in mindestens einer Haftvermittlerschicht der mindestens eine UV-Absorber eingesetzt wird, beispielsweise silbrigfarbene Pigmente eingebracht sein. Eine diesbezügliche beispielhafte Schichtfolge bei einer 7-Schicht-Folie ist PE/PE/HV/PA/HV/PE/PE. Bei einer dreischichtigen Folie, beispielsweise PA / HV / PE, ist vorzugsweise der mindestens eine UV-Absorber in der Haftvermittlerschicht enthalten, während in der PE-Schicht die silbrigfarbenen Pigmente enthalten sind. Hierbei bedeutet die Formulierung „PE-Schicht“ bzw. „PA-Schicht“, dass die betreffende Schicht überwiegend Polyethylen bzw. Polyamid enthält.

[0038] Wenn die Folie als Außenschlauchfolie ausgebildet ist, ist gemäß einer vorteilhaften Ausführungsform der mindestens eine UV-Absorber in eine Schicht eingebracht, die an eine der Außenschichten der Außenfolie angrenzt. Hierdurch wird zumindest ein Teil der UV-Strahlung in der dem Harz am nächsten liegenden Schicht abgefangen. Wenn in der angrenzenden Außenschicht zudem die besagten silbrigfarbenen Pigmente vorhanden sind und/oder die besagte Metallisierung aufgebracht ist, gelangt ohnehin nur ein kleinerer Anteil an Strahlung in die Schicht mit dem mindestens einen UV-Absorber.

[0039] Eine weitere vorteilhafte Ausführungsform der erfindungsgemäßen Folie als Schlauchaußenfolie sieht vor, dass mindestens ein UV-Absorber in mindestens zwei Schichten der schlauchförmigen Außenfolie eingebracht ist. In diesem Zusammenhang ist es bevorzugt, dass diese beiden Schichten jeweils innenseitig an eine der Außenschichten der Außenfolie angrenzen. In den Außenschichten sind beispielsweise die silbrigfarbenen Pigmente eingebracht (bzw. eine Metallisierung aufgebracht) und in den beiden nach innen angrenzenden Schichten der oder die UV-Absorber.

[0040] Auch sind Ausführungsformen möglich, bei denen in einer Schicht sowohl silbrigfarbene Pigmente als auch mindestens ein UV-Absorber eingebracht sind.

[0041] Die Schichten, in denen die silbrigfarbenen Pigmente und/oder UV-Absorber eingebracht sind, enthalten besonders bevorzugt mindestens ein thermoplastisches Olefin-Homo- oder Copolymer, gegebenenfalls modifiziert. Ist beispielsweise der mindestens eine UV-Absorber in einer Haftvermittlerschicht (s.o.) aus einem Olefin-Homo- oder Copolymer vorhanden, ist dieses vorzugsweise mit mindestens einer organischen Säure oder einem cyclischen organischen Säureanhydrid modifiziert, bevorzugt mit Maleinsäureanhydrid.

[0042] Mindestens eine, vorzugsweise beide Außenschichten der erfindungsgemäßen Mehrschichtfolie enthalten bevorzugt mindestens ein thermoplastisches Olefin-Homo- oder Copolymer, gegebenenfalls modifiziert. Auch ggf. vorhandene Haftvermittlerschichten sind vorzugsweise derartig aufgebaut.

[0043] Bevorzugte Olefin-Homo- oder Copolymere sind solche von α,β -ungesättigten Olefinen mit 2–10 Kohlenstoffatomen. Es eignen sich hierbei vorzugsweise Ethylen-Homopolymere (Polyethylen, PE), vorzugsweise LDPE (Polyethylen hoher Dichte im Bereich von 0,86–0,93 g/cm³), LLDPE (Linear Low Density Polyethylen), HDPE (Polyethylen hoher Dichte im Bereich von 0,94 und 0,97 g/cm³) und mPE (auf Basis von Metallocen-Katalysatoren polymerisierte PE), Propylen-Homopolymere (Polypropylen, PP), Butylen-Homopolymere (Polybutylen, PB) und Isobutylen-Homopolymere (Polyisobutylene, PI) oder Mischungen aus mindestens zwei der genannten Polymere. Diese Olefin-Homo- oder Copolymere können in den Schichten, die silbrigfarbene Pigmente und/oder UV-Absorber enthalten, eingesetzt werden.

[0044] Insbesondere für die Rohrsanierung ist es sehr vorteilhaft, wenn mindestens eine innenliegende Barrierschicht gegen den Durchtritt von Gasen und/oder chemischen Substanzen vorgesehen ist, wobei die Barrierschicht vorzugsweise Ethylenvinylalkohol (EVOH) oder Polyamid (PA) oder Cyclo-Olefin-Copolymer (COC) oder eine Kombination von diesen enthält, bevorzugt jeweils mit bis zu 100 Gew.-% aus diesen Verbindungen. Als Polyamide können vorzugsweise Homo- oder Copolyamide verwendet werden, vorzugsweise PA 6, PA 12, PA 66, PA 6I und PA 6T. Auch entsprechende Copolymere oder Mischungen aus mindestens zwei Polyamiden sind ohne weiteres möglich.

[0045] Ist beispielsweise eine PA-Barrierschicht vorgesehen, kann diese entweder zu einer Seite oder zu ihren beiden Seiten mit jeweils einer Haftvermittlerschicht mit jeweils einer Schicht, vorzugsweise jeweils einer Außenschicht, verbunden werden. Enthalten diese beiden äußeren Schichten überwiegend (bis zu 100 Gew.-%) ein thermoplastisches Olefin-Homo- oder Copolymer, gegebenenfalls modifiziert, wird der schon oben genannte 5-Schicht-Aufbau PE / HV / PA / HV / PE erhalten, wobei in den PE- und HV-Schichten die silbrigfarbenen Pigmente bzw. der besagte mindestens eine UV-Absorber enthalten sind.

[0046] Bevorzugt beträgt die Gesamtdicke der erfindungsgemäßen Folie zwischen 10 μ m und 1000 μ m, vorzugsweise zwischen 20 μ m und 500 μ m, und besonders bevorzugt zwischen 30 μ m und 400 μ m.

[0047] Die erfindungsgemäße Folie kann auch noch mit einer anderen Folie oder mit einem für Harz und Flüssigkeiten saugfähigen Material und insbesondere mit einem für Harz und Flüssigkeiten saugfähigen Material ein- oder beidseitig kaschiert werden, um einen entsprechenden Verbund zu erhalten. Beispielsweise kann die erfindungsgemäße Folie, wenn diese als Schlauchaußenfolie ausgebildet ist, mit einer Gleitfolie kaschiert sein, um ein gleitreibungsreduziertes, beschädigungsfreies Einbringen dieses Verbundes in ein zu sanierendes Rohr zu realisieren.

[0048] Alternativ oder zusätzlich kann die erfindungsgemäße Folie mit einer Schicht aus einem für Harz und/oder Flüssigkeiten saugfähigen Material kaschiert werden. Es wird damit ein Verbund erhalten, der die erfindungsgemäße UV-Lichtschutzfolie mit einer z.B. mit Harz zu tränkenden oder getränkten Vliesschicht kombiniert und somit das Handling wesentlich vereinfacht. Insbesondere kann damit die Anbindung der UV- und lichtundurchlässigen Außenfolie an den das Harz inklusive Träger erreicht werden, was zu einer erhöhten Stabilität des Liners führt. Schließlich wird – durch die Verbindung mit einem für Harz oder Flüssigkeiten saugfähigen Material – ein enges Anschmiegen der Außenfolie mit dem mit Harz getränkten Trägermaterial erzielt. So bietet die Außenfolie keine Angriffsfläche, um beim Einziehen des Schlauchliners beschädigt zu werden, indem die Außenfolie zu weit vom Trägermaterial mit Harz absteht. Als bzgl. Harz oder Flüssigkeiten saugfähige Materialien (oder damit tränkbare bzw. imprägnierbare Materialien) können insbesondere aus Fasern bestehende Materialien verwendet werden, vorzugsweise Vliese, Filze, Gewebe, Gewirke, Gestricke, Gelege, Textilien allgemein, aber auch Schaumstoffe. Saugfähig bedeutet dabei, dass die Flüssigkeit oder das Harz vom Material – zumindest teilweise – aufgenommen werden kann. Im Idealfall wird das Material von Harz und Flüssigkeit durchtränkt.

[0049] Im Rahmen dieser Erfindung wird unter dem Begriff „Vlies“ ein Gebilde aus Fasern begrenzter Länge, Endlosfasern oder geschnittenen Garnen jeglicher Art und jeglichen Ursprungs verstanden, die auf irgendeine Weise zu einem Vlies bzw. einer Faserschicht oder einem Faserflor zusammengefügt und auf irgendeine Weise miteinander verbunden worden sind. Hierunter fallen nicht das Verkreuzen bzw. Verschlingen von Garnen, wie es beim Weben, Wirken, Stricken, der Spitzenherstellung, dem Flechten und der Herstellung von getufteten Erzeugnissen geschieht. Der überwiegende Teil der Vliesstoffe sind flexible textile Flächengebilde, da sie aus textilen Fasern als Hauptstrukturelement aufgebaut sind.

[0050] Als Gewebe kann beispielsweise ein Jeansstoff verwendet werden. Auch andere Gewebe, Gestricke, Gewirke etc. können verwendet werden, solange sie Harz oder Flüssigkeiten aufsaugen können oder damit getränkt werden können.

[0051] Teil der Erfindung ist auch ein Einlegeschlauch für das Schlauchlining-Verfahren zur Rohrsanierung, insbesondere zur grabenlosen Kanalsanierung, wobei der erfindungsgemäße Einlegeschlauch die zuvor beschriebene schlauchförmige Außenfolie umfasst, sowie eine schlauchförmige, für UV-Strahlung durchlässige Innenfolie, und ein zwischen diesen beiden Folien angeordnetes Trägermaterial, das mit einem reaktiven Kunststoffharz getränkt ist. Die Erfindung betrifft ebenfalls die entsprechende Verwendung eines solchen Einlegeschlauchs zur Sanierung eines Rohrs, vorzugsweise eines unterirdisch verlegten Kanalrohrs.

[0052] Die genannte UV-durchlässige Innenfolie ist bevorzugt gemäß dem Stand der Technik aufgebaut, wie beispielsweise in der WO 2013/026568 A1 beschrieben.

[0053] In alternativen Verwendungen kann die erfindungsgemäße Folie als schützendes Verpackungsmaterial für Lebensmittel oder für den sog. Non-Food-Bereich, als Außenverkleidung, als außenliegende Abdeckung von Gebäudeteilen, als Bag-in-Box-Folie, als Membranfolie, als Folie für Sicherheitsgläser, Solarmodule oder Airbags, als Klebefolie, Tape oder Band, für die Kabelummantelung, in Schutzanzügen, bei Textilien und Bekleidungen, als Dekorfolie bei Laminaten für Holz-, Naturfaser- und Kunststoffverbundwerkstoffe, als Schutzfolie im Prepreg-Bereich (preimpregnated fibers, vorimprägnierte Fasern), als Schutzfolie, für Schilder sowie Anzeigetafeln, für medizinische Anwendungen wie Pflaster, für Hygieneartikel wie Windeln, für Displays oder als Isoliermaterial eingesetzt werden.

[0054] Die oben genannten vorteilhaften Ausführungsformen sind – soweit sie sich nicht gegenseitig technisch ausschließen – ohne weiteres miteinander kombinierbar.

Ausführungsbeispiele:

[0055] Die nachfolgenden Beispiele und Vergleichsbeispiele dienen zur Erläuterung der Erfindung und sind nicht einschränkend auszulegen. Im Folgenden werden verschiedene Vergleichsbeispiele (Folien V1–V7) und

erfindungsgemäße Beispielfolien (Folien B1–B5) vorgestellt, die hinsichtlich ihrer Reflexions- und Transmissions-eigenschaften untersucht wurden.

I. Verwendete Materialien

[0056] Das in vielen der nachfolgenden Beispielen verwendete LDPE ist Lupolen 2420 F von der Firma LyondellBasell Polymers. Auch das eingesetzte Lupolen 3010D ist ein LDPE von LyondellBasell Polymers.

[0057] Durethan C38 F von Lanxess ist ein Copolyamid mittlerer Viskosität.

[0058] Admer NF498E von Mitsui Chemicals ist ein mit Maleinsäureanhydridgruppen modifiziertes LDPE, besitzt eine große Adhäsion zu PET, EVOH und PA, ist sehr gut verarbeitbar und weist eine thermische Stabilität auf, die äquivalent zu gewöhnlichem PE ist.

[0059] Luvofilm 9679 ist ein Prozesshilfsmittel der Firma Lehmann & Voss & Co. KG, das in einem LDPE Masterbatch mit Fluorelastomer vorlag.

[0060] Eingesetzte silbrigfarbene Pigmente der Firma GRAFE Color Batch GmbH waren:

Grafe 13-08486: ca. 5 µm, „fein“; 30 Gew.-% Pigment

Grafe 13-08485: ca. 10 µm, „grob“; 30 Gew.-% Pigment

Grafe 13-08487: ca. 20 µm, „sehr grob“; 35 Gew.-% Pigment

[0061] Constab UVA 01490 LD der Firma CONSTAB Polyolefin Additives GmbH ist ein UV-Absorber Konzentrat zur Ausrüstung von Erzeugnissen auf Basis PE und dessen Copolymere, das UV-Barriereaufgaben zum Schutz des darunterliegenden Gutes erfüllen soll. Die Dichte beträgt 1,830 g/cm³ (nach ISO 1183) und 970 kg/m³ (nach ISO 60). Die jeweilig verwendeten Konzentrationsangaben bzgl. dieses UV-Absorbers sind in den nachfolgenden Tabellen wiedergegeben, wobei beispielsweise die Angabe „4%“ bedeutet, dass 4 Gew.-% UV-Absorber in beispielsweise 96 Gew.-% PE-LD vorhanden sind.

II. Herstellung der Mehrschichtfolien

[0062] Die in den folgenden Tabellen aufgeführten Folien wurden durch Blasfolien-Extrusion hergestellt.

III. Vermessung der Folien

[0063] Die Messung der Reflexion der Folien wurde bei den Wellenlängen 350 nm, 400 nm und 450 nm mit dem Gerät Specord 200 plus von Analytik Jena durchgeführt. Der Messbereich reichte von 200 bis 800 nm. Es war ein Messwinkel von 8° eingestellt.

[0064] Die Messung der Transmission erfolgte ebenso mit dem o.g. Gerät Specord 200 plus. Der Messbereich reichte ebenfalls von 200 bis 800 nm.

IV. Vermessene Folien

[0065] Die Gewichtsprozentangaben beziehen sich jeweils auf das Gesamtgewicht der jeweiligen Schicht.

[0066] Die Beispiele B1–B5 sind erfindungsgemäße Mehrschichtfolien, während die Vergleichsfolien V1–V7 nicht erfindungsgemäß ausgebildet sind.

Beispiel B1:

Silbrigfarbene Folie mit UV-Absorber; Farbbatch: Grafe 13-08485

Schicht-Nummer	Zusammensetzung	Anteil in Schicht in %	Dicke in µm
1	<ul style="list-style-type: none"> • Luvofilm 9679 • Lupolen 2420 F • Farbbatch silber 	<ul style="list-style-type: none"> • 0,5 • 79,5 • 20 	75

2	<ul style="list-style-type: none"> • Haftvermittler Mitsui Admer NF 498 E • UV-Absorber Constab UVA 01490 LD 	<ul style="list-style-type: none"> • 96 • 4 	12
3	• Durethan C 38 F	• 100	26
4	<ul style="list-style-type: none"> • Haftvermittler Mitsui Admer NF 498 E • UV-Absorber Constab UVA 01490 LD 	<ul style="list-style-type: none"> • 96 • 4 	12
5	<ul style="list-style-type: none"> • Luvofilm 9679 • Lupolen 2420 F • Farbbatch silber 	<ul style="list-style-type: none"> • 0,5 • 79,5 • 20 	75
			200 µm

Beispiel B2:

Silbrigfarbene Folie mit UV-Absorber; Farbbatch silber: Grafe 13-08486

Schicht-Nummer	Zusammensetzung	Anteil in Schicht in %	Dicke in µm
1	<ul style="list-style-type: none"> • Luvofilm 9679 • Lupolen 2420 F • Farbbatch silber 	<ul style="list-style-type: none"> • 0,5 • 79,5 • 20 	75
2	<ul style="list-style-type: none"> • Haftvermittler Mitsui Admer NF 498 E • UV-Absorber Constab UVA 01490 LD 	<ul style="list-style-type: none"> • 96 • 4 	12
3	• Durethan C 38 F	• 100	26
4	<ul style="list-style-type: none"> • Haftvermittler Mitsui Admer NF 498 E • UV-Absorber Constab UVA 01490 LD 	<ul style="list-style-type: none"> • 96 • 4 	12
5	<ul style="list-style-type: none"> • Luvofilm 9679 • Lupolen 2420 F • Farbbatch silber 	<ul style="list-style-type: none"> • 0,5 • 79,5 • 20 	75
			200 µm

Beispiel B3:

Silbrigfarbene Folie mit UV-Absorber; Farbbatch silber: Grafe 13-08487

Schicht-Nummer	Zusammensetzung	Anteil in Schicht in %	Dicke in µm
1	<ul style="list-style-type: none"> • Luvofilm 9679 • Lupolen 2420 F • Farbbatch silber 	<ul style="list-style-type: none"> • 0,5 • 84,5 • 15 	75
2	<ul style="list-style-type: none"> • Haftvermittler Mitsui Admer NF 498 E • UV-Absorber Constab UVA 01490 LD 	<ul style="list-style-type: none"> • 96 • 4 	12
3	• Durethan C 38 F	• 100	26
4	<ul style="list-style-type: none"> • Haftvermittler Mitsui Admer NF 498 E • UV-Absorber Constab UVA 01490 LD 	<ul style="list-style-type: none"> • 96 • 4 	12

5	<ul style="list-style-type: none"> • Luvofilm 9679 • Lupolen 2420 F • Farbbatch silber 	<ul style="list-style-type: none"> • 0,5 • 84,5 • 15 	75
			200 µm

Beispiel B4:

Einseitig metallisierte Folie mit UV-Absorber

Schicht-Nummer	Zusammensetzung	Anteil in Schicht in %	Dicke in µm
1	<ul style="list-style-type: none"> • Luvofilm 9679 • Lupolen 2420 F 	<ul style="list-style-type: none"> • 0,5 • 99,5 	75
2	<ul style="list-style-type: none"> • Haftvermittler Mitsui Admer NF 498 E • UV-Absorber Constab UVA 01490 LD 	<ul style="list-style-type: none"> • 96 • 4 	12
3	• Durethan C 38 F	• 100	26
4	<ul style="list-style-type: none"> • Haftvermittler Mitsui Admer NF 498 E • UV-Absorber Constab UVA 01490 LD 	<ul style="list-style-type: none"> • 96 • 4 	12
5	<ul style="list-style-type: none"> • Luvofilm 9679 • Lupolen 2420 F 	<ul style="list-style-type: none"> • 0,5 • 99,5 	75
			200 µm

Beispiel B5:

Beidseitig metallisierte Folie mit UV-Absorber

Schicht-Nummer	Zusammensetzung	Anteil in Schicht in %	Dicke in µm
1	<ul style="list-style-type: none"> • Luvofilm 9679 • Lupolen 2420 F 	<ul style="list-style-type: none"> • 0,5 • 99,5 	75
2	<ul style="list-style-type: none"> • Haftvermittler Mitsui Admer NF 498 E • UV-Absorber Constab UVA 01490 LD 	<ul style="list-style-type: none"> • 96 • 4 	12
3	• Durethan C 38 F	• 100	26
4	<ul style="list-style-type: none"> • Haftvermittler Mitsui Admer NF 498 E • UV-Absorber Constab UVA 01490 LD 	<ul style="list-style-type: none"> • 96 • 4 	12
5	<ul style="list-style-type: none"> • Luvofilm 9679 • Lupolen 2420 F 	<ul style="list-style-type: none"> • 0,5 • 99,5 	75
			200 µm

Vergleichsbeispiele:

[0067] Vergleichsbeispiele V1 bis V5: Wie die Beispiele 1 bis 5, nur ohne den UV-Absorber Constab UVA 01490 LD, also z.B. für

Vergleichsbeispiel V1:

Farbbatch silber: Grafe 13-08485

Schicht-Nummer	Zusammensetzung	Anteil in Schicht in %	Dicke in μm
1	• Luvofilm 9679 • Lupolen 2420 F • Farbbatch silber	• 0,5 • 79,5 • 20	75
2	• Haftvermittler Mitsui Admer NF 498 E	• 100	12
3	• Durethan C 38 F	• 100	26
4	• Haftvermittler Mitsui Admer NF 498 E	• 100	12
5	• Luvofilm 9679 • Lupolen 2420 F • Farbbatch silber	• 0,5 • 79,5 • 20	75
			200 μm

Vergleichsbeispiel V6:

[0068] Wie Beispiel 1, nur ohne UV-Absorber und ohne Farbbatch silber.

Schicht-Nummer	Zusammensetzung	Anteil in Schicht in %	Dicke in μm
1	• Luvofilm 9679 • Lupolen 2420 F	• 0,5 • 99,5	75
2	• Haftvermittler Mitsui Admer NF 498 E	• 100	12
3	• Durethan C 38 F	• 100	26
4	• Haftvermittler Mitsui Admer NF 498 E	• 100	12
5	• Luvofilm 9679 • Lupolen 2420 F	• 0,5 • 99,5	75
			200 μm

Vergleichsbeispiel V7:

[0069] Hier wurde die 5-schichtige Folie aus dem Beispiel 1 der WO 2013/026568 A1 gemessen, deren Dicke 200 μm betrug. In der zur Außenumgebung gerichteten Außenschicht waren 1,5 Gew.-% Euthylenblau 69-2025 Granulat, in der anschließenden Schicht 6 Gew.-% Remafin Schwarz &E-AE (40% Ruß) und in der nach innen gerichteten Außenschicht 20 Gew.-% Remafin Weiss RCL enthalten.

V. Ergebnisse

[0070] Die folgende Tabelle gibt eine Übersicht über die gemessene Reflexion bei den Wellenlängen 350 nm, 400 nm, 450 nm für die Beispielfolien B1–B5 und die Vergleichsfolien V1–V7. Bei der beidseitig metallisierten Folie des Beispiels B5 sind die Messwerte von beiden Folienseiten angegeben.

Bezeichnung	Reflexion in % bei 200 nm	Reflexion in % bei 350 nm	Reflexion in % bei 400 nm	Reflexion in % bei 450 nm	Reflexion in % bei 600 nm
B1	49,3	33,6	57,1	58,7	56,7
B2	45,1	30,3	55,1	55,8	50,0
B3	58,9	63,4	58,6	56,4	57,5

B4	91,6	91,7	91,2	91,0	91,2
B5	93,6/93,4	93,9/93,7	93,3/93,4	92,9/93,1	93,0/93,0
V1	Wie B1				
V2	Wie B2				
V3	Wie B3				
V4	Wie B4				
V5	Wie B5				
V6	1,7	3,2	3,4	4,0	4,1
V7	7,2	9,3	11,4	14,3	15,6

[0071] Die folgende Tabelle gibt eine Übersicht über die gemessene Transmission bei den Wellenlängen 350 nm, 400 nm, 450 nm für die Beispielfolien B1–B5 und die Vergleichsfolien V1–V7:

Bezeichnung	Transmission in % bei 200 nm	Transmission in % bei 350 nm	Transmission in % bei 400 nm	Transmission in % bei 450 nm	Transmission in % bei 600 nm
B1	0,014	0,015	0,016	0,014	0,013
B2	0,009	0,008	0,007	0,009	0,008
B3	0,020	0,020	0,021	0,025	0,024
B4	0,009	0,010	0,009	0,009	0,009
B5	0,007	0,007	0,007	0,007	0,007
V1	0,57	0,55	0,65	0,66	0,66
V2	0,33	0,31	0,42	0,39	0,40
V3	1,11	1,00	1,00	1,10	1,12
V4	0,12	0,12	0,12	0,11	0,12
V5	0,09	0,09	0,08	0,08	0,09
V6	83,91	86,42	92,94	93,22	94,12
V7	0,82	0,72	0,69	0,63	0,65

[0072] Mit $E_{\lambda} = -\log_{10} T$ kann aus den obigen Transmissionswerten die Extinktion (optische Dichte) bei den jeweiligen Wellenlängen berechnet werden. Bei den Beispielen B1 bis B5 resultieren hierbei Extinktionswerte von 1,60 (Transmission $T = 0,025$) bis 2,16 (Transmission $T = 0,007$).

VI. Auswertung und Interpretation:

[0073] Eine hohe Reflexion von sowohl sichtbarem Licht als auch von UV-Strahlung wird bei den Folien aus den Beispielen B1 bis B3 und den Vergleichsbeispielen V1 bis V3 zum einen durch Zugabe eines Farbbatches mit silbrigfarbenen Metallpigmenten in die Folien, bevorzugt in die beiden Außenschichten (mindestens jedoch in eine Schicht), erreicht. Die verwendeten silbrigfarbenen Farbbatche enthielten Aluminium-Metallpigmente, deren Größe sich je nach Farbbatch unterschied. Bei den Beispielen B2 und dem Vergleichsbeispiel V2 wiesen die Metallpigmente eine mittlere Größe von etwa 5 μm auf und werden als „fein“ bezeichnet. Bei den Beispielen B1 und dem Vergleichsbeispiel V1 wiesen die Metallpigmente eine mittlere Größe von etwa 10 μm auf und werden als „grob“ bezeichnet. Bei den Beispielen B3 und dem Vergleichsbeispiel V3 wiesen die Metallpigmente eine mittlere Größe von etwa 20 μm auf und werden als „sehr grob“ bezeichnet.

[0074] Es stellte sich im Rahmen dieser Erfindung heraus, dass je feiner die Metallpigmente im verwendeten silbrigen Farbbatch waren, ein abnehmendes Reflexionsvermögen bei den Folien gegenüber sichtbarem Licht und insbesondere gegenüber UV-Licht (z.B. bei Wellenlänge 350 nm) beobachtet wurde. So lag die Reflexion bei dem Beispiel B2 und dem Vergleichsbeispiel V2 im UV-Bereich von 350 nm bei 30,3%.

[0075] Der Einsatz eines Farbbatches mit etwas größeren Metallpigmenten (B1 und V1) führte zu einer Reflexion bei 350 nm von 33,6%. Bei Verwendung eines Farbbatches mit noch größeren Metallpigmenten (Beispiel B3 und Vergleichsbeispiel V3) wurde im Rahmen dieser Messreihe mit 63,4% die höchste Reflexion gefunden.

[0076] Überraschenderweise hat die Größe der im Farbbatch enthaltenen Metallpigmente mit zunehmender Wellenlänge – insbesondere ab dem Bereich der Wellenlänge des sichtbaren Lichts (400 nm) – nur noch einen geringen Einfluss auf das Reflexionsvermögen der Folie. So finden sich bei B1 bis B3 und V1 bis V3 bei einer Wellenlänge von 400 nm und 450 nm mit Werten für die Reflexion im Bereich 55,1 bis 58,7% fast identische Werte. Das sind Werte, die für eine sehr gute Reflexion sprechen. Auch die Reflektionswerte bei 600 nm liegen mit 56,7 % (B1 und V1), 50,0 % (B2 und V2) und 57,5 % (B3 und V3) in diesem Bereich.

[0077] Eine noch höhere Reflexion von sowohl sichtbarem Licht als auch von UV-Strahlung wurde bei den Folien aus den Beispielen B4 bis B5 und den Vergleichsbeispielen V4 bis V5 zum anderen dadurch erreicht, dass die Folie auf wenigstens einer Seite metallisiert wurde, zum Beispiel durch Bedampfung mit Aluminium. Die Arten der Metallisierung sind dem Fachmann bekannt. Mit einer Metallisierung wird demnach mit Abstand das höchste Reflexionsvermögen der Folie realisiert, das bei der hier verwendeten Aluminium-Bedampfung der Folie nahezu unabhängig von der Wellenlänge des UV- und sichtbaren Lichts ist. So werden bei B4, B5, V4 und V5 bei allen gemessenen Wellenlängen 200 nm, 350 nm, 400 nm, 450 nm und 600 nm Reflexionswerte von weit über 90% erzielt. Aufgrund des Spiegel-Effekts wird die UV- und Lichtstrahlung nahezu vollständig reflektiert.

[0078] Die transparente Folie aus dem Vergleichsbeispiel V6, die weder ein Metallpigment enthält noch metallisiert ist, hat demgegenüber nur ein geringes Reflexionsvermögen, wie die Werte im Bereich 1,7 bis 4,0% bei den Wellenlängen 200, 350, 400, 450 und 600 nm zeigen.

[0079] Überraschenderweise wurde bei der Folie aus Vergleichsbeispiel V7 eine deutlich geringere Reflexion ermittelt, als in dem Patent WO2013/026568 beschrieben. Der Einsatz einer weißen Schicht, bei einer darunter liegenden schwarzen Schicht, führte lediglich zu Reflexionswerten zwischen 7,2% (200 nm) und 15,6% (600 nm).

[0080] Dies zeigt, dass ein hohes Reflexionsvermögen einer Folie bevorzugt und idealerweise durch den Einsatz von silbrigfarbenen Metallpigmenten oder durch Metallisierung erhalten wird.

[0081] Trotzdem hat sich gezeigt, dass die UV- und Lichtschutzwirkung von Folien, die entweder silbrigfarbene Metallpigmente enthalten oder metallisiert sind und daher eine hohe Reflexion aufweisen, für deren Einsatz etwa als Außenfolien für Schlauchliner oftmals immer noch nicht optimal ist. Dies belegen die Vergleichsbeispiele V1 bis V6 mit Blick auf die Werte für die Transmission bei den Wellenlängen 350 nm, 400 nm und 450 nm. Die geringsten Transmissionswerte werden mit 0,08 bis 0,09% bei der beidseitig metallisierten Folie aus Vergleichsbeispiel V5 gefunden. Schon die einseitig metallisierte Folie aus Vergleichsbeispiel V4 hat mit Werten von 0,11 bis 0,12% bereits deutlich höhere Werte bei der Transmission.

[0082] Noch höher liegen die Transmissionswerte bei den Folien, die mit Hilfe von silbrigfarbenen Farbbatches eingefärbt wurden. Trotz hoher Konzentration an Silber-Farbbatch in beiden Außenschichten der Folien zeigen die Folien aus den Vergleichsbeispielen V1, V2 und V3 Transmissionswerte im Bereich 0,31% (V2 bei 350 nm) bis 1,10% (V3 bei 450 nm).

[0083] Zusätzlich gilt, dass je gröber die in die Folie eingebrachten Metallpigmente sind, umso höher deren Transmission ist. Dadurch besteht bei längerer Einwirkung von Licht – insbesondere von UV-Licht im Bereich 350 bis 380 nm – immer die Gefahr, dass bei einem Schlauchliner das unter der UV- und Lichtschutzaußenfolie befindliche reaktive Harz durch Aktivierung des Photoinitiators vorzeitig photochemisch ausgehärtet werden kann, womit der Schlauchliner unbrauchbar wird.

[0084] Somit zeichnen sich bisher im Stand der Technik verwendete Außenfolien, die entweder Metallpigmente enthalten oder metallisiert sind, zwar durch sehr hohe Werte für die Licht-Reflexion aus. Sie weisen aber immer noch zu hohe Transmissionswerte auf, d.h. der Anteil der durch die Folie dringenden UV- und Lichtstrahlung ist für viele Anwendungsfälle immer noch zu hoch.

[0085] Wie den Beispielen B1 bis B5 entnommen werden kann, wird die Transmission erheblich verringert, wenn der Folie noch in wenigstens einer Schicht, bevorzugt aber in zwei oder mehr Schichten, ein UV-Absorber zugegeben wird. So wird die Transmission von UV-Strahlung (350 nm) um einen Faktor von 50 verringert, wie

der Vergleich von Beispiel B3 mit Vergleichsbeispiel V3 zeigt. Hier konnte die Transmission durch Zugabe von UV-Absorber von 1,00% auf 0,02% gesenkt werden.

[0086] Gleiches gilt für die Verringerung der Transmission von sichtbarem Licht bei Wellenlängen von 400 nm und 450 nm. Hier ergab sich eine Verringerung der Transmission um einen Faktor von über 40, wenn die Folien mit UV-Absorber versetzt waren. Selbst bei den metallisierten Folien aus den Vergleichsbeispielen V4 und V5, die bereits ohnehin schon geringe Transmissionswerte haben, kann deren Transmission im UV- und Lichtbereich nochmals um mehr als einen Faktor 10 verringert werden, was die Beispiele B4 und B5 belegen.

[0087] Vergleichsbeispiel V6 zeigt, dass eine transparente Folie ohne UV-Absorber UV- und sichtbares Licht nahezu ungehindert durchlassen. Die Transmissionswerte liegen weit über 80%.

[0088] Die im Stand der Technik beschriebene Vergleichsfolie V7 ist in Bezug auf UV- und Lichttransmission ebenfalls noch ungenügend. Im Wellenlängenbereich von 350 nm bis 450 nm lag die Transmission zwischen 0,63 und 0,72%. Hier lagen die Werte für die Transmission in der Größenordnung einer silbrigen Folie mit Metallpigmenten ohne UV-Absorber (V1 bis V3).

[0089] Die Erfindung ist nicht auf die beschriebenen Ausführungsbeispiele beschränkt. Abwandlungen innerhalb der Ansprüche und Kombinationen von Merkmalen der einzelnen Ansprüche sind ohne weiteres möglich.

ZITATE ENTHALTEN IN DER BESCHREIBUNG

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Zitierte Patentliteratur

- WO 2013026568 A1 [0004]
- DE 29700236 U1 [0005]
- WO 2013/026568 A1 [0052]
- WO 2013026568 [0069]
- WO 2013/026568 [0079]

Patentansprüche

1. Folie, vorzugsweise mehrschichtig, **dadurch gekennzeichnet**, dass einerseits in ein oder mehreren Schichten der Folie silbrigfarbene Pigmente eingebracht sind und/oder eine Metallisierung auf mindestens einer Außenschicht der Folie aufgebracht ist, und dass andererseits in mindestens einer oder mehreren Schichten der Folie mindestens ein UV-Absorber eingebracht ist, so dass in Abstimmung mit der bzw. den Schichtdicken und der Gesamtdicke der Folie die gesamte Folie für UV- und sichtbares Licht in einem Wellenlängenbereich von 200 bis 800 nm zu weniger als 0,1% durchlässig ist und für einen Betrachter als opak, undurchsichtig und blickdicht wahrgenommen wird, und die UV- und sichtbare Strahlung in einem Wellenlängenbereich von 200 bis 800 nm zu mehr als 20% reflektiert wird.
2. Folie nach Anspruch 1, **dadurch gekennzeichnet**, dass die Folie eine schlauchförmige mehrschichtige Außenfolie für einen Einlegeschlauch eines Rohrsanierungssystems ist, bei welchem die Außenfolie ein schlauchförmiges Trägersystem mit aushärtbarem Harz umgibt und das Trägersystem eine schlauchförmige Innenfolie umgibt, mit mindestens einer zum sanierenden Kanal weisenden Außenschicht, und einer zum Schlauchinneren gerichteten Außenschicht.
3. Folie nach Anspruch 1 oder 2, **dadurch gekennzeichnet**, dass durch den Zusatz von silbrigfarbenen Pigmenten und/oder durch besagte Metallisierung einerseits und durch den mindestens einen UV-Absorber andererseits die gesamte Folie für UV- und sichtbares Licht zumindest in einem Wellenlängenbereich von 200 bis 800 nm zu weniger als 0,075%, vorzugsweise zu weniger als 0,05%, besonders bevorzugt zu weniger als 0,025% durchlässig ist.
4. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass durch den Zusatz von silbrigfarbenen Pigmenten und/oder durch besagte Metallisierung sichtbare Strahlung zumindest in einem Wellenlängenbereich von 200 bis 800 nm zu mehr als 20%, vorzugsweise mehr als 30%, am meisten bevorzugt zu mehr als 40%, reflektiert wird.
5. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass die mindestens eine silbrigfarbene Pigmente enthaltende Schicht bzw. die metallisierte Schicht eine Außenschicht der Folie ist.
6. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass in mindestens zwei Schichten silbrigfarbene Pigmente eingebracht sind bzw. dass beide Außenschichten metallisiert sind.
7. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass die silbrigfarbenen Pigmente ausgewählt sind aus der Gruppe umfassend:
 - Metallische Pigmente, vorzugsweise vom Leafing-Typ;
 - Metalleffektpigmente, basierend auf z.B. Aluminium, Silber, Nickel, Chrom, Quecksilber, Amalgam, oder Legierungen besagter Metalle;
 - Perlglanzpigmente;
 - Metallisierte Träger, z.B. metallisierte Perlglanzpigmente (Glimmerpigmente), beispielsweise durch Aluminium Bedampfung.
8. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass die mittleren Pigmentgrößen der silbrigfarbenen Pigmente im Bereich von 0,1 µm bis 100 µm liegen, vorzugsweise im Bereich von 1 µm bis 75 µm, besonders bevorzugt im Bereich von 5 µm bis 50 µm.
9. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass die Pigmente in der silbrigfarbenen Schicht in einer Konzentration von 0,1 bis 50 Gew.-%, bevorzugt von 1 bis 30 Gew.-%, enthalten sind.
10. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass im Falle der Ausbildung der Folie als Schlauchaußenfolie in der zum Kanal weisenden Außenschicht der Schlauchaußenfolie neben den silbrigfarbenen Farbstoffen oder Farbpigmenten auch andersfarbige Farbstoffe und Farbpigmente eingebracht sind.
11. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass die mindestens eine Schicht, in welcher silbrigfarbene Pigmente eingebracht sind oder eine Metallisierung

aufgebracht ist, mindestens ein thermoplastisches Olefin-Homo- oder Copolymer, gegebenenfalls modifiziert, enthält.

12. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass durch die Zugabe des mindestens einen UV-Absorbers in mindestens einer Schicht die Strahlung in der gesamten Folie in einem Wellenlängenbereich von 200 bis 450 nm, insbesondere von 250 bis 400 nm, zu mehr als 95%, vorzugsweise zu mehr als 98%, besonders bevorzugt zu mehr als 99,5% absorbiert wird.

13. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass der besagte mindestens eine UV-Absorber ausgewählt ist aus der Gruppe, die folgende Verbindungen umfasst:

- Anorganische Verbindungen, wie z.B. Metalloxide, einschließlich Übergangsmetalloxide, wie z.B. Titanoxid, Eisenoxid und Zinkoxid, sowie Metalloxydhydrate, einschließlich Übergangsmetalloxydhydrate;
- Organische Verbindungen, wie z.B. Benzotriazole, Triazine, Benzophenone und Cyanoacrylate;
- Derivate der vorgenannten Verbindungen;
- Mischungen aus den vorgenannten Verbindungen.

14. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass der mindestens eine UV-Absorber in der besagten Schicht in einer Konzentration von 0,01 bis 20 Gew.-%, bevorzugt von 0,1 bis 10 Gew.-%, am meisten bevorzugt von 0,5 bis 5 Gew.-%, enthalten ist.

15. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass die mindestens eine Schicht, welche mindestens einen UV-Absorber enthält, eine Dicke von weniger als 100 µm aufweist, vorzugsweise weniger als 50 µm, besonders bevorzugt zwischen 5 µm und 30 µm.

16. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass der mindestens eine UV-Absorber in eine Haftvermittlerschicht der Folie eingebracht ist.

17. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass der mindestens eine UV-Absorber in eine Schicht der Folie eingebracht ist, die innenseitig an eine der Außenschichten der Folie angrenzt.

18. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass der mindestens eine UV-Absorber in zwei Schichten eingebracht sind, vorzugsweise jeweils in innenseitig an jeweils eine der Außenschichten der Folie angrenzende Schichten.

19. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass die mindestens eine Schicht, in welcher der mindestens eine UV-Absorber eingebracht ist, mindestens ein thermoplastisches Olefin-Homo- oder Copolymer, gegebenenfalls modifiziert, enthält.

20. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass eine und vorzugsweise beide ihrer Außenschichten mindestens ein thermoplastisches Olefin-Homo- oder Copolymer, gegebenenfalls modifiziert, enthalten.

21. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass eine oder beide ihrer Außenschichten mindestens ein Polyamid, gegebenenfalls modifiziert, enthalten.

22. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass eine oder beide ihrer Außenschichten mindestens ein Thermoplastisches Elastomer (TPE), insbesondere TPU, gegebenenfalls modifiziert, enthalten.

23. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass mindestens eine innenliegende Barrierschicht gegen den Durchtritt von Gasen und/oder chemischen Substanzen vorgesehen ist, wobei die Barrierschicht vorzugsweise Ethylenvinylalkohol (EVOH) oder Polyamid (PA) oder Cyclo-Olefin-Copolymer (COC) oder eine Kombination von diesen enthält, bevorzugt jeweils mit bis zu 100 Gew.-% aus diesen Verbindungen.

24. Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass die Gesamtdicke der Folie zwischen 10 µm und 1000 µm, vorzugsweise zwischen 20 µm und 500 µm, besonders bevorzugt zwischen 30 µm und 400 µm, beträgt.

25. Verbund mit einer Folie nach einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, dass die besagte Folie mit mindestens einer weiteren Folie oder einem Woven- oder Nonwoven-Material und insbesondere mit einem für Harz und Flüssigkeiten saugfähigen Material kaschiert ist.

26. Einlegeschlauch für die Rohrsanierung, insbesondere die grabenlose Kanalsanierung, umfassend eine Folie als schlauchförmige Außenfolie nach einem oder mehreren der vorhergehenden Ansprüche, sowie eine schlauchförmige, für UV-Strahlung durchlässigen Innenfolie, sowie einem zwischen diesen beiden Folien angeordneten Trägermaterial, das mit einem reaktiven Kunststoffharz getränkt ist.

27. Verwendung eines Einlegeschlauchs nach dem vorhergehenden Anspruch zur Sanierung eines Rohres, vorzugsweise einem unterirdisch verlegten Rohr, insbesondere einem Kanalrohr.

28. Verwendung einer Folie bzw. eines Verbundes nach einem der Ansprüche 1 bis 25, als schützendes Verpackungsmaterial für Lebensmittel oder für den sog. Non-Food-Bereich, als Außenverkleidung, als außenliegende Abdeckung von Gebäudeteilen, als Bag-in-Box-Folie, als Membranfolie, als Folie für Sicherheitsgläser, Solarmodule oder Airbags, als Klebefolie, Tape oder Band, für die Kabelummantelung, in Schutzanzügen, bei Textilien und Bekleidungen, als Dekorfolie bei Laminaten für Holz-, Naturfaser- und Kunststoffverbundwerkstoffe, als Schutzfolie im Prepreg-Bereich (preimpregnated fibers, vorimprägnierte Fasern), als Schutzfolie, für Schilder sowie Anzeigetafeln, für medizinische Anwendungen wie Pflaster, für Hygieneartikel wie Windeln, für Displays oder als Isoliermaterial.

Es folgen keine Zeichnungen



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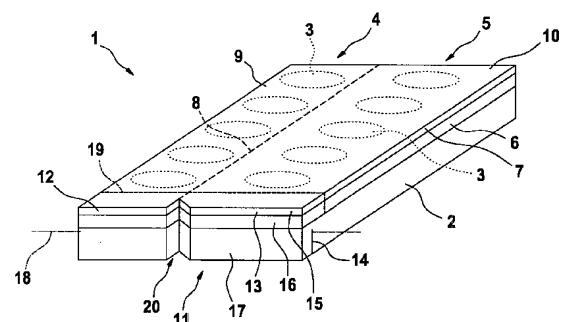
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(54) Bezeichnung: **Peel-Push-Blisterverpackung**

(57) Hauptanspruch: Blisterverpackung mit einer Kavitäten (3) aufweisenden Bodenfolie (2), und mit einer die Kavitäten (3) überdeckenden, durchdrückbaren Deckschicht (6), wobei die Blisterverpackung (1) entweder entlang einer einzigen Trennlinie (8) oder entlang mehrerer sich nicht-kreuzender Trennlinien (8) in einen ersten, mindestens eine der Kavitäten (3) aufweisenden Verpackungsabschnitt (9) und in mindestens einen zweiten, mindestens eine der Kavitäten (3) aufweisenden Verpackungsabschnitt (10) aufteilbar ist, dadurch gekennzeichnet, dass oberhalb der Deckschicht (6) eine abziehbare Peel-Schicht (7) angeordnet ist, und dass zum erleichterten Abziehen der Peel-Schicht (7) entlang des ersten Verpackungsabschnitts (9) mindestens ein erster, randseitiger Greifabschnitt (12) und zum erleichterten Abziehen der Peel-Schicht (7) entlang des zweiten Verpackungsabschnitts (10) mindestens ein zweiter, randseitiger Greifabschnitt (13) vorgesehen ist.



Beschreibung

[0001] Die Erfindung betrifft eine Blisterverpackung mit einer mehrere (mindestens zwei) Kavitäten aufweisenden Bodenfolie, und mit einer die Kavitäten überdeckenden, durchdrückbaren Deckschicht, wobei die Blisterverpackung entweder entlang einer einzigen Trennlinie oder entlang mehrerer sich nicht-kreuzender Trennlinien in einen ersten, mindestens eine der Kavitäten aufweisenden Verpackungsabschnitt und in mindestens einen zweiten, mindestens eine der Kavitäten aufweisenden Verpackungsabschnitt aufteilbar (auftrennbar) ist.

[0002] Ferner betrifft die Erfindung eine Blisterverpackung mit einer, mehrere (mindestens zwei) Kavitäten aufweisenden, Bodenfolie, wobei die Blisterverpackung entlang von sich kreuzenden Trennlinien in, jeweils mindestens eine der Kavitäten aufweisende, Verpackungsabschnitte aufteilbar (auftrennbar) ist, und mit einer die Kavitäten überdeckenden, durchdrückbaren Deckschicht, sowie mit einer oberhalb der Deckschicht angeordneten, abziehbaren Peel-Schicht, wobei jedem Verpackungsabschnitt jeweils mindestens ein Greifabschnitt zum Abziehen der Peel-Schicht entlang des jeweiligen Verpackungsabschnittes zugeordnet ist.

[0003] Als kindersichere Blisterverpackungen zur Verpackung von Medikamenten sind sogenannte, in Fig. 5 gezeigte Peel-Push-Blisterverpackungen **100** bekannt geworden. Derartige Peel-Push-Blisterverpackungen machen sich die Erkenntnis zu nutze, dass Kleinkinder einen aus mehreren separaten Teilschritten bestehenden Öffnungsvorgang nicht einfach durchschauen und Ausführen können. Die in Fig. 5 gezeigte, bekannte Peel-Push-Blisterverpackung weist mehrere, sich kreuzende, als Perforationen ausgebildete Trennlinien **101** auf, entlang derer die Peel-Push-Blisterverpackung **100** in, in dem gezeigten Ausführungsbeispiel acht, Verpackungsabschnitte mit jeweils einer Kavität **102** aufgeteilt werden kann. Die Kavitäten **102** sind in einer, in der gezeigten Draufsicht gemäß Fig. 5 nicht zu erkennen, unteren Bodenfolie (Bodenteil) in an sich bekannter Weise eingebracht, wobei die Kavitäten in ihrem Öffnungsbereich von einer durchdrückbaren Deckschicht überdeckt sind. Oberhalb der Deckschicht wiederum befindet sich eine sogenannte, von der Deckschicht abziehbare Peel-Schicht **103**, die selbst nicht durchdrückbar ist. Dies führt dazu, dass zunächst die Peel-Schicht **103** von der darunter befindlichen Deckschicht entfernt werden muss, bevor ein Medikament aus einer Kavität **102** durch die in Fig. 5 von der Peel-Schicht **103** verdeckte Deckschicht zum Entnehmen des Medikaments durchgedrückt werden kann. Um ein Abziehen der Peel-Schicht **103** zu erleichtern, ist jedem Verpackungsabschnitt **104** ein Greifabschnitt **105** der Peel-Schicht **103** zugeordnet. Die Greifabschnitte

105 werden gebildet von nicht versiegelten Bereichen **106**, in denen die Deckschicht nicht mit der Bodenfolie versiegelt ist. Dabei befinden sich die nicht versiegelten Bereiche **106** jeweils in zentrischen Bereichen der Peel-Push-Blisterverpackung **100**, in denen jeweils vier Verpackungsabschnitte **104** aneinander angrenzen. Um nun eine Peel-Schicht **103** von der Deckschicht entfernen zu können, muss der zugehörige Greifabschnitt durch Aufbrechen der Peel-Push-Blisterverpackung **100** entlang von Trennlinien **101** frei gelegt werden. Daraufhin kann der entsprechende Greifabschnitt **105** zwischen zwei Fingern gegriffen und in Richtung des gegenüberliegenden Ecks des betreffenden Verpackungsabschnitts **104** abgezogen werden, woraufhin das entsprechende Medikament durch die freigelegte Deckschicht gedrückt werden kann. Nachteilig bei der bekannten Peel-Push-Blisterverpackung ist, dass diese ein ganz spezielles Blisterformat erfordert. Insbesondere werden Peel-Push-Blisterverpackungen **100** mit sich kreuzenden Trennlinien **101** benötigt, um die zentrisch angeordneten Greifabschnitte **105** nach einem entsprechenden Aufteilen der Peel-Push-Blisterverpackung **100** in Verpackungsabschnitte komfortabel greifen zu können. Das Vorsehen von sich kreuzenden Trennlinien **101** bedingt jedoch sowohl in Längs- als auch in Querrichtung jeweils zwischen benachbarten Kavitäten einen Mindestabstand einzuhalten, um eine Diffusion von Feuchtigkeit aus einem Bereich der Trennlinie in Richtung in die Kavität hinein sicher zu verhindern.

[0004] Ferner sind reine Push-Blisterverpackungen bekannt, bei denen auf eine Peel-Schicht verzichtet wird. Diese Push-Blisterverpackungen weisen ausschließlich in Längsrichtung oder in Querrichtung der Blisterverpackung verlaufende Trennlinien auf, so dass ausschließlich streifenförmige Verpackungsabschnitte erhalten werden können. Die jeweils in einer Reihe nebeneinander angeordneten Kavitäten können mangels dazwischen liegender Trennlinie mit einem geringen Abstand zueinander angeordnet werden, wodurch der Flächenverbrauch der Blisterverpackung minimiert wird. Lediglich quer zur Längserstreckung der Verpackungsabschnitte muss ein ausreichender Abstand zwischen zwei nebeneinander angeordneten Kavitäten vorgesehen werden. Nachteilig bei den bekannten Push-Blisterverpackungen ist jedoch die mangelnde Kindersicherheit.

[0005] Der Erfindung liegt zum einen die Aufgabe zugrunde, Blisterverpackungen ohne sich kreuzende Trennlinien kindersicher zu gestalten. Dabei soll die kindersichere Blisterverpackung vorzugsweise auf den bisher eingesetzten Produktionsmaschinen herstellbar sein, ohne dass erhebliche Anpassungen der Produktionsmaschine notwendig sind. Ferner besteht die Aufgabe darin, besonders kindersichere Blisterverpackungen mit sich kreuzenden Trennlinien vorzuschlagen.

[0006] Diese Aufgabe wird hinsichtlich einer Blisterverpackung, die keine sich kreuzenden, sondern entweder eine einzige, zum Aufteilen der Blisterverpackungen in jeweils mindestens eine Kavität aufweisende Verpackungsabschnitte ausgebildete, und angeordnete Trennlinie oder mehrere sich nicht-kreuzende, zum Aufteilen der Blisterverpackung in mehrere jeweils mindestens eine Kavität aufweisende Verpackungsabschnitte ausgebildete, und angeordnete Trennlinien aufweist, dadurch gelöst, dass oberhalb, d. h. auf der von der Bodenfolie abgewandten Seite der Deckschicht, eine abziehbare, vorzugsweise nicht-durchdrückbare, ein- oder mehrschichtige Peel-Schicht angeordnet ist, die vor dem Durchdrücken der Deckschicht mittels einer in einer Kavität befindlichen Ware, insbesondere eines Medikaments, zu entfernen ist. Dabei kann die Peel-Schicht unmittelbar auf der Deckschicht angeordnet werden oder es kann zwischen der Deckschicht und der Peel-Schicht mindestens eine weitere Schicht vorgesehen werden. Um ein erleichtertes Abziehen der Peel-Schicht zu ermöglichen, ist bei einer nach dem Konzept der Erfindung ausgebildeten Blisterverpackung die Peel-Schicht für jeden, insbesondere streifenförmigen, durch Trennen der Blisterverpackung entlang der mindestens einen Trennlinie (z. B. Perforation oder Knicklinie) zu erhaltenden und mindestens eine der Kavitäten aufweisenden, Verpackungsabschnitt, jeweils mindestens ein, einen Peel-Schichtabschnitt umfassender, Greifabschnitt vorgesehen, wobei die den Verpackungsabschnitten zugeordneten Greifabschnitte nicht wie im Stand der Technik in einem Bereich innerhalb der Blisterverpackung, sondern randseitig an der Blisterverpackung, vorzugsweise jeweils an einer Schmalseite eines Verpackungsabschnitts angeordnet sind. Eine nach dem Konzept der Erfindung ausgebildete Blister-Verpackung vereint auf geschickte Weise die Vorteile einer Blisterverpackung mit sich nicht-kreuzenden Trennlinien, bei der in einer Richtung beabstandete Kavitäten in einem geringen Abstand zueinander angeordnet werden können als in einer zweiten Richtung, und einer kindersicheren Peel-Push-Blisterverpackung. Besonders bevorzugt ist eine Ausführungsform der Blisterverpackung, bei der die mindestens eine Trennlinie von einer die Blisterverpackung, bevorzugt vollständig, durchdringenden, insbesondere gestanzten, Perforationslinie gebildet ist. Dabei ist es wesentlich, dass die mindestens eine, alternativ auch als Schnitt-Linie ausgebildete, Trennlinie nicht von weiteren Trennlinien gekreuzt wird, sondern dass allenfalls mehrere, vorzugsweise parallel zueinander angeordnete, Trennlinien vorgesehen sind. Die Blisterverpackung ohne sich kreuzende Trennlinien, d. h. die kreuzlinienfreie Blisterverpackung, kann auf verschiedene Weisen geöffnet werden. So ist es möglich, die Deckschicht oberhalb nur einer der Verpackungsabschnitte abzuziehen, ohne dass es notwendig wäre, die Blisterverpackung entlang der Trennlinie in mindestens zwei, insbesondere streifenförmige,

Verpackungsabschnitte zu unterteilen, da der dem entsprechenden Verpackungsabschnitt zugeordnete Greifabschnitt randseitig an der Blisterverpackung angeordnet ist. Alternativ ist es jedoch auch möglich, die Blisterverpackung zunächst entlang der mindestens einen, vorzugsweise ausschließlich einen, Trennlinie in mindestens zwei Verpackungsabschnitte zu unterteilen und erst dann die Peel-Schicht eines gebildeten, separaten Verpackungsabschnittes durch Greifen und Abziehen des zugehörigen Greifabschnittes zu entfernen. Bevorzugt sind in der vorgeschlagenen Blisterverpackung Medikamente, vorzugsweise Feststoffmedikamente und/oder Medikamente mit einer Feststoffhülle, die beispielsweise mit Flüssigkeit gefüllt ist, verpackt.

[0007] Vorteilhafte Weiterbildungen der Erfindung sind in den Unteransprüchen angegeben. In den Rahmen der Erfindung fallen sämtliche Kombinationen aus zumindest zwei von in der Beschreibung, den Ansprüchen und/oder den Figuren offenbarten Merkmalen.

[0008] Von besonderem Vorteil ist eine Ausführungsform der Blisterverpackung, bei der die Kavitäten in Reihen angeordnet sind, wobei sich die mindestens eine Trennlinie entlang der Reihen erstreckt. Dabei kann die Richtung, in der sich die Reihen und damit die mindestens eine Trennlinie erstreckt mit der Längserstreckung der Blisterverpackung übereinstimmen oder die Richtung kann winklig, insbesondere rechtwinklig zur Längserstreckung der Blisterverpackung verlaufen. Wesentlich ist lediglich, dass sich kreuzende Trennlinien zur Bildung von Verpackungsabschnitten vermieden werden, wodurch der Flächenbedarf der Blisterverpackung insgesamt minimiert werden kann, ohne dabei Abstriche bei der Dichtheit der Kavitäten machen zu müssen. Bevorzugt ist eine Ausführungsform, bei der die Trennlinien, im Falle des Vorsehens mehrerer Trennlinien parallel zueinander verlaufen.

[0009] In Weiterbildung der Erfindung ist mit Vorteil vorgesehen, dass zwischen jeweils zwei benachbarten Reihen von Kavitäten eine Trennlinie angeordnet ist. Im Falle des Vorsehens von ausschließlich zwei nebeneinander angeordneten Reihen reicht dabei das Vorsehen einer einzigen Trennlinie auf der Blisterverpackung aus. Im Falle des Vorsehens mehrerer, sich beispielsweise in Längsrichtung der Blisterverpackung oder quer dazu erstreckenden Reihen, ist das Vorsehen von mehreren, sich nicht-kreuzenden, vorzugsweise parallelen, Trennlinien von Vorteil, wobei sich bevorzugt zwischen jeweils zwei benachbarten Reihen mindestens eine, vorzugsweise ausschließlich eine Trennlinie befindet, wodurch die Blisterverpackung entlang der Trennlinien in insbesondere streifenförmige Verpackungsabschnitte unterteilbar ist. Es ist auch eine Ausführungsform möglich, bei der nicht zwischen sämtlichen Reihen von Kavitäten

ten eine Trennlinie angeordnet ist. So ist beispielsweise eine Ausführungsform realisierbar, bei der die Blisterverpackung entlang nur einer einzigen Trennlinie in zwei Verpackungsabschnitte unterteilbar ist, wobei beispielsweise einer der Verpackungsabschnitte mehrere Reihen von Kavitäten umfasst.

[0010] Von besonderem Vorteil ist eine Ausführungsform der kreuztrennlinien-freien Blisterverpackung, bei der die Greifabschnitte durch das Vorsehen mindestens einer Knicklinie in der Bodenfolie gebildet sind. Anders ausgedrückt wird eine Schwächungslinie in die Bodenfolie, vorzugsweise durch Stanzen, eingebracht, die bevorzugt die Bodenfolie nicht vollständig entlang ihrer Dickenerstreckung durchsetzt, sodass das Abziehen der Peel-Schicht zunächst ein manuelles Abbrechen des Greifabschnittes von der Bodenfolie notwendig macht. Die Knicklinie (Schwächungslinie) stellt dabei die Grenze des Greifabschnittes zur restlichen Blisterverpackung dar. Bevorzugt umfassen die Greifabschnitte bei der beschriebenen Ausführungsform zusätzlich zu einem Peel-Schichtabschnitt, einen Bodenfolienabschnitt und einen zwischen Bodenfolie und Peel-Schicht angeordneten Abschnitt der Deckschicht. Die Bildung der Greifabschnitte durch das Vorsehen mindestens einer, vorzugsweise ausschließlich einer, Knicklinie ist in soweit von erheblichem Vorteil, als dass eine derart ausgebildete Blisterverpackung in bekannten Blisterverpackungsproduktionsmaschinen hergestellt werden kann, ohne dass erhebliche Änderungen an der Maschine vorgenommen werden müssen. Anders ausgedrückt ermöglicht es insbesondere eine derartige Bauform, auf einfache Weise eine bestehende Produktionsmaschine (Herstellungsmaschine) zum Herstellen der Blisterverpackung mit randseitigem Greifabschnitt nachzurüsten. Hierzu ist es lediglich notwendig, das Stanzwerkzeug zu ändern, sodass beim Stanzprozess, bei dem bevorzugt die mindestens eine Trennlinie eingebracht wird gleichzeitig auch die Knicklinie gestanzt wird.

[0011] Besonders bevorzugt ist eine Ausführungsform der Blisterverpackung, bei der sich die mindestens eine Knicklinie quer zur Längserstreckung der Verpackungsabschnitte erstreckt. Anders ausgedrückt ist eine Ausführungsform bevorzugt, bei der die Greifabschnitte an einem Schmalseitenrand der Blisterverpackung angeordnet sind, um zu ermöglichen, die Peel-Schicht in Richtung der Längserstreckung des zugehörigen Verpackungsabschnittes abzuziehen.

[0012] Alternativ zu durch das Vorsehen von mindestens einer Knicklinie gebildeten Greifabschnitten ist eine Ausführungsform realisierbar, bei der die beispielsweise als Polyethylenterephthalat(PET)-Peel-Folie ausgebildete Peel-Schicht nicht zusammen mit einem Bodenfolienabschnitt gegriffen werden muss – auf einen separaten Abknickprozess

beim Öffnungsvorgang wird dabei verzichtet.

[0013] Um beim Abziehen der Peel-Schicht sicher zu verhindern, dass die darunter befindliche Deckschicht bis in einen Bereich oberhalb einer Kavität mit abgezogen wird, beispielsweise weil die Haftung der Peel-Schicht an der Deckschicht besser ist als die Haftung der Deckschicht an der Bodenfolie, ist eine Ausführungsform bevorzugt, bei der benachbart zu mindestens einem der Greifabschnitte, vorzugsweise benachbart zu sämtlichen Greifabschnitten mindestens eine Sollbruchlinie für die Deckschicht vorgesehen ist, an der die Deckschicht beim Abziehen der Peel-Schicht an- und/oder abreißt. Besonders bevorzugt ist es dabei diese Sollbruchlinie als Perforationslinie auszubilden, die zumindest die Deckschicht durchsetzt. Im Falle des Vorsehens mindestens einer zur Ausbildung des Greifabschnittes ausgebildeten Knicklinie, ist eine Ausführungsform bevorzugt, bei der die Sollbruchlinie parallel zu der Knicklinie, mit geringem Abstand zu dieser verläuft.

[0014] Um auch für den anfänglich beschriebenen Fall, dass die Verpackungsabschnitte vor dem Abziehen der Peel-Schicht nicht voneinander entlang der Trennlinie getrennt werden, zu verhindern, dass nicht gleichzeitig unbeabsichtigt die Peel-Schicht von zwei benachbarten Verpackungsabschnitten abgezogen wird, ist in Weiterbildung der Erfindung mit Vorteil vorgesehen, dass zwei nebeneinander angeordnete Greifabschnitte durch eine Ausstanzung voneinander getrennt sind. Durch das Vorsehen mindestens einer zwei benachbarte Greifabschnitte voneinander trennenden Ausstanzung kann gewährleistet werden, dass durch das Greifen und Abziehen eines Greifabschnittes nicht die Peelfolie im benachbarten Verpackungsabschnitt mit abgezogen wird.

[0015] Insbesondere um eine Abzieh-Richtung für den Benutzer vorzugeben bzw. zu kennzeichnen, ist eine Ausführungsform bevorzugt, bei der die Ausstanzung zwischen zwei benachbarten Greifabschnitten V-förmig ausgebildet ist, die Ausstanzung randseitig offen ist und in Richtung des Blisterverpackungsinners spitz zuläuft.

[0016] Von besonderem Vorteil ist eine Ausführungsform, bei der der Abstand zwischen zwei in Längsrichtung der Reihen unmittelbar nebeneinander angeordneten Kavitäten geringer ist als der Abstand zwischen zwei in benachbarten Reihen nebeneinander angeordneten Kavitäten. Diese Raumeinsparung wird möglich, da auf quer zur Längserstreckung der Verpackungsabschnitte verlaufende Trennlinien verzichtet wird.

[0017] Im Hinblick auf die Ausbildung der durchdrückbaren, d. h. aufbrechbaren, Deckschicht gibt es unterschiedliche Möglichkeiten. Bevorzugt ist eine Ausführungsform, bei der die Deckschicht eine Dicke

aus einem Bereich zwischen etwa 6 µm und etwa 40 µm aufweist. Dabei kann die Deckschicht je nach zu verpackender Ware als Monolayer- oder Multilayer-Schicht ausgebildet sein, also als eine aus einer einzigen Schicht gebildete Deckschicht oder als eine aus einer Anzahl von Unterschichten gebildete Schicht. Besonders bevorzugt ist es, wenn die Deckschicht eine Aluminiumschicht und/oder eine Aluminiumlegierungsschicht aufweist oder als solche ausgebildet ist. Dabei kann die Schicht weich oder hart getempert sein. Alternativ zu einer aluminiumhaltigen Schicht ist das Vorsehen mindestens einer aluminiumfreien, durchdrückbaren Deckschicht realisierbar. Hierzu eignet sich beispielsweise eine Purelay®-Schicht.

[0018] Auch im Hinblick auf die Ausbildung der Peel-Schicht gibt es mehrere Möglichkeiten. So ist es möglich, die Peel-Schicht als Monolayer-Schicht oder als Multilayer-Schicht, also bestehend aus mehreren Unterschichten, auszubilden. Dabei kann die Peel-Schicht mindestens eine der im Folgenden genannten Schichten bzw. Unterschichten umfassen bzw. aus einer solchen gebildet sein: orientiertes Polyamid (oPA), oder Polyester (PET), oder orientierter Polyester (oPET) oder orientiertes Polypropylen (oPP), oder auf Kunststoff laminiertes Papier, wobei der Kunststoff vorzugsweise eine Dicke zwischen 12 µm und 70 µm und/oder das Papier vorzugsweise ein Flächengewicht aus einem Bereich zwischen etwa 20 g/m² und etwa 80 g/m² aufweist. Weiterhin ist von Vorteil, wenn die Peel-Schicht auf ihrer Außenseite, vorzugsweise im Digitaldruck, im Flexodruck oder im Rotationsgravurdruck, etc. bedruckbar ist. Insbesondere wird bevorzugt der Greifabschnitt mit relevanter Information bedruckt. Als Druckvorrichtungen kann bevorzugt folgende Ausrüstung eingesetzt werden: HAPA, CSAT, Laser-Drucker, UV-Flexodrucker, Tintenstrahldrucker, Thermotransferdrucker, etc.

[0019] Auch im Hinblick auf die Ausbildung der die Kavitäten bildenden Bodenfolie gibt es unterschiedliche Möglichkeiten. Auch hier ist es möglich, die Bodenfolie entweder als Monolayer (eine einzige Schicht) oder als Multilayer, bestehend aus einer Vielzahl von Unterschichten auszubilden. Ferner ist es möglich, die Bodenfolie aus einem thermoverformbaren Material oder aus einem kaltverformbaren Material auszubilden. Im Hinblick auf thermoverformbares Material ist der Einsatz von folgenden Materialien entweder einzeln oder in Kombination von Vorteil: Polyvinylchlorid (PVC), Polyvinylidencchlorid (PVDC), eine Aclar/PVC-Schichtkombination, einer Aclar/Polyethylen (PE)/PVC-Schichtkombination, Polypropylen (PP), Polyethylenentrephalath (PET), Polyethylen (PE), hochdichtes Polyethylen (HDPE), einer Cyclo-Olefin-Copolymer (COC)/Polypropylen-Schichtkombination, eine COC/Polyvinylchlorid (PVC)-Schichtkombination.

[0020] Im Falle der Ausbildung der Bodenfolie aus kaltverformbarem Material ist eine Ausführungsform bevorzugt, bei der die Bodenfolie Aluminium und/oder eine Aluminiumlegierung umfasst oder aus diesen Materialien besteht.

[0021] Von besonderem Vorteil ist eine Ausführungsform der Blisterverpackung, bei der auf der die Kavitäten bildenden Bodenfolie eine Mehrschicht-Folie (insbesondere Folienlaminat) festgelegt ist, die die Deckschicht und die Peel-Schicht als Schichten umfasst. Bevorzugt umfasst die Mehrschicht-Folie folgenden Schichtaufbau oder besteht aus einem derartigen Schichtaufbau (von der der Bodenfolie zugewandten Seite her betrachtet): Siegelschicht, Deckschicht, lösbare Klebeschicht, Peel-Schicht. Dabei dient die Siegelschicht zum flüssigkeitsdichten Verbinden der durchdrückbaren Deckschicht und den an dieser festgelegten Schichten mit der Bodenfolie. Bevorzugt handelt es sich um eine heißsiegelbare Siegelschicht. Die lösbare Klebeschicht, die bevorzugt zwischen der Deckschicht und der Peel-Schicht vorgesehen ist, ist bevorzugt derart ausgebildet, dass ein leichtes Abziehen der Peel-Schicht von der darunter befindlichen Deckschicht ermöglicht wird.

[0022] Die Erfindung führt auch auf eine Blisterverpackung, die zusätzlich zu mindestens einer in eine erste Richtung verlaufenden Trennlinie mindestens eine zweite quer, zu der ersten Trennlinie verlaufende Trennlinie aufweist, sodass Verpackungsabschnitte sowohl durch Auftrennen in die eine als auch in die andere, vorzugsweise rechtwinklig zu der vorgenannten Richtung verlaufende Richtung erhalten werden können. Erfindungsgemäß ist vorgesehen, dass die Greifabschnitte zum Greifen der Peel-Schicht durch das Vorsehen mindestens einer Knicklinie in der Bodenfolie gebildet sind. Hierdurch ist es möglich, auf einfache Weise in bestehenden Blisterverpackungsherstellungsmaschinen Peel-Push-Blisterverpackungen herzustellen. Besonders bevorzugt ist dabei eine Ausführungsform, bei der zumindest ein Teil der Greifabschnitte, vorzugsweise sämtliche Greifabschnitte randseitig an der Blisterverpackung angeordnet sind. Auf nicht versiegelte Bereiche, wie diese im Stand der Technik zur Bildung der Greifabschnitte notwendig sind, kann dabei mit Vorteil verzichtet werden. Bevorzugt ist/sind in der vorgeschlagenen Blisterverpackung Medikamente, vorzugsweise Feststoffmedikamente und/oder Medikamente mit einer Feststoffhülle, die beispielsweise mit Flüssigkeit gefüllt ist, verpackt.

[0023] In Weiterbildung der Erfindung ist mit Vorteil vorgesehen, dass benachbart zu der mindestens einen Knicklinie eine Sollbruchlinie für die Deckschicht vorgesehen ist, die ein zu weites Abziehen der Deckschicht zusammen mit der Peel-Schicht sicher verhindert, da die Deckschicht an der Sollbruchlinie aufbricht. Bevorzugt ist die Sollbruchlinie dabei als Per-

foration ausgebildet und/oder parallel zur Knicklinie verlaufend angeordnet.

[0024] Um zu verhindern, dass die Peelfolie gleichzeitig unbeabsichtigt von benachbart zueinander angeordneten Verpackungsabschnitten abgezogen wird, ist eine Ausführungsform bevorzugt, bei der zwei benachbarte Greifabschnitte durch eine Ausstanzung voneinander getrennt sind. Bevorzugt ist diese Ausstanzung V-förmig ausgebildet.

[0025] Im Hinblick auf mögliche Ausbildungen der zur Anwendung kommenden Folien und Schichten wird zur Vermeidung von Wiederholungen auf die vorhergehende Beschreibung verwiesen.

[0026] Die Erfindung führt auch auf eine Verwendung von zuvor beschriebenen Blisterverpackungen als Medikamentenverpackung, vorzugsweise für Feststoffmedikamente oder für Medikamente mit einer Feststoffhülle.

[0027] Weitere Vorteile, Merkmale und Einzelheiten der Erfindung ergeben sich aus der nachfolgenden Beschreibung bevorzugter Ausführungsbeispiele sowie anhand der Zeichnungen. Diese zeigen in:

[0028] Fig. 1a eine schematische Darstellung eines Blisterverpackungsaufbaus mit ausschließlich einer in einer einzigen Richtung orientierten Trennlinie zum Aufteilen der Blisterverpackung in zwei Verpackungsabschnitte,

[0029] Fig. 1b einen bevorzugten Schichtaufbau einer zur Herstellung einer Blisterverpackung gemäß Fig. 1a einsetzbaren Mehrschicht-Folie (Deckfolie),

[0030] Fig. 2 die Blisterverpackung gemäß Fig. 1a mit einer teilweise abgezogenen Peel-Schicht an einer der beiden Verpackungsabschnitte,

[0031] Fig. 3 eine Draufsicht auf ein alternatives Ausführungsbeispiel einer Blisterverpackung mit sich kreuzenden Trennlinien,

[0032] Fig. 4 eine Seitenansicht der Blisterverpackung gemäß Fig. 3 und

[0033] Fig. 5 eine Darstellung einer Peel-Push-Blisterverpackung nach dem Stand der Technik mit innenliegenden Greifabschnitten und sich kreuzenden Trennlinien.

[0034] In den Figuren sind gleiche Bauteile und Bauteile mit der gleichen Funktion mit den gleichen Bezugszeichen gekennzeichnet.

[0035] In Fig. 1a ist eine in erster Näherung rechteckige, kindersichere Blisterverpackung 1 in einer Ansicht von schräg oben gezeigt. In der Zeichnungsebene

unten weist die Blisterverpackung 1 eine in diesem Ausführungsbeispiel als 300 µm dicke PVC-Folie ausgebildete Bodenfolie 2 auf. In der Bodenfolie 2 sind nach in der Zeichnungsebene unten ragende, nicht eingezeichnete Kavitäten eingestrichelt. Die Lage der Kavitäten ist durch die mit dem Bezugszeichen 3 gekennzeichneten, strichliert dargestellten Kreise gekennzeichnet. Wie sich aus Fig. 1a weiter ergibt, sind die Kavitäten 3 in Reihen angeordnet, nämlich in einer sich in Längsrichtung der Blisterverpackung 1 erstreckenden, ersten Reihe 4 und in einer parallel zu der ersten Reihe 4 verlaufenden, zweiten Reihe 5. Jede Reihe 4, 5 weist in dem gezeigten Ausführungsbeispiel fünf in Längsrichtung der Blisterverpackung 1 nebeneinander angeordnete Kavitäten 3 auf.

[0036] Auf der offenen in der Zeichnungsebene nach oben weisenden Seite der Kavitäten 3 sind diese von einer als 20 µm dicke Aluminiumfolie ausgebildeten, durchdrückbaren Deckschicht 6 überdeckt. In dem gezeigten Ausführungsbeispiel überdeckt die Deckschicht 6 die Kavitäten 3 und ist mit der Bodenfolie 2 heißversiegelt. Auf die Deckschicht 6 ist eine nicht durchdrückbare, als monoaxial gereckte Kunststoffschicht ausgebildete Peel-Schicht 7 aufgebracht. Die Peel-Schicht 7 muss zunächst von der Deckschicht 6 abgezogen, d. h. abgepeelt werden, um ein Durchdrücken von in den Kavitäten 3 aufgenommenen Medikamenten durch die Deckschicht 6 zu ermöglichen.

[0037] Wie sich weiter aus Fig. 1a ergibt, weist die Blisterverpackung 1 eine einzige, sich in Längsrichtung der Blisterverpackung 1 erstreckende Trennlinie 8 auf. Die Trennlinie 8 ist als Perforationslinie ausgebildet, die zumindest die Peel-Schicht 7, vorzugsweise die gesamte Blisterverpackung 1, in Richtung ihrer Dickenerstreckung durchsetzt. Die Blisterverpackung 1 kann entlang der Trennlinie 8 in zwei separate Verpackungsabschnitte, nämlich einen ersten Verpackungsabschnitt 9 und einen zweiten Verpackungsabschnitt 10 aufgeteilt werden, wobei in dem gezeigten Ausführungsbeispiel jeder Verpackungsabschnitt 9, 10 eine Reihe 4, 5 mit jeweils 5 Kavitäten 3 umfasst. Die Trennlinie 8 befindet sich zumindest näherungsweise mittig zwischen den Reihen 4, 5 von Kavitäten 3. Bei Bedarf kann die Blisterverpackung 1 in der Zeichnungsebene nach rechts und/oder links mit weiteren, nicht gezeigten Reihen von Kavitäten erweitert werden, wobei sich bevorzugt jeweils zwischen zwei Reihen eine Trennlinie befindet und wobei diese Trennlinien bevorzugt parallel zueinander verlaufen und sich in dem gezeigten Ausführungsbeispiel von in der Zeichnungsebene vorne nach in der Zeichnungsebene hinten erstrecken.

[0038] Alternativ ist ein nicht gezeigtes Ausführungsbeispiel realisierbar, bei dem mehrere Trennlinien vorgesehen sind, die sich von in der Zeichnungsebene links nach in der Zeichnungsebene rechts,

also quer zur Längserstreckung der Blisterverpackung 1 erstrecken und eine Aufteilung der Blisterverpackung 1 in fünf separate Verpackungsabschnitte mit je zwei in Reihe angeordneten Kavitäten ermöglichen. Wesentlich ist bei einer derartigen Ausführungsform, dass auf eine die in Querrichtung verlaufenden Trennlinien kreuzende Trennlinie verzichtet wird.

[0039] An dem in der Zeichnungsebene vorderen Rand 11 der Blisterverpackung 1 sind zwei nebeneinander angeordnete, jeweils einen Peel-Schichtabschnitt umfassende Greifabschnitte, nämlich ein erster Greifabschnitt 12 und ein zweiter Greifabschnitt 13, zum komfortablen Greifen der Peel-Schicht 7 vorgesehen. Dabei ist der erste Greifabschnitt 12 dem ersten Verpackungsabschnitt 9 und der zweite Greifabschnitt 13 dem zweiten Verpackungsabschnitt 10 zugeordnet. Mit Hilfe des ersten Greifabschnittes 12 kann die Peel-Schicht 7 (bzw. ein Peel-Schichtbereich) entlang der Längserstreckung des ersten Verpackungsabschnittes 9 und mit Hilfe des zweiten Greifabschnittes 13 kann die Peel-Schicht 7 (bzw. ein Peel-Schichtbereich) entlang der Längserstreckung der zweiten Verpackungsabschnittes 10 abgezogen werden. Jeder Greifabschnitt 12, 13 wird gebildet von einer gemeinsamen Knicklinie 14, die vom Boden her (also von in der Zeichnungsebene unten her) in die Bodenfolie 2 eingestanz ist, wobei die Knicklinie 14 die Bodenfolie 2 in dem gezeigten Ausführungsbeispiel nicht vollständig in Richtung ihrer Dickenerstreckung durchsetzt, sondern kurz vor der Deckschicht 6 endet. Zum Abziehen der Peel-Schicht 7, ausschließlich auf dem gesamten zweiten Verpackungsabschnitt 10, muss der zweite Greifabschnitt 13, umfassend einen zweiten Peel-Schichtabschnitt 15, einen zweiten Deckschichtabschnitt 16 und einen zweiten Bodenfolienabschnitt 17, in der Zeichnungsebene nach oben geknickt werden, um eine gedachte, sich quer zur Längserstreckung der Blisterverpackung erstreckende mit der Knicklinie 14 zusammenfallende Schwenkachse 18 (Knickachse). Um bei dem Öffnungsvorgang zu verhindern, dass die Deckschicht 6 zusammen mit der Peel-Schicht 7 bis zu den Kavitäten 3 abgezogen wird, ist in Richtung der Längserstreckung der Blisterverpackung 1, relativ zu der Knicklinie 14 beabstandet, eine als Perforationslinie ausgebildete Sollbruchlinie 19 realisiert, die sich wie die Knicklinie 14 quer zur Trennlinie 8 erstreckt. Die die Deckschicht 16 durchsetzende Sollbruchlinie 19, die durch Stanzen hergestellt ist, gewährleistet, dass die Deckschicht beim Abreißvorgang im Bereich der Sollbruchlinien 19, vor Erreichen der ersten Kavität 3 abreißt.

[0040] Zum Abziehen der Peel-Schicht 7 entlang eines der Verpackungsabschnitte 9, 10 kann die Blisterverpackung 1 durch Reißen oder Knicken zunächst entlang der Trennlinie 8 in die beiden Verpackungsabschnitte 9, 10 aufgeteilt werden. Es ist auch

möglich die Peelfolie bei nicht aufgeteilter Blisterverpackung 1 definiert nur auf einem der Verpackungsabschnitte 9, 10 abzureißen. Um sicherzugehen, dass beim Abziehen der Peel-Schicht 7 von dem zweiten Verpackungsabschnitt 10 nicht auch die Peel-Schicht 7 von dem ersten Verpackungsabschnitt 9 abgezogen wird, sind die Greifabschnitte 12, 13 durch eine randseitige, V-förmige Ausstanzung 20, die die gesamte Blisterverpackung 1 in Richtung ihrer Dickenerstreckung durchsetzt, voneinander getrennt. Der Querschnitt der V-förmigen Ausstanzung verjüngt sich in eine Richtung von dem Rand 11 weg und symbolisiert so die Abziehrichtung für die Peel-Schicht 7.

[0041] Wie sich aus **Fig. 1a** ergibt, ist der Abstand zwischen zwei in unterschiedlichen Reihen 4, 5 befindlichen, nebeneinander angeordneten Kavitäten 3 größer als der Abstand zwischen jeweils 2 in einer der Reihen 4, 5 unmittelbar nebeneinander angeordneten Kavitäten 3. Dies ist darauf zurückzuführen, dass zwischen in einer Reihe 4, 5 angeordneten Kavitäten keine Trennlinie angeordnet ist.

[0042] In **Fig. 2** ist die Blisterverpackung 1 gemäß **Fig. 1** mit teilweise abgezogener Peel-Schicht 7 dargestellt. In dem gezeigten Ausführungsbeispiel wurde die Peel-Schicht 7 definiert ausschließlich auf dem zweiten Verpackungsabschnitt 10 ein Stück weit in Richtung der Längserstreckung der Reihen 4, 5 abgezogen. Zu erkennen ist, dass die Trennlinie 8 zusammen mit der Ausstanzung 20 ein zusätzliches, ungewolltes Abziehen der Peel-Schicht 7 von dem ersten Verpackungsabschnitt 9 verhindert. Zu erkennen ist weiterhin, dass der zweite Bodenfolienabschnitt 17 durch Abknicken an der Knicklinie 14 um die Schwenkachse 18 vollständig von der restlichen Bodenfolie 2 abgetrennt wurde. Ferner ist zu erkennen, dass sich auch der zweite Deckschichtabschnitt 16 im Bereich der Sollbruchlinie 19 vollständig von der restlichen Deckschicht 6 gelöst hat. Lediglich die Peel-Schicht 7 ist nicht abgetrennt und verbindet den zweiten Greifabschnitt 13 mit der weiteren Peel-Schicht 7 auf dem zweiten Verpackungsabschnitt 10, wobei die Peel-Schicht 7 entlang der Trennlinie 8 von der auf dem ersten Verpackungsabschnitt 9 befindlichen Peel-Schicht 7 abreißt.

[0043] Bevorzugt handelt es sich bei der Deckschicht 6 und der Peel-Schicht 7 um Schichten einer in **Fig. 1b** gezeigten, laminierten Mehrschicht-Folie 21. In dem gezeigten Ausführungsbeispiel ist die Mehrschicht-Folie 21 durch Heißversiegeln flüssigkeits- und gasdicht mit der Bodenfolie 2 verbunden. Wie sich aus **Fig. 1b** ergibt, weist die Mehrschicht-Folie 21 auf der in der Zeichnungsebene unteren, der Bodenfolie 2 zugewandten Seite eine heißsiegelfähige Siegelschicht 22 auf, oberhalb derer sich die durchdrückbare Deckschicht 6 befindet. An die Deckschicht 6 grenzt eine Klebeschicht 23 an, mit

der die darauf angeordnete Peel-Schicht 7 lösbar mit der Deckschicht 6 verklebt ist.

[0044] In den **Fig. 3** und **Fig. 4** ist ein alternatives Ausführungsbeispiel einer Blisterverpackung 50 gezeigt. Die Blisterverpackung 50 weist eine Vielzahl von sich kreuzenden Trennlinien 51 auf, wobei ein Teil der Trennlinien 51 sich in Richtung der Längserstreckung der Blisterverpackung 50 und sich ein anderer Teil der Trennlinien 51 quer zur Längserstreckung der Blisterverpackung 50 erstreckt. Die Blisterverpackung 1 kann durch Auftrennen entlang der sich kreuzenden Trennlinien 51 in in dem gezeigten Ausführungsbeispiel insgesamt zwölf, jeweils eine Kavität 52 umfassende Verpackungsabschnitte 53 aufgeteilt werden.

[0045] Wie sich aus **Fig. 3** ergibt, die eine Ansicht auf die von der nicht gezeigten Bodenfolie abgewandte Seite der Blisterverpackung 50 zeigt, ist jedem Verpackungsabschnitt 53 ein Greifabschnitt 54 zugeordnet, wobei die Greifabschnitte 54, wie die Greifabschnitte 12, 13 bei dem Ausführungsbeispiel gemäß **Fig. 1a** und **Fig. 2** ausgebildet sind. Die Position der entsprechenden Knicklinien ist mit dem Bezugszeichen 55 gekennzeichnet. Die in der Zeichnungsebene oben und unten befindlichen Greifabschnitte 54 befinden sich randseitig an der Blisterverpackung 1, wohingegen sich dazwischen angeordnete Greifabschnitte 54 innerhalb der Blisterverpackung 1 befinden. Diese inneren Greifabschnitte 54 sind über eine in Längsrichtung der Blisterverpackung 1 verlaufende Trennlinie 51 mit unmittelbar benachbarten Verpackungsabschnitten 53 verbunden. Es ist auch eine Ausführungsform einer Blisterverpackung 50 realisierbar, bei der ausschließlich randseitige Greifabschnitte 54 vorgesehen sind. Jeweils zwei nebeneinander angeordnete Greifabschnitte 54 sind über eine dazwischenliegende V-förmige Ausstanzung 56 voneinander getrennt, um ein unbeabsichtigtes Abziehen der Peel-Schicht 57 von benachbarten Verpackungsabschnitten 54 zu vermeiden.

[0046] In **Fig. 4** ist eine Seitenansicht der Blisterverpackung 50 gemäß **Fig. 3** gezeigt. Zu erkennen ist grob der Schichtaufbau der Blisterverpackung, wobei ein möglicher exakter Aufbau einer oberhalb einer Bodenfolie 58 angeordneten Mehrschicht-Folie 21 aus **Fig. 1b** ersichtlich ist. Zu erkennen ist die unten angeordnete Bodenfolie 58 mit den nach unten weisenden und nach oben öffnenbaren Kavitäten 53. Darüber befindet sich eine durchdrückbare Deckschicht 59, auf der sich wiederum die Peel-Schicht 57 befindet, wobei die Peel-Schicht 57 mit einer nicht gezeigten Klebeschicht auf der Deckschicht 59 aufgebracht ist und die Deckschicht 59 mit Hilfe einer nicht gezeigten heißsiegelfähigen Siegelschicht an der Bodenfolie 58 festgelegt ist.

Schutzansprüche

1. Blisterverpackung mit einer Kavitäten (3) aufweisenden Bodenfolie (2), und mit einer die Kavitäten (3) überdeckenden, durchdrückbaren Deckschicht (6), wobei die Blisterverpackung (1) entweder entlang einer einzigen Trennlinie (8) oder entlang mehrerer sich nicht-kreuzender Trennlinien (8) in einen ersten, mindestens eine der Kavitäten (3) aufweisenden Verpackungsabschnitt (9) und in mindestens einen zweiten, mindestens eine der Kavitäten (3) aufweisenden Verpackungsabschnitt (10) aufteilbar ist, **dadurch gekennzeichnet**, dass oberhalb der Deckschicht (6) eine abziehbare Peel-Schicht (7) angeordnet ist, und dass zum erleichterten Abziehen der Peel-Schicht (7) entlang des ersten Verpackungsabschnitts (9) mindestens ein erster, randseitiger Greifabschnitt (12) und zum erleichterten Abziehen der Peel-Schicht (7) entlang des zweiten Verpackungsabschnitts (10) mindestens ein zweiter, randseitiger Greifabschnitt (13) vorgesehen ist.

2. Blisterverpackung nach Anspruch 1, dadurch gekennzeichnet, dass die Kavitäten (3) in einer ersten Reihe (4) und in mindestens einer zweiten, zu der ersten Reihe (4) parallelen, Reihe (5) angeordnet sind, und dass die einzige Trennlinie (8) bzw. die sich nicht-kreuzenden Trennlinien (8) in Richtung der Längserstreckung der Reihen (4, 5) verläuft/verlaufen.

3. Blisterverpackung nach Anspruch 2, dadurch gekennzeichnet, dass die einzige Trennlinie (8) zwischen den Reihen (4, 5) angeordnet ist bzw. dass jeweils eine der sich nicht-kreuzenden Trennlinien (8) zwischen jeweils zwei Reihen (4, 5) angeordnet ist.

4. Blisterverpackung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass der erste und der zweite Greifabschnitt (12, 13) durch das Vorsehen mindestens einer Knicklinie (14) in der Bodenfolie (2) gebildet sind.

5. Blisterverpackung nach Anspruch 4, dadurch gekennzeichnet, dass sich die Knicklinie (14) quer zur Längserstreckung der Verpackungsabschnitte (9), vorzugsweise über die gesamte Breitenerstreckung mindestens eines der Greifabschnitte (12, 13), erstreckt.

6. Blisterverpackung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, dass die Bodenfolie (2) im Bereich des Greifabschnittes (12, 13) ausgestanzt ist.

7. Blisterverpackung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass benachbart zu den Greifabschnitten (12, 13) mindestens eine, vorzugsweise parallel zu der Knicklinie (14) verlaufende, insbesondere als Perforation aus-

gebildete, Sollbruchlinie (19) für die Deckschicht (6) vorgesehen ist.

8. Blisterverpackung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass der erste Greifabschnitt (12) benachbart zu dem zweiten Greifabschnitt (13) angeordnet ist, wobei die Greifabschnitte (12, 13) durch eine Ausstanzung (20), zumindest zum Teil, vorzugsweise vollständig, voneinander getrennt sind.

9. Blisterverpackung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass die Ausstanzung (20) V-förmig ist.

10. Blisterverpackung nach einem der Ansprüche 2 bis 9, dadurch gekennzeichnet, dass der Abstand zwischen zwei in Längsrichtung der ersten und/oder der zweiten Reihe (4, 5) nebeneinander angeordneten Kavitäten (3) geringer ist, als der Abstand zwischen zwei nebeneinander in benachbarten Reihen (4, 5) angeordneten Kavitäten (3).

11. Blisterverpackung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass die als Monolayer oder Multilayer ausgebildete Deckschicht (6) eine Aluminiumschicht und/oder eine Aluminiumlegierungsschicht, vorzugsweise mit einer Dicke aus einem Bereich zwischen etwa 10 µm und etwa 40 µm, umfasst.

12. Blisterverpackung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass die als Monolayer oder Multilayer ausgebildete Peel-Schicht (7) PET, und/oder oPA und/oder auf Kunststoff, insbesondere PET, vorzugsweise mit einer Dicke aus einem Bereich zwischen etwa 12 µm und etwa 70 µm, laminiertes Papier, vorzugsweise mit einem Flächengewicht aus einem Bereich zwischen etwa 20 g/m² und etwa 80 g/m², umfasst.

13. Blisterverpackung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass die als Monolayer oder Multilayer ausgebildete Bodenfolie thermoverformbares Material umfasst, vorzugsweise PVC, und/oder PVDC beschichtetes PVC und/oder eine Aclar/PVC-Schichtkombination und/oder eine Aclar/PE/PVC-Schichtkombination und/oder PP und/oder PET und/oder PE und/oder HDPE und/oder eine COC/PP-Schichtkombination und/oder eine COC/PVC-Schichtkombination.

14. Blisterverpackung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass die als Monolayer oder Multilayer ausgebildete Bodenfolie (2) kalt-verformbares Material, vorzugsweise Aluminium und/oder eine Aluminiumlegierung umfasst.

15. Blisterverpackung nach einem der vorherge-

henden Ansprüche, dadurch gekennzeichnet, dass die Deckschicht (6) und die Peel-Schicht (7) Bestandteile einer Mehrschicht-Folie (21) sind.

16. Blisterverpackung nach Anspruch 15, dadurch gekennzeichnet, dass die Mehrschicht-Folie (21) folgenden Schichtaufbau umfasst: Siegelschicht (22), Deckschicht (6), lösbare Klebeschicht (23), Peel-Schicht (7).

17. Blisterverpackung mit einer Kavitäten (52) aufweisenden Bodenfolie (58), wobei die Blisterverpackung (50) entlang von sich kreuzenden Trennlinien (51) in jeweils mindestens eine Kavität (52) aufweisende Verpackungsabschnitte aufteilbar ist, und mit einer die Kavitäten (52) überdeckenden, drückbaren Deckschicht (59), sowie mit einer oberhalb der Deckschicht (59) angeordneten abziehbaren Peel-Schicht (57), wobei jedem Verpackungsabschnitt (53) jeweils mindestens ein Greifabschnitt (54) zum erleichterten Abziehen der Peel-Schicht (57) entlang des jeweiligen Verpackungsabschnittes (53) zugeordnet ist, dadurch gekennzeichnet, dass die Greifabschnitte (54) durch das Vorsehen mindestens einer Knicklinie (55) in der Bodenfolie (58) gebildet sind.

18. Blisterverpackung nach Anspruch 17, dadurch gekennzeichnet, dass benachbart zu der Knicklinie (55) mindestens eine, vorzugsweise parallel zu der Knicklinie (55) verlaufende, insbesondere als Perforation ausgebildete, Sollbruchlinie für die Deckschicht (59) vorgesehen ist.

19. Blisterverpackung nach einem der Ansprüche 17 oder 18, dadurch gekennzeichnet, dass zwei benachbarte Greifabschnitte (54) durch eine Ausstanzung (56) voneinander getrennt sind.

20. Blisterverpackung nach Anspruch 17, dadurch gekennzeichnet, dass die Ausstanzung (56) V-förmig ist.

21. Verwendung einer Blisterverpackung (50) nach einem der vorhergehenden Ansprüche als Medikamentenverpackung, vorzugsweise für Feststoff-mediakamente oder für Medikamente mit einer Feststoffhülle.

Es folgen 3 Blatt Zeichnungen

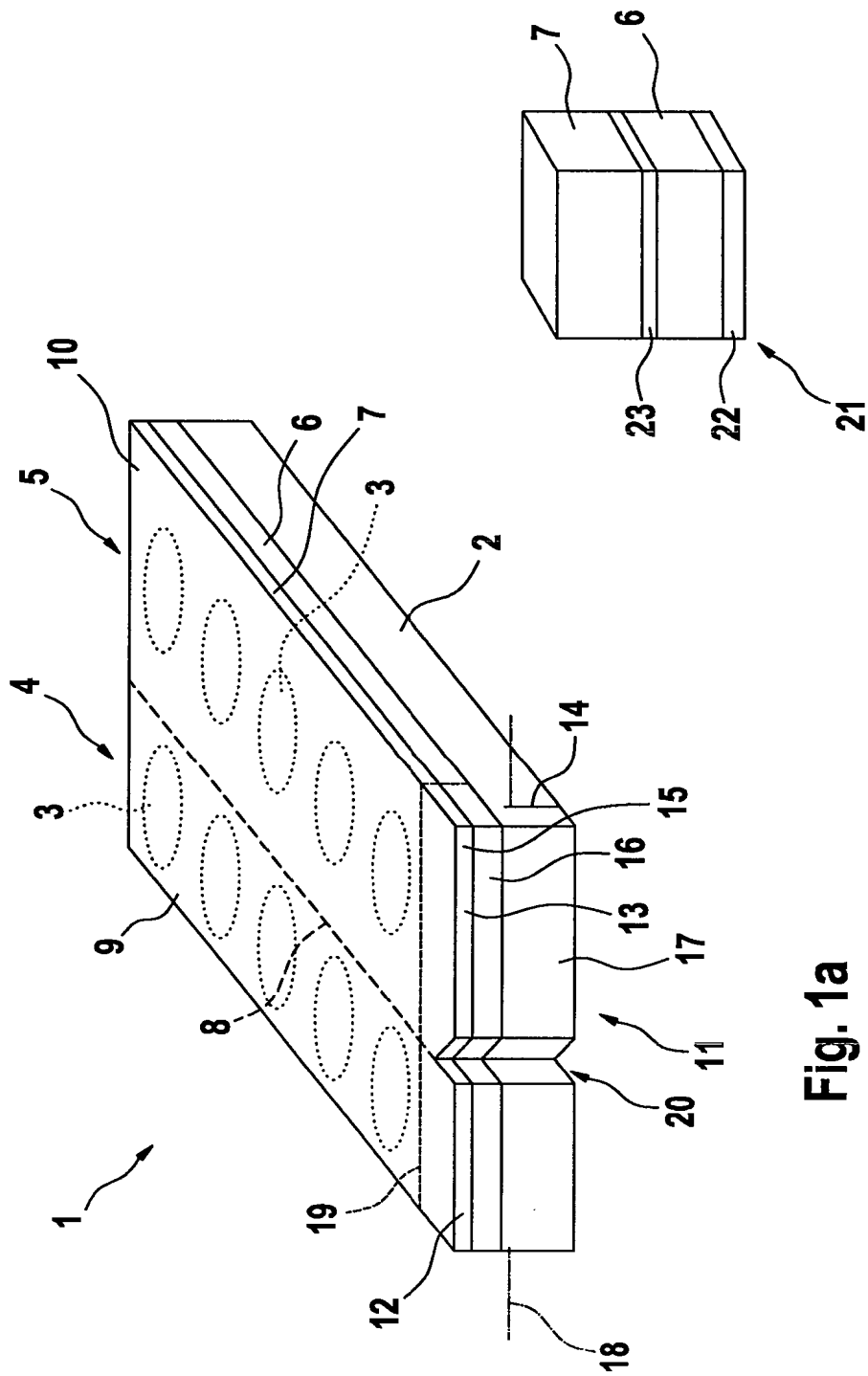


Fig. 1a

Fig. 1b

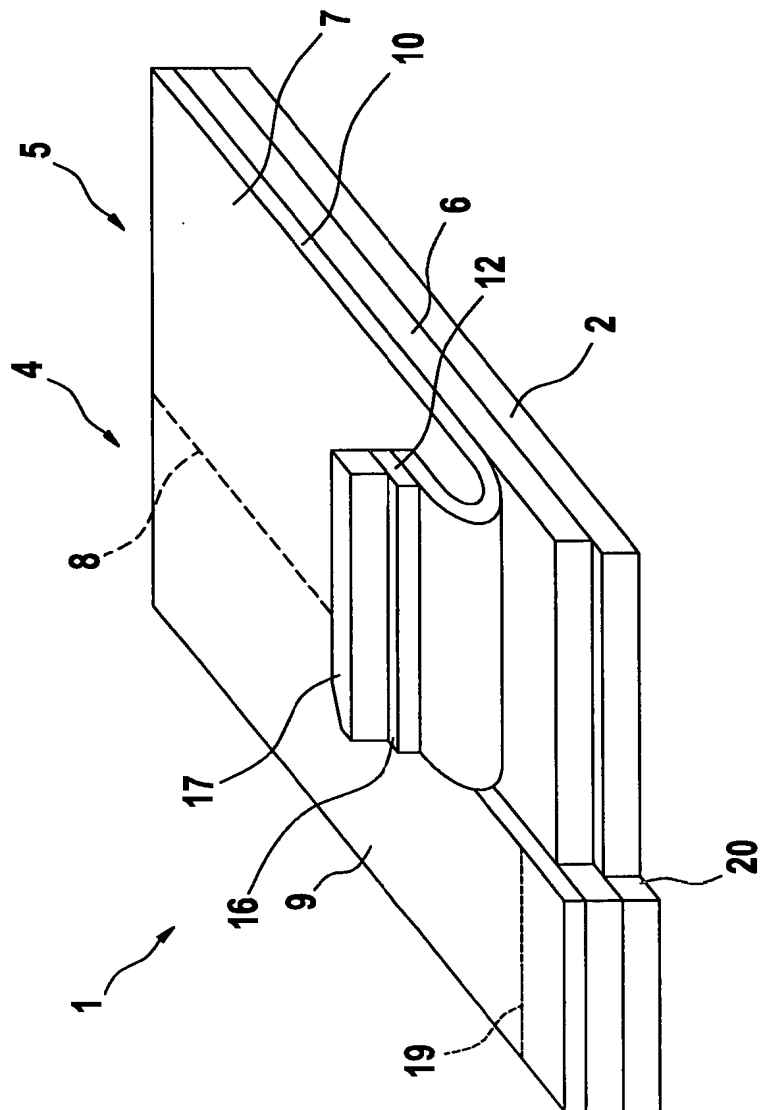


Fig. 2

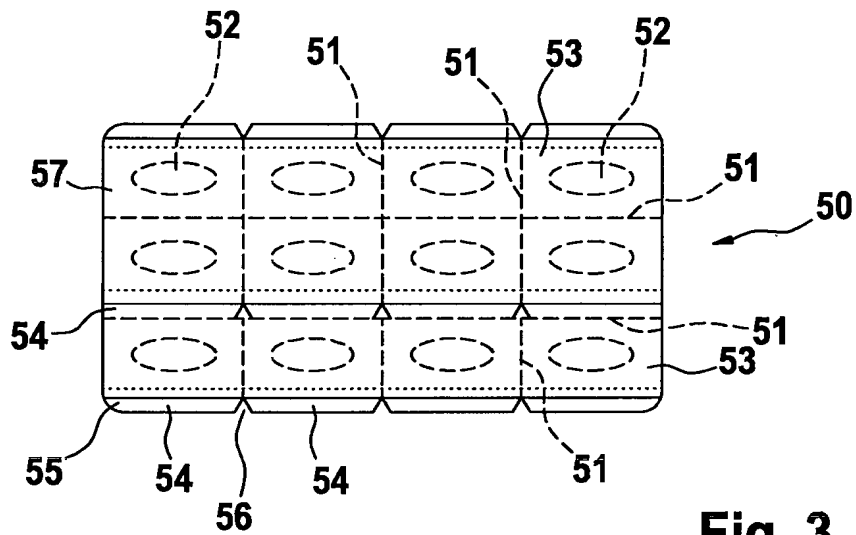


Fig. 3

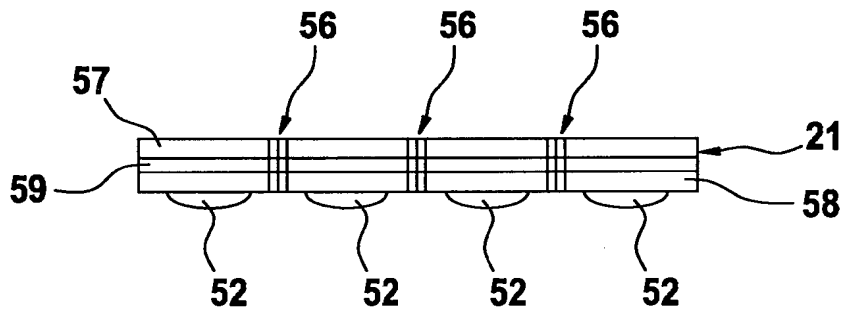


Fig. 4

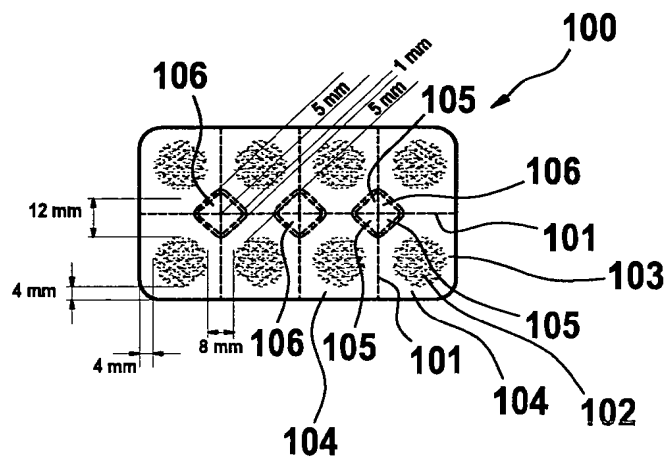


Fig. 5

Stand der Technik

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(54) Multi-layer laminate, packaging material and packages made therefrom

Mehrschichtlaminat, Verpackungsmaterial und aus diesem Material hergestellte Verpackungen

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Description

[0001] The present invention relates to a multi-layer packaging material, particularly for the protection of moisture sensitive food and non-food goods, such as detergents, washing powder, zeolithe-free washing powder, moisture sensitive chemicals and foodstuffs, such as cereals, cornflakes, dried soups, chocolates, cookies and the like.

[0002] It has been tried to make packages for perishable liquid or dry foods, such as milk products, juices, cereals, moisture, oxygen and aroma proof for improving the durability.

[0003] JP-A-0813480 (Mitsui) discloses a laminated paper product comprising paper base material laminated with a layer of cyclic-olefin based resins used as a packaging material with improved moisture barrier properties.

[0004] JP-A-10237234 (Tamapori) discloses a laminated packaging film composed of three layers. The middle layer is composed of a blend of 5-50 wt% COC (cycloolefin copolymer) and 50-95 wt% LLDPE (linear low density polyethylene) having a good balance of strength and tear properties to axis- and cross-directions.

[0005] EP-A-1302311 (Nihon Tetra Pak, Nippon Zeon) discloses a container comprised of a plastic-paper laminate, where the plastic composition contains a blend of LLDPE (100 parts per weight) and norbornene-based polymers (10 to 20 parts per weight). The container is suitable for packaging food and beverages because of its good heat resistance, heat sealability and low moisture permeability.

[0006] The traditional procedure has been to provide the fiber-based packaging material with a grey aluminum foil, which provides an efficient protection against the penetration of moisture and oxygen and the escape of aromas in the packed product. However, the use of aluminum foil used for a long time is now decreasing due to its high costs, environmental hazards and regulations concerning the recycling of materials.

[0007] Aluminum is undecomposable on dumping areas, and it is difficult to regenerate packaging cardboard lined with aluminum.

[0008] Aluminum used as an oxygen and aroma barrier in food packages has been

[0009] replaced by polymers to an increasing extent; the most important polymers being ethyl vinyl alcohol copolymer (EVOH), polyamide (PA), and polyethylene terephthalate (PET). By combining these polymers with binding agents and heat sealing polymers, multi-layer cardboard has been formed, with which gas barrier characteristics almost comparable with aluminum have at best been achieved. A disadvantage of these materials are their permeability to water vapor, so these materials all have a high Moisture Vapor Transition Rate (MVTR).

[0010] This disadvantage has attempted to be overcome by the usage of polyolefin layers as moisture barriers, either alone or in combination with the polymers above. Low Density Polyethylene (PE-LD) is a widely used polyolefin used for this purpose. For even lower Moisture Vapor Transition Rates (MVTR), PE-LD layers may be combined with high density polyethylene layers (PE-HD).

[0011] A disadvantage of these solutions are high film thicknesses. Another trend also depending on material costs and tightening environmental regulations has been to decrease the amount of polymer used for the coating of packaging cardboard.

[0012] It was an object of the present invention to provide a packaging material having a lower MVTR at a given thickness and to achieve higher overall moisture barrier properties / lower MVTR, respectively. This object has been accomplished by a multi-layer laminate comprising at least one layer of fiber material and at least one layer of plastic laminated thereto, which plastic layer comprises a blend of more than 50 weight percent of a cycloolefin copolymer and polyethylene.

[0013] The invention also relates to packaging materials consisting of multi-layer laminates according to the invention, and to packagings made thereof. Such packagings may have the shape of boxes, tumblers or may be boxes or tumblers with at least one handle. The MVTR of multi-layer laminates according to the invention are generally about 3 to about 5 times lower than the MVTR of multi-layer laminates equipped with PE-LD as moisture vapor barrier layer and about 2 to about 3 times lower than the MVTR of multi-layer laminates equipped with a layer sequence of PE-LD / PE-HD / PE-LD as moisture vapor barrier layer, when the MVTR is measured at a temperature of 23 °C and 85% of relative humidity. According to the invention multi-layer laminates can be provided having an MVTR of 1.0 g per square meter and day with a coating thickness of 23 g/m²; the barrier properties are about equal to more than 100 g/m² of PE-LD as moisture vapor barrier layer, and the amount of plastic in packaging materials according to the invention are preferably equal or less than 5 percent by weight of the total packaging. As the base material for multi-layer laminates according to the invention, a fibre material such as board, paper, kraft paper, cardboard of bleached sulphate pulp may be used. The multi-layer laminate may contain more than one layer of board or paper. In a preferred embodiment, the multi-layer laminate comprises at least one further layer consisting essentially of polyethylene.

[0014] In general, any type of polyethylene may be used for the purposes mentioned above, like PE-HD or PE-LLD, although the use of PE-LD is preferred. Suitable polyolefins are described in Saechtling, Kunststoff-Taschenbuch, Hanser-Verlag, 27th edition, 1998 on pages 375 to 415, which document is incorporated by reference for all useful purposes.

[0015] In a further preferred embodiment the plastic layer comprising a cycloolefin copolymer consists essentially of

at least one cycloolefin copolymer. This embodiment is preferred if maximum barrier properties are desired, however, such a layer can sometimes be difficult to laminate to the fibre material. An option to improve the adhesion between the plastic layer comprising a cycloolefin copolymer and other materials is a surface treatment of this layer, which treatment preferably leads to a partial oxidation of the surface. Examples are corona treatment, flame treatment or the like. Preferably, the plastic layer comprising a cycloolefin copolymer comprises more than 60 percent by weight, preferably 60 to 80 percent by weight, of a cycloolefin copolymer. The usage of this embodiment provides improved adhesion to the fiber material and may be easily laminated to the fiber material, particularly if the plastic layer comprising a cycloolefin copolymer is a blend of about 60 to about 80 percent by weight of the cycloolefin copolymer with PE-LD. Even types of paper which are particularly difficult to be laminated thereto may easily adhere to such a plastic layer. Cycloolefin copolymers usually show a high neck-in on film extrusion which can be reduced by coextrusion or blending of the cycloolefin copolymer with PE-LD. The PE-LD used preferably has a Melt Flow Index (MFI) of about 4 to about 7.5.

[0016] In further preferred embodiments, different layer sequences may be created to optimize the multi-layer laminate for various purposes. Such preferred layer sequences are:

- Fiber material / plastic layer comprising a cycloolefin copolymer
- Fiber material / plastic layer comprising a cycloolefin copolymer / PE-LD
- Fiber material / PE-LD / plastic layer comprising a cycloolefin copolymer / PE-LD, wherein the fiber material is preferably board or paper.

[0017] Particularly preferable multi-layer laminates have one of the following layer sequences:

- board / PE-LD / plastic layer comprising a cycloolefin copolymer / PE-LD / paper
- board / plastic layer comprising a cycloolefin copolymer / PE-LD / paper
- board / plastic layer comprising a cycloolefin copolymer / paper
- board / Blend of PE-LD and a cycloolefin copolymer / paper

[0018] Such multi-layer laminates are preferred if contact between plastic and the content is to be avoided, or if the illusion of a pure paper packaging is desired. Such multi-layer laminates are particularly useful for foodstuffs or detergents, particularly washing powder. Usage of such packaging is of particular advantage for washing powder which do not contain zeolithes. Such washing powders are more moisture sensitive than washing powders containing zeolithes; however, such washing powders often leave light spots on dark clothing, which can be avoided by using zeolithe-free washing powders.

[0019] If oxygen barrier properties and/or aroma barrier properties are desired, appropriate polymers with such properties are for example EVOH and polyamides, particularly amorphous polyamides such as Selar® obtainable from Dupont. Preferable layer sequences are for example :

- fiber material / EVOH / tie / plastic layer comprising a cycloolefin copolymer / PE-LD
- fiber material / tie / EVOH / tie / plastic layer comprising a cycloolefin copolymer / PE-LD
- fiber material / tie / plastic layer comprising a cycloolefin copolymer / tie / Polyamide. In these embodiments board is preferably used as fiber material. The tie layer may be necessary to ensure adhesion between the layers, particularly between the plastic layer comprising a cycloolefin copolymer and the EVOH and the polyamide.

[0020] The tie layer may comprise a modified polyolefin, and preferably consists essentially of a modified polyolefin. The modified polyolefin comprises at least a group like carboxyl, carboxyl anhydride, metal carboxylate, carboxy ester, imino, amino or epoxy group in an amount of 1 percent by weight to 50 percent by weight of the modified polyolefin. Examples for such modified polyolefins comprise modified polyolefin copolymers or grafted copolymers, which may be obtained by incorporating groups like maleic anhydride, fumaric anhydride, citric anhydride, n-phenylmaleimide, n-cyclohexylmaleimide, glycidyl acrylate, glycidyl methacrylate, glycidyl vinyl benzoate, N-[4-(2,3-epoxpropoxy)-3,5-dimethylbenzyl]acrylamide (AXE), alkylmethacrylate and/or derivatives thereof into polyolefins like polyethylene, polypropylene, ethylene/propylene copolymers or polyamide grafted polyolefins. Such products can be obtained by compounding the polyolefin with maleic anhydride or other substances as mentioned above together with a radical initiator, like for example AIBN or benzoyl peroxide.

[0021] The modified polyolefin is not limited in its degree of polymerization and may be an oligomer as well. Preferred modified polyolefins are

Maleic anhydride modified polyethylene,
Maleic anhydride modified polypropylene,
Maleic anhydride modified polyethylene/polypropylene-copolymer,

Fumaric acid modified polyethylene,
 Fumaric acid modified polypropylenes,
 Fumaric acid modified polyethylene/polypropylene-copolymer,
 Glycidylmethacrylate modified polyethylene,
 Glycidylmethacrylate modified polypropylene,
 AXE modified polyethylene,
 AXE modified polypropylene.

[0022] Further materials suitable to be used in the tie layer are copolymers of ethylene with unsaturated esters like vinyl acetate, (meth)acrylic esters, for example ethyl methacrylate, and copolymers of ethylene with vinylalcohol.

[0023] Particular preference is given to maleic-acid grafted polyethylene and maleic-acid grafted polypropylene.

[0024] The plastic layer comprising a cycloolefin copolymer may comprise usual additives in an amount of up to 0.5 percent by weight, such as lubricants or antioxidants, like Irganox® available from Ciba Specialty Chemicals.

[0025] The layer thicknesses for the plastic layer comprising a cycloolefin copolymer are generally in the range of about 10 g/m² to about 50 g/m². If this film is a blend of a cycloolefin copolymer, the thickness is preferably in the range of about 10 g/m² to about 20 g/m².

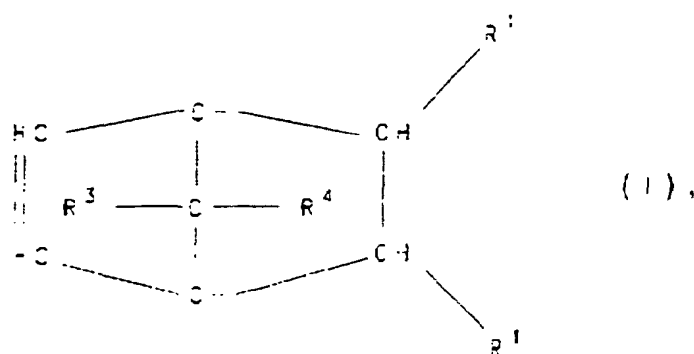
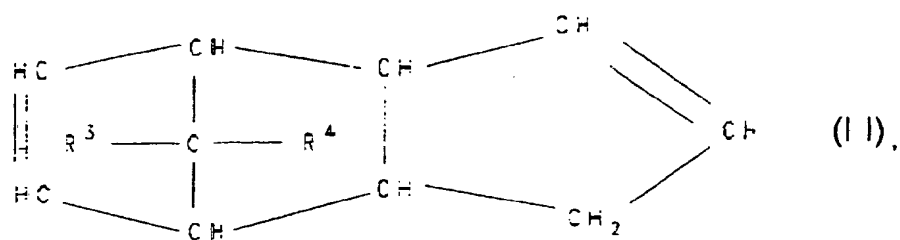
[0026] Additional layers made of PE-LD preferably have a thickness of from about 1 g/m² to about 10 g/m².

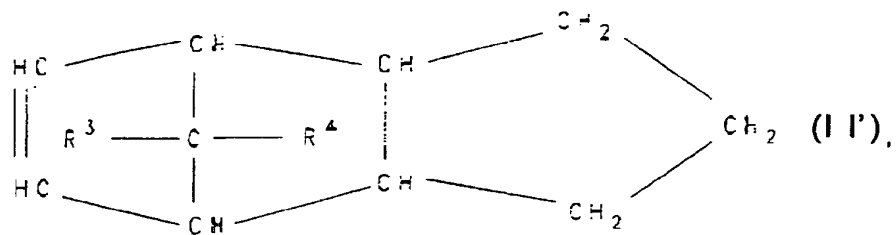
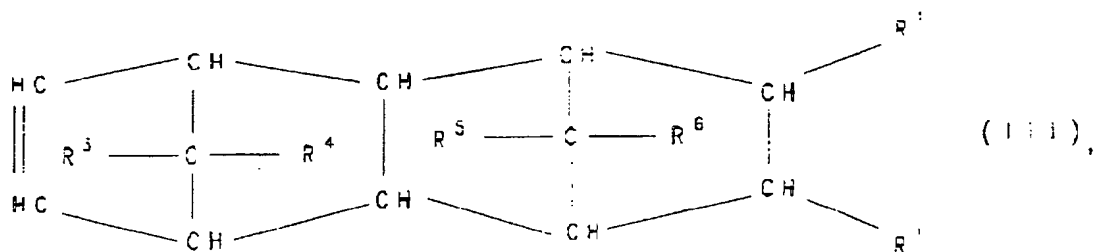
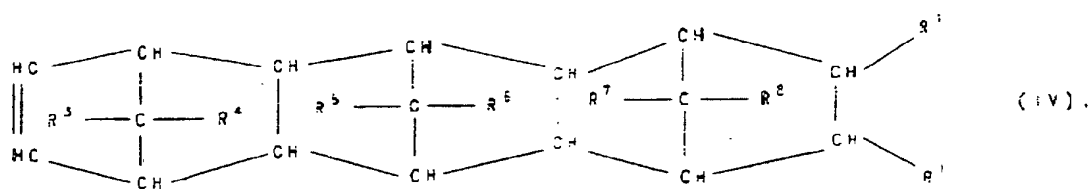
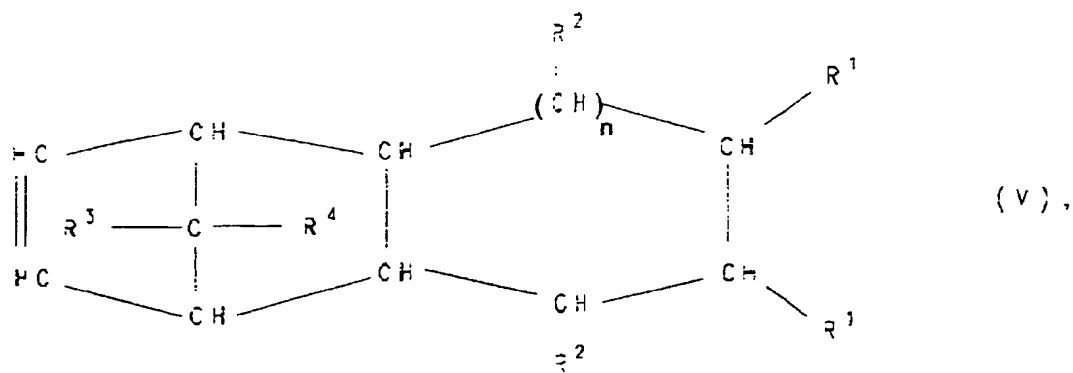
[0027] The thickness of the layer made of polyamide or EVOH has to be adjusted to meet the desired oxygen barrier properties.

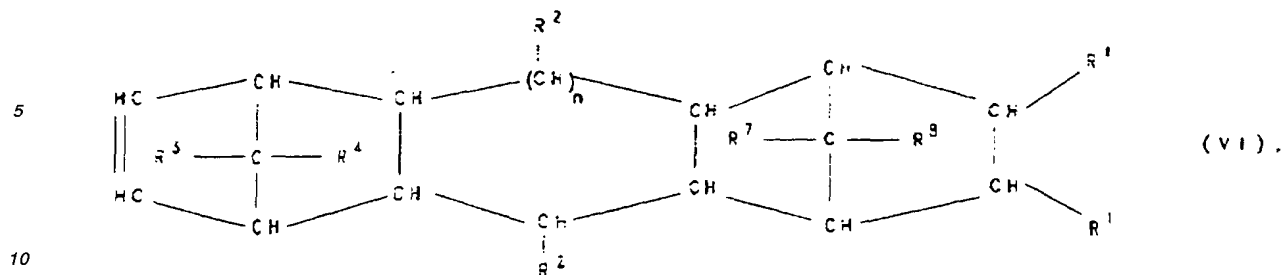
[0028] The thickness of the fiber material layers and the plastic layers may be adjusted to meet the desired barrier properties or a given weight percentage of plastic content of the multi-layer laminate.

[0029] The overall thickness of the polymer layer on the fiber material generally is between about 5 µm and about 100 µm, preferably between about 12 µm and about 50 µm, more preferably between about 25 to about 40 µm. If the overall thickness exceeds 100µm, the processing becomes more difficult so the thickness should preferably be less than 100 µm.

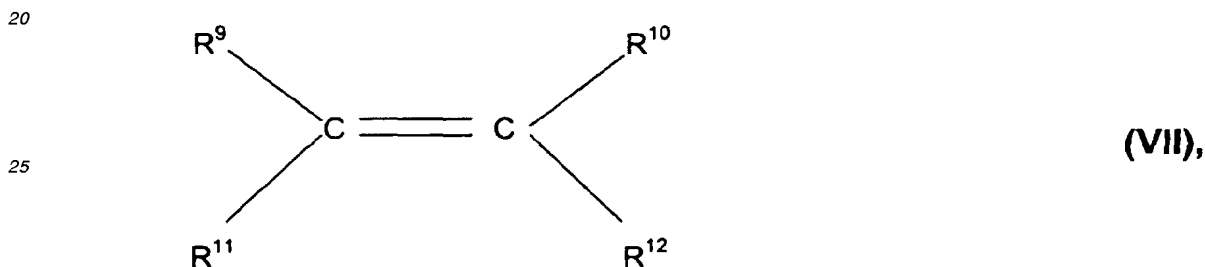
[0030] The cycloolefin copolymer preferably has a glass transition temperature from about 60°C to about 150°C, preferably about 70°C to about 100°C. Most preferably, the glass transition temperature is about 80°C. The cycloolefin copolymer is preferably a polymer comprising 0.1 - 99 mole %, preferably 3 - 75 mole %, particularly preferably 10 mole % to 65 mole % of cycloolefin copolymers, polymerized units of at least one cyclic olefin of the formulae I, II, II', III, IV, V or VI







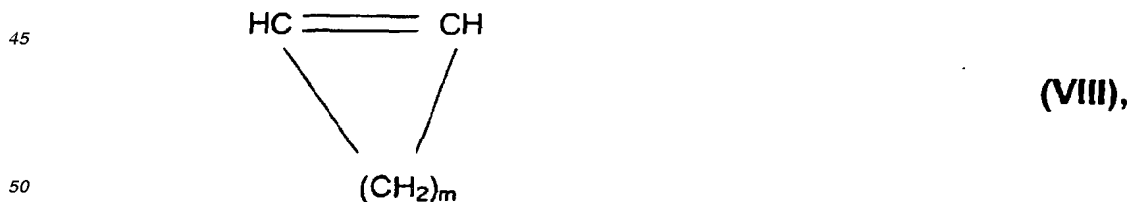
wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 and R^8 are the same or different and are hydrogen or a C_1 - C_{20} -hydrocarbon rest, like a linear or branched C_1 - C_8 -alkyl rest, C_6 - C_{18} -aryl radical, C_7 - C_{20} -alkylenaryl rest, a cyclic or acyclic C_2 - C_{20} -alkenyl rest, or may form a saturated, unsaturated or aromatic ring, wherein equal rests R^1 to R^8 in different formulae I to VI can be different, wherein n is an integer of from 0 to 5, and comprises 25 to 97 mole %, preferably 35 mole % to 90 mole % polymerized units which are derived from at least one acyclic olefin of formula VII



wherein R^9 , R^{10} , R^{11} and R^{12} are the same or different and are a hydrogen, a linear, branched, saturated or unsaturated C_1 - C_{20} -hydrocarbon rest such as a C_1 - C_8 -alkyl rest or a C_6 - C_{18} -aryl rest. Preferably, the acyclic olefin is an α -olefin or ethylene. Particularly preferably, the cycloolefin copolymer is a copolymer of ethylene, propylene or another alpha olefin having preferably 2 to 20 carbon atoms with at least one cyclic olefin of the formulae I, II, II', III, IV, V or VI. Particularly preferably, the cycloolefin copolymer is a copolymer of norbornene or tetracyclododecene with ethylene or an alpha olefin, like propylene. Most preferably, the cycloolefin copolymer is a copolymer of ethylene and norbornene or ethylene and tetracyclododecene.

[0031] Cycloolefin copolymers may be obtained by ring opening polymerization of at least one monomer of the formulae I to VI, followed by a hydration step.

[0032] The cycloolefin copolymer may further comprise 0 to 45 mol-% polymerized units which are derived from one or more monocyclic olefins of the formula VIII



wherein m is an integer from 2 to 10.

The amount of polymerized units which are derived from cyclic, particularly polycyclic olefins is preferably from about 3 mol-% to about 75 mol-%. The amount of polymerized units derived from the acyclic olefin is preferably from about 5 mol-% to about 80 mol-% of the cycloolefin copolymer.

[0033] Preferably the cycloolefin copolymer consists of polymerized units derived from one or more polycyclic olefins, particularly polycyclic olefins of the formulae I or III, and polymerized units which are derived from one or more acyclic

olefins of the formula VII, particularly α -olefins with 2 to 20 carbon atoms. Particularly preferred are cycloolefin copolymers consisting of polymerized units derived from a polycyclic olefin of the formulae I or III and an acyclic Olefin of the formula VII. Further preferred are terpolymers, which consist of polymerized units derived from a polycyclic monoolefin of the formula I or III, an acyclic monoolefin of the formula VII and a cyclic or acyclic olefin, comprising at least

two double bonds (polyene), particularly cyclic, preferably polycyclic dienes like norbornadiene or cyclic, particularly preferably polycyclic alkenes carrying a C_2-C_{20} -alkenyl rest, like for example vinylnorbornene.

[0034] The cycloolefin copolymer can be prepared at temperatures of about -78°C to about 200°C and a pressure of about 0.001 to about 200 bar in the presence of one or more catalyst systems comprising at least one transition metal compound and optionally a cocatalyst a optionally a carrier material. Suitable transition metal compounds are

Examples for suitable transition metal compounds are

rac-dimethylsilylbis(1-indenyl)zirconium dichloride,
 rac-dimethylgermylbis(1-indenyl)zirconium dichloride,
 rac-phenylmethylsilylbis(1-indenyl)zirconium dichloride,
 rac-phenylvinylsilylbis(1-indenyl)zirconium dichloride,
 1-silacyclobutylbis(1-indenyl)zirconium dichloride,
 rac-diphenylsilylbis(1-indenyl)hafnium dichloride,
 rac-phenylmethylsilylbis(1-indenyl)hafnium dichloride,
 rac-diphenylsilylbis(1-indenyl)zirconium dichloride,
 rac-ethylene-1,2-bis(1-indenyl)zirconium dichloride,
 dimethylsilyl(9-fluorenyl)(cyclopentadienyl)zirconium dichloride,
 diphenylsilyl(9-fluorenyl)(cyclopentadienyl)zirconium dichloride,
 bis(1-indenyl)zirconium dichloride,
 diphenylmethylene(9-fluorenyl)cyclopentadienylzirconium dichloride,
 isopropylene(9-fluorenyl)cyclopentadienylzirconium dichloride,
 rac-isopropylidene-bis(1-indenyl)zirconium dichloride,
 rac-isopropylidene-bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride,
 phenylmethylmethylene(9-fluorenyl)cyclopentadienylzirconium dichloride,
 isopropylene(9-fluorenyl)(1-(3-isopropyl)cyclopentadienyl)zirconium dichloride,
 isopropylene(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)zirconium dichloride,
 diphenylmethylene(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)zirconium dichloride,
 methylphenylmethylene(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)zirconium dichloride,
 dimethylsilyl(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)zirconium dichloride,
 diphenylsilyl(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)zirconium dichloride,
 diphenylmethylene(9-fluorenyl)(1-(3-tert-butyl)cyclopentadienyl)zirconium dichloride,
 isopropylene(9-fluorenyl)(1-(3-tert-butyl)cyclopentadienyl)zirconium dichloride,
 isopropylene(cyclopentadienyl)(1-indenyl)zirconium dichloride,
 diphenylcarbonyl(cyclopentadienyl)(1-indenyl)zirconium dichloride,
 dimethylsilyl(cyclopentadienyl)(1-indenyl)zirconium dichloride,
 isopropylene(methylcyclopentadienyl)(1-indenyl)zirconium dichloride,
 4-(η^5 -cyclopentadienyl)-4,7,7-trimethyl(η^5 -4,5,6,7-tetrahydroindenyl)-zirconium dichloride,
 [4-(η^5 -cyclopentadienyl)-4,7,7-triphenyl(η^5 -4,5,6,7-tetrahydroindenyl)]zirconium dichloride,
 [4-(η^5 -cyclopentadienyl)-4,7-dimethyl-7-phenyl(η^5 -4,5,6,7-tetrahydroindenyl)]zirconium dichloride,
 [4-(η^5 -3'-tert-butylcyclopentadienyl)-4,7,7-triphenyl(η^5 -4,5,6,7-tetrahydroindenyl)]zirconium dichloride,
 [4-(η^5 -3'-tert-butylcyclopentadienyl)-4,7-dimethyl-7-phenyl(η^5 -4,5,6,7-tetrahydroindenyl)]zirconium dichloride,
 [4-(η^5 -3'-methylcyclopentadienyl)-4,7,7-trimethyl(η^5 -4,5,6,7-tetrahydroindenyl)]zirconium dichloride,
 [4-(η^5 -3'-methylcyclopentadienyl)-4,7,7-triphenyl(η^5 -4,5,6,7-tetrahydroindenyl)]zirconium dichloride,
 [4-(η^5 -3'-methylcyclopentadienyl)-4,7-dimethyl-7-phenyl(η^5 -4,5,6,7-tetrahydroindenyl)]zirconium dichloride,
 [4-(η^5 -3'-isopropylcyclopentadienyl)-4,7,7-trimethyl(η^5 -4,5,6,7-tetrahydroindenyl)]zirconium dichloride,
 [4-(η^5 -3'-isopropylcyclopentadienyl)-4,7,7-triphenyl(η^5 -4,5,6,7-tetrahydroindenyl)]zirconium dichloride,
 [4-(η^5 -3'-isopropylcyclopentadienyl)-4,7-dimethyl-7-phenyl(η^5 -4,5,6,7-tetrahydroindenyl)]zirconium dichloride,
 [4-(η^5 -cyclopentadienyl)(η^5 -4,5-tetrahydropentalene)]zirconium dichloride,
 [4-(η^5 -cyclopentadienyl)-4-methyl(η^5 -4,5-tetrahydropentalene)]zirconium dichloride,
 [4-(η^5 -cyclopentadienyl)-4-phenyl(η^5 -4,5-tetrahydropentalene)]zirconium dichloride,
 [4-(η^5 -cyclopentadienyl)-4-phenyl(η^5 -4,5-tetrahydropentalene)]zirconium dichloride,

[4-(η^5 -3'-methylcyclopentadienyl)(η^5 -4,5-tetrahydropentalene)]zirconium dichloride,
 [4-(η^5 -3'-isopropylcyclopentadienyl)(η^5 -4,5-tetrahydropentalene)]zirconium dichloride,
 [4-(η^5 -3'-benzylcyclopentadienyl)(η^5 -4,5-tetrahydropentalene)]zirconium dichloride,
 [2,2,4-trimethyl-4-(η^5 -cyclopentadienyl)(η^5 -4,5-tetrahydropentalene)]zirconium dichloride
 5 [2,2,4-trimethyl-4-(η^5 -(3,4-diisopropyl)cyclopentadienyl)(η^5 -4,5-tetrahydropentalene)]zirconium dichloride.

The multi-layer laminates may be used for manufacturing packaging materials, which preferably consist of the multi layer laminates according to the invention. From these packaging materials packages for various products can be produced, which can have different shapes, like boxes, tumblers or the like. Preferably, these packages having the shape of tumblers or boxes have at least one handle. Such packages can be advantageously for protection of moisture sensitive food and non-food goods, such as detergents, washing powder, zeolite-free washing powder, moisture sensitive chemicals and foodstuffs, such as cereals, cornflakes, dried soups, pet food, chocolates, cookies and the like. If desired, the package can be equipped to be heat-sealable. Such packagings can be used for packaging for milk, soft-drinks, juices or the like, in which cases particularly tight packages are desired which have low permeation rates. These packages are preferably in the shape of milk boxes. For heat-sealable equipment of the packages, the fiber material can preferably be equipped with materials and/or layer sequences as described in US 5693414 and US 5861208, which documents are incorporated by reference for all useful purposes.

Examples / Best Modes

[0035] The cycloolefin copolymer (COC) used was TOPAS® 8007, Ticona GmbH, Kelsterbach.

The PE-LD used had a density of 922 kg/m³, an MFI of 7g/10 minutes.

The PE-HD used had a density of 964 kg/m³ and an MFI 4 g/10minutes.

The modified polyethylene used as tie layer was Byne® available from Dupont.

As amorphous polyamide Selar® from Dupont was used.

The board used had a thickness of 385 g/m².

The kraft paper used had a thickness of 65 g/m².

MVTR measured under tropical conditions means at a temperature of 38°C and a relative humidity of 90%, normal conditions means at a temperature of 23°C and a relative humidity of 85%. MVTR are given in g/m² 24h. The MVTR was measured according to DIN 53122.

Comparative Example 1

[0036] The board used was covered with different layer sequences by means of coextrusion.

The overall plastic layer thickness was 24 g/m².

The layer thicknesses in examples B and C were 3/18/3 g/m²

A) board / PE-LD

B) board / PE-LD / PE-HD / PE-LD

C) board / PE-LD / COC / PE-LD

A, B and C are Comparative Examples.

Table 1 shows the results. The MVTR can be significantly improved with substitution of even PE-HD with COC.

Table 1

Example	MVTR normal	MVTR trop.
A	4.8	19
B	2.5	9.2
C	1.0	3.2

Example 2

[0037] Different multi-layer laminates of board with COC-LDPE blends were produced with different layer thicknesses (given in μ m).

Table 2

Material		100 μm		25 μm		12 μm	
		38°C/ 90%	23°C/ 85%	38°C/ 90%	23°C/ 85%	38°C/ 90%	23°C/ 85%
COC*		1,0	0,3	4	1,2	8	2,4
Blends	20% LDPE	1,2	0,3	5	1,2	10	2,6
	40% LDPE	1,5	0,4	6	1,4	13	2,9
	60% LDPE*	2,4	0,4	10	1,7	20	3,5
	80% LDPE*	3,9	0,6	16	2,3	32	4,8
PE-LD*		4,8	0,9	19	3,7	40	7,7

* not according to the claims

Comparative Example 3

[0038] Different multi layer laminates were produced by coextrusion to investigate the influence of layer thicknesses of COC on the MVTR under tropical conditions. A is a comparative example with a single PE-LD layer (thickness 13 g/m²). MVTR given in g / m² 24h

A) PE-LD MVTR: 35

B) PE-LD / COC /PE-LD, layer thicknesses 2 / 4 / 7 g/m² MVTR: 15C) PE-LD / COC /PE-LD layer, thicknesses 2 / 9 / 2 g/m² MVTR: 9

Comparative Example 4

[0039] To obtain a laminated article with maximum barrier properties and moderate weight, a layer sequence was extruded with the layer sequence board / PE-LD (2 g/m²) / COC (19 g/m²) / PE-LD (2 g/m²) / kraft paper. The MVTR at normal conditions was determined being 1 g/m² 24h. The barrier properties are roughly equivalent to 100 g/m² PE-LD coating weight. This laminating material combines excellent moisture barrier while containing less than 5% plastic weight.

Comparative Example 5

[0040] To obtain a laminated article having excellent moisture barrier board was coated with a COC layer of 40 μm and a PE-LD layer of 10 μm thickness. MVTR tropical is 2 g/m² 24h. This Comparative example has the maximum barrier properties with a practical layer thickness.

Comparative Example 6

[0041] To obtain a laminated article with excellent MVTR and oxygen transmission rate (OTR) a laminated article with the layer sequence board / tie (3 g/m²) / COC (10 g/m²) / tie (3 g/m²) / amorphous polyamide (5 μm) was produced. The MVTR was 9 g/m² 24h, the OTR 80 cm³/m² 24h bar.

Claims

- Multi-layer laminate comprising at least one layer of fibre material and at least one layer of plastic laminated thereto, wherein the plastic layer comprises a blend of more than 50 percent by weight of cycloolefin copolymer and polyethylene.
- Multi-layer laminate according to claim 1, comprising at least one further layer consisting essentially of polyethylene.
- Multi-layer laminate according to claim 2, wherein the polyethylene is a low density polyethylene (PE-LD).

4. Multi-layer laminate according to one or more of the preceding claims, wherein the polyethylene comprised in the blend is a low density polyethylene (PE-LD).
5. Multi-layer laminate according to claim 4, wherein the plastic layer comprising a cycloolefin copolymer comprises more than 60 percent by weight, preferably 60 to 80 percent by weight of a cycloolefinic copolymer.
6. Multi-layer laminate according to one or more of the preceding claims having a layer sequence: Fiber material, preferably board or paper / Plastic layer comprising a cycloolefin copolymer / PE-LD.
7. Multi-layer laminate according to one or more of the preceding claims having a layer sequence: Fiber material, preferably board or paper / PE-LD / Plastic layer comprising a cycloolefin copolymer / PE-LD.
8. Multi-layer laminate according to one or more of the preceding claims comprising an oxygen barrier layer consisting essentially of an ethylvinyl alcohol or an amorphous polyamide.
9. Packaging material consisting of a multi layer laminate according to one or more of the preceding claims.
10. Package for moisture sensitive chemicals, detergents, washing powder, zeolithe-free washing powder, dry food-stuffs, dry soups, cereals, pet food, chocolates, cookies, cornflakes and the like, consisting of a packaging material according to claim 9.
11. Package according to claim 10 having a shape of a box, tumbler, box or tumbler with at least one handle.

Patentansprüche

1. Mehrschichtlaminat mit mindestens einer Fasermaterialschicht und mindestens einer darauf auflaminierten Kunststoffschicht, bei dem die Kunststoffschicht eine Mischung von mehr als 50 Gewichtsprozent Cycloolefincopolymer und Polyethylen enthält.
2. Mehrschichtlaminat nach Anspruch 1 mit mindestens einer weiteren Schicht, die im wesentlichen aus Polyethylen besteht.
3. Mehrschichtlaminat nach Anspruch 2, bei dem es sich bei dem Polyethylen um ein Polyethylen niedriger Dichte (PE-LD) handelt.
4. Mehrschichtlaminat nach einem oder mehreren der vorhergehenden Ansprüche, bei dem es sich bei dem in der Mischung enthaltenen Polyethylen um ein Polyethylen niedriger Dichte (PE-LD) handelt.
5. Mehrschichtlaminat nach Anspruch 4, bei dem die ein Cycloolefincopolymer enthaltende Kunststoffschicht mehr als 60 Gewichtsprozent und vorzugsweise 60 bis 80 Gewichtsprozent eines Cycloolefincopolymers enthält.
6. Mehrschichtlaminat nach einem oder mehreren der vorhergehenden Ansprüche mit der Schichtenfolge: Fasermaterial, vorzugsweise Pappe oder Papier / Kunststoffschicht, enthaltend ein Cycloolefincopolymer / PE-LD.
7. Mehrschichtlaminat nach einem oder mehreren der vorhergehenden Ansprüche mit der Schichtenfolge: Fasermaterial, vorzugsweise Pappe oder Papier / PE-LD / Kunststoffschicht, enthaltend ein Cycloolefincopolymer / PE-LD.
8. Mehrschichtlaminat nach einem oder mehreren der vorhergehenden Ansprüche mit einer Sauerstoffbarrierschicht, die im wesentlichen aus einem Ethylvinylalkohol oder einem amorphen Polyamid besteht.
9. Verpackungsmaterial, bestehend aus einem Mehrschichtlaminat nach einem oder mehreren der vorhergehenden Ansprüche.
10. Verpackung für feuchtigkeitsempfindliche Chemikalien, Wasch- und Reinigungsmittel, Waschpulver, zeolithfreies Waschpulver, Trockenlebensmittel, Trockensuppen, Müsli, Haustierfutter, Pralinen, Kekse, Cornflakes und dergleichen, bestehend aus einem Verpackungsmaterial nach Anspruch 9.

11. Verpackung nach Anspruch 10 in Form einer Schachtel, eines Tumblers, einer Schachtel mit mindestens einem Griff oder eines Tumblers mit mindestens einem Griff.

5 **Revendications**

1. Stratifié multicouche comprenant au moins une couche de matière fibreuse et au moins une couche de plastique stratifiée par-dessus, dans lequel la couche de plastique comprend un mélange de plus de 50 pour cent en poids de copolymère de cyclooléfine et de polyéthylène.
2. Stratifié multicouche selon la revendication 1, comprenant au moins une autre couche constituée essentiellement de polyéthylène.
3. Stratifié multicouche selon la revendication 2, dans lequel le polyéthylène est un polyéthylène basse densité (PE-LD).
4. Stratifié multicouche selon une ou plusieurs des revendications précédentes, dans lequel le polyéthylène compris dans le mélange est un polyéthylène basse densité (PE-LD).
5. Stratifié multicouche selon la revendication 4, dans lequel la couche de plastique comprenant un copolymère de cyclooléfine comprend plus de 60 pour cent en poids, de préférence 60 à 80 pour cent en poids, d'un copolymère cyclooléfinique.
6. Stratifié multicouche selon une ou plusieurs des revendications précédentes comportant la suite de couches : matière fibreuse, de préférence carton ou papier/couche de plastique comprenant un copolymère de cyclooléfine/PE-LD.
7. Stratifié multicouche selon une ou plusieurs des revendications précédentes comportant la suite de couches : matière fibreuse, de préférence carton ou papier/PE-LD/couche de plastique comprenant un copolymère de cyclooléfine/PE-LD.
8. Stratifié multicouche selon une ou plusieurs des revendications précédentes comprenant une couche de barrière à l'oxygène constituée essentiellement d'un alcool éthylvinyle ou d'un polyamide amorphe.
9. Matériau d'emballage constitué d'un stratifié multicouche selon une ou plusieurs des revendications précédentes.
10. Emballage pour produits chimiques sensibles à l'humidité, détergents, poudre à laver, poudre à laver sans zéolithe, denrées alimentaires sèches, soupes déshydratées, céréales, aliments pour animaux, chocolats, petits gâteaux, flocons de maïs et analogues, constitué d'un matériau d'emballage selon la revendication 9.
11. Emballage selon la revendication 10 ayant la forme d'une boîte, d'un tonneau, d'une boîte ou d'un tonneau doté d'au moins une poignée.



Espacenet

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Coextruded, heat-sealable and peelable polyesterfilm, process for its production and its use

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Abstract of EP1475228 (A2)

A polyester film comprises a base layer and a heatsealable top layer which is peelable from amorphous polyethylene terephthalate. The top layer contains 60-97 wt.% polyester and 3-30 wt.% polyester-incompatible polymer. The polyester comprises 25-95 mol.% units derived from aromatic dicarboxylic acid(s) and 5-75 mol.% units derived from aliphatic dicarboxylic acid(s). The layer thickness of the top layer is 0.7-2.5 μ m. An independent claim is also included for a process for producing a sealable and peelable polyester film, comprising feeding polymers for the base layer (B) and the top layer (A) specified above and top layer (C) to separate extruders. The melts are then shaped and layered on top of one another in a multilayer die to give flat melt films. The

multilayer film is drawn off with the aid of a chill roll and optionally further rolls, solidified and then biaxially stretch-oriented and heat-set. The biaxial stretching is carried out in succession, first longitudinally (in machine direction) and then transversely (at right angles to machine direction) that the longitudinal stretching is carried out at 60-130 [deg]C and the transverse stretching is at 90-140[deg]C, and the longitudinal stretching ratio is set at 2:1 to 5.5:1 and the transverse stretching ratio is at 2.4:1 to 5:1.

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(54) **Coextrudierte, heissiegelbare und peelfähige Polyesterfolie, Verfahren zu ihrer Herstellung und ihre Verwendung**

Coextruded, heat-sealable and peelable polyesterfilm, process for its production and its use

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Beschreibung

[0001] Die Erfindung betrifft eine coextrudierte, peelfähige, transparente und biaxial orientierte Polyesterfolie mit einer Basisschicht (B) und mindestens einer auf dieser Basisschicht (B) aufgetragenen Deckschicht (A). Die Deckschicht (A) ist heißsiegelbar und zeichnet sich durch eine leichte bis feste Peelbarkeit, insbesondere zu APET/CPET-Menüschalen (APET = amorphes Polyethylenterephthalat (PET); CPET = kristallines PET), aus. Die heißsiegelbare und peelfähige Deckschicht (A) enthält Polyester auf Basis von aromatischen und aliphatischen Säuren und aliphatischen Diolen. Des Weiteren enthält die Deckschicht (A) ein mit Polyester unverträgliches Polymer (anti-PET-Polymer) in einer bestimmten Konzentration. Die Erfindung betrifft weiterhin ein Verfahren zur Herstellung der Folie und ihre Verwendung.

[0002] Für Fertiggerichte (engl. ready-prepared meals) sind in Europa die Zuwachsraten derzeit zweistellig. Die Fertiggerichte werden nach ihrer Zubereitung in Menüschalen (engl. trays) eingefüllt (vgl. Figur 1). Auf den Rand der Menüschale wird eine Folie heißgesiegelt, die die Verpackung verschließt und das Fertiggericht gegen äußere Einflüsse schützt. Die Fertiggerichte sind z. B. für die Erhitzung in der Mikrowelle, für die Erhitzung im Backofen oder für die Erhitzung in der Mikrowelle und im Backofen geeignet. Im letztgenannten Fall muss das Fertiggericht und die Verpackung "dual ovenable" (= Mikrowellen- und Backofen fähig) sein. Auf Grund der im Backofen vorherrschenden Temperaturen (bis 220 °C) werden an das Verpackungsmaterial (Menüschale und Deckelfolie) besonders hohe Anforderungen gestellt.

[0003] Sowohl für die Menüschale als auch für die Deckelfolie kommen für "dual ovenable"-Anwendungen nur ausgewählte Materialien in Frage. Typische Materialien für die Menüschalen sind in diesem Fall CPET, Aluminium, mit PET oder mit PET-Folie beschichteter Karton oder Schalen aus APET/CPET. Menüschalen aus APET/CPET (vgl. Figur 1) bestehen außen aus einer CPET-Schicht und innen (d.h. zum Fertigmenü hin) aus einer APET-Schicht. Die dicke kristalline und meist pigmentierte, d. h. mit Partikeln gefüllte CPET-Schicht liefert die Stabilität der Schale, auch bei den vergleichsweise hohen Temperaturen im Backofen. Das amorphe PET verbessert dagegen im Wesentlichen die Haftung der Folie auf der Menüschale.

[0004] Bei "dual ovenable"-Anwendungen wird für die Deckelfolie in der Regel PET verwendet, das selbst bei 220 °C formstabil und fest genug ist. Materialien wie PP oder PE scheiden hier wegen ihrer niedrigen Schmelzpunkte von vornherein aus. Die Anforderungen an die Deckelfolie werden am besten von biaxial orientierter Polyesterfolie erfüllt.

[0005] Bei der Zubereitung des Fertiggerichtes im Ofen wird die Polyesterfolie kurz vor der Erhitzung oder kurz nach der Erhitzung von der Menüschale mit der Hand abgezogen. Hierbei darf die Polyesterfolie auf keinen Fall ein- bzw. ein- und weiter- oder abreißen. Das Abziehen der Folie von der Menüschale, ohne dass dabei die Folie ein-, weiter- oder abreißt, wird in der Lebensmittelbranche auch mit "Peelen" bezeichnet. Für diese Anwendung muss die Polyesterfolie daher nicht nur heißsiegelbar, sondern insbesondere auch peelfähig sein. Bei vorgegebenem Material und vorgegebener Gesamtdicke der Folie wird die Peelfähigkeit der Folie hauptsächlich von den Eigenschaften der Oberflächenschicht der Folie, die auf der Menüschale gesiegelt ist, bestimmt.

[0006] Die Peelfähigkeit von Folien lässt sich labormäßig relativ einfach mit einem Spannungs-Dehnungstester (z. B. Zwick) feststellen (vgl. Figur 2). Für diesen Test werden zunächst aus der Polyesterfolie und der Menüschale zwei 15 mm breite und ca. 50 mm lange Streifen ausgeschnitten und gegeneinander gesiegelt. Die gesiegelten Streifen werden - wie in der Figur 2 dargestellt - in die Kluppen des Testers eingespannt. Der "Winkel" zwischen der in der oberen Kluppe eingespannten Folie und dem Menüschalenstreifen beträgt 180°. Bei diesem Test werden die Kluppen des Testers mit einer Geschwindigkeit von 200 mm/min auseinander gefahren, wobei die Folie im günstigsten Fall von der Menüschale vollständig abgeschält wird (in Anlehnung an ASTM-D 3330).

[0007] Bei diesem Test ist im Wesentlichen zwischen zwei unterschiedlichen Mechanismen zu unterscheiden.

[0008] Im ersten Fall steigt beim Ziehvorgang die Zugkraft schnell bis zu einem Maximum an (vgl. Figur 3a) und fällt danach direkt wieder auf Null zurück. Beim Erreichen der Maximalkraft reißt die Folie ein oder vor dem Delaminieren von der Menüschale ab, wodurch die Kraft sofort wieder auf Null zurückgeht. Die Folie ist in diesem Fall nicht peelfähig, da sie zerstört wird. Das Verhalten der Folie lässt sich eher als eine Art "Verschweißen" (engl. weldable) mit der Menüschale beschreiben. Die Zerstörung der Folie beim Abziehen von der Menüschale ist unerwünscht, weil damit das saubere und leichte Öffnen der Verpackung (engl. easy opening) ohne Werkzeuge wie Schere oder Messer erschwert wird.

[0009] Eine peelfähige Folie wird dagegen erhalten, wenn die Zug- oder die Schälkraft bis zu einem bestimmten Wert (bzw. bis zu einem bestimmten Plateau) ansteigt und dann über die Strecke, über die die beiden Streifen miteinander gesiegelt sind, in etwa konstant bleibt (vgl. Figur 3b). In diesem Fall reißt die Folie nicht ein, sondern lässt sich wie gewünscht von der Menüschale mit geringem Kraftaufwand abschälen (engl. peelen).

[0010] Die Höhe der Peelkraft wird in erster Linie von den in der Siegelschicht (A) verwendeten Polymeren bestimmt (vgl. Figur 4, Polymer 1 und Polymer 2). Daneben ist die Höhe der Peelkraft insbesondere abhängig von der angewandten Heißsiegeltemperatur. Die Peelkraft steigt in der Regel mit der Heißsiegeltemperatur an. Mit zunehmender Heißsiegeltemperatur wächst dabei die Gefahr, dass die Siegelschicht ihre Peelfähigkeit verliert. D. h. eine Folie, die bei Anwendung einer geringen Heißsiegeltemperatur peelfähig ist, verliert diese Eigenschaft, wenn eine genügend hohe Heißsiegeltemperatur angewendet wird. Dieses Verhalten ist insbesondere bei Polymeren zu erwarten, die die in Figur 4 für Polymer

1 gezeigte Charakteristik aufzeigen. Diesem tendenziell allgemeingültigen aber für die Anwendung eher ungünstigen Verhalten muss bei der Gestaltung der Siegelschicht Rechnung getragen werden. Die Folie muss in einem genügend großen Temperaturbereich heißgesiegelt werden können, ohne dass dabei die gewünschte Peelfähigkeit verloren geht (vgl. Polymer 2 in Figur 4). In der Praxis beträgt dieser Temperaturbereich im Allgemeinen 150 bis 220 °C, bevorzugt 150 bis 200 °C und besonders bevorzugt 150 bis 190 °C.

[00111] Die heißsiegelbare und peelfähige Schicht wird nach dem Stand der Technik in der Regel mittels so genannter off-line-Methoden (d. h. in einem zusätzlichen, der Folienherstellung nachgeordneten Prozessschritt) auf die Polyesterfolie aufgebracht. Bei dieser Methode wird zunächst eine "Standardpolyesterfolie" nach einem üblichen Verfahren hergestellt. Die so hergestellte Polyesterfolie wird dann in einem weiteren Verarbeitungsschritt in einer Beschichtungsanlage "off-line" mit einer heißsiegelbaren und peelfähigen Schicht beschichtet. Bei diesem Verfahren wird das heißsiegelbare und peelfähige Polymer zunächst in einem organischen Lösungsmittel aufgelöst. Die fertige Lösung wird dann über ein geeignetes Antragsverfahren (Messergießer, Rasterwalze, Düse) auf die Folie appliziert. In einem nachgeschalteten Trockenofen wird das Lösungsmittel verdunstet und das peelfähige Polymer bleibt als feste Schicht auf der Folie zurück.

[0012] Solch ein off-line-Antrag der Siegelschicht ist aus mehreren Gründen vergleichsweise kostspielig. Erstens muss die Beschichtung der Folie in einem separaten Schritt in einer speziellen Apparatur erfolgen. Zweitens muss das verdampfte Lösemittel wieder kondensiert und rückgewonnen werden, um somit die Umwelt über die Abluft möglichst wenig zu belasten. Drittens ist ein großer Kontrollaufwand erforderlich, um sicherzustellen, dass der Restlösemittelgehalt in der Beschichtung möglichst gering ist.

[0013] Außerdem kann in einem wirtschaftlichen Verfahren das Lösemittel nie vollständig während der Trocknung aus der Beschichtung entfernt werden, insbesondere weil der Trocknungsvorgang nicht beliebig lang sein kann. In der Beschichtung verbleibende Spuren des Lösemittels migrieren anschließend über die auf dem Tray befindliche Folie in die Speisen, wo sie den Geschmack verfälschen oder sogar den Konsumenten gesundheitlich schädigen können.

[0014] Auf dem Markt werden verschiedene off-line hergestellte peelfähige heißsiegelbare Polyesterfolien angeboten. Die Polyesterfolien unterscheiden sich im Aufbau und in der Zusammensetzung der Deckschicht (A). Sie gelangen entsprechend ihrer (Peel)-Eigenschaften in unterschiedliche Anwendungen. Es ist z. B. üblich, die Folien von Seiten der Anwendung in Folien mit leichter Peelbarkeit (easy peel), mit fester Peelbarkeit (medium peel) und mit starker, widerstandsfähiger Peelbarkeit (strong peel) zu unterteilen. Wesentliches quantifizierbares Unterscheidungsmerkmal zwischen diesen Folien ist die Höhe der jeweiligen Peelkraft entsprechend der Figur 3b. Eine Einteilung wird an dieser Stelle wie folgt vorgenommen:

Leichte Peelbarkeit (easy peel)	Peelkraft im Bereich von ungefähr 1 bis 4 N je 15 mm Streifenbreite
Feste Peelbarkeit (medium peel)	Peelkraft im Bereich von ungefähr 3 bis 8 N je 15 mm Streifenbreite
Starke, widerstandsfähige Peelbarkeit (strong peel)	Peelkraft im Bereich von mehr als 5 N je 15 mm Streifenbreite

[0015] Einige siegelbare PET-Folien sind bereits bekannt.

[0016] In der EP-A 0 035 835 wird eine coextrudierte siegelfähige Polyesterfolie beschrieben, der zur Verbesserung des Wickel- und des Verarbeitungsverhaltens in der Siegelschicht Partikel beigelegt werden, deren mittlere Teilchengröße die Schichtdicke der Siegelschicht übersteigt. Das Polymer der Versiegelungsfolienschiicht ist im Wesentlichen ein Polyester-copolymer, das auf Basis von aromatischen Dicarbonsäuren sowie aliphatischen Diolen aufgebaut ist. Durch die teilchenförmigen Zusatzstoffe werden Oberflächenvorsprünge gebildet, die ein unerwünschtes Blocken und Kleben der Folie an Walzen oder Führungen verhindern. Durch Wahl von Partikeln mit größerem Durchmesser als die Siegelschicht wird das Siegelverhalten der Folie verschlechtert. Angaben zum Siegeltemperaturbereich der Folie werden in der Schrift nicht gemacht. Die Siegelnahtfestigkeit wird bei 140 °C gemessen und liegt in einem Bereich von 63 bis 120 N/m (entsprechend 0,97 bis 1,8 N/15 mm Folienbreite). Über das Peelverhalten der Folie gegen Menüschen aus APET, CPET und APET/CPET finden sich in der Schrift keine Hinweise.

[0017] In der EP-A 0 379 190 wird eine coextrudierte, biaxial orientierte Polyesterfolie beschrieben, die eine Trägerfolienschiicht aus Polyester und mindestens eine Versiegelungsfolienschiicht aus einer Polyester-Zusammensetzung umfasst. Die Versiegelungsfolienschiicht kann aliphatische und aromatische Dicarbonsäuren sowie aliphatische Dirole enthalten. Das Polymer für die Versiegelungsfolienschiicht enthält zwei unterschiedliche Polyester A und B, von denen zumindest einer (Polyester B) aliphatische Dicarbonsäuren und/oder aliphatische Dirole enthält. Die Versiegelungsenergie, die zwischen zwei sich gegenüberliegenden, miteinander verbundenen Versiegelungsfolienschiichten gemessen wird (= fin-Siegelung), beträgt mehr als $400 \text{ g}_{\text{force}} \cdot \text{cm}/15 \text{ mm}$ (mehr als $4 \text{ N} \cdot \text{cm}/15 \text{ mm}$), wobei die Versiegelungsfolienschiicht anorganische und/oder organische feine Teilchen enthalten kann, die im Polyester nicht löslich sind und wobei die feinen Teilchen in einer Menge von 0,1 bis 5 Gew.-% vorhanden sind, bezogen auf das Gesamtgewicht der

Versiegelungsfolienschnitt. In den Beispielen der EP-A 0 379 190 werden organische Partikel - sofern sie überhaupt eingesetzt werden - in Mengen von maximal 0.3 Gew.-% eingesetzt. Die Folie zeichnet sich zwar durch gute Peeleigenschaften (mit Plateau-Charakter im Peeldiagramm [s. o.]) gegen sich selbst aus (d. h. Versiegelungsfolienschnitt gegen Versiegelungsfolienschnitt), über das Peelverhalten gegen Menüschnalen aus APET, CPET und APET/CPET finden sich dort jedoch keine Hinweise. Insbesondere aber ist die Folie gemäß dieser Erfindung verbesserungswürdig in ihrer Herstell- und ihrer Verarbeitbarkeit (die Rohstoffe neigen zum Kleben).

[0018] In der WO A- 96/19333 wird ein Verfahren zur Herstellung peelfähiger Folien beschrieben, bei dem die heißsiegelbare, peelfähige Schicht in-line auf die Polyesterfolie aufgebracht wird. Bei dem Verfahren werden vergleichsweise geringe Mengen von organischen Lösungsmitteln verwendet. Die heißsiegelbare, peelfähige Schicht enthält einen Copolyester, bei dem a) 40 bis 90 Mol-% einer aromatischen Dicarbonsäure, b) 10 bis 60 Mol-% einer aliphatischen Dicarbonsäure, c) 0,1 bis 10 Mol-% einer Dicarbonsäure enthaltend eine freie Säuregruppe oder ein Salz davon, d) 40 bis 90 Mol-% eines Glykols enthaltend 2 bis 12 Kohlenstoffatome und e) 10 bis 60 Mol-% eines Polyalkyldiols zur Bildung des Copolyesters verwendet wurden. Die Beschichtung wird aus einer wässrigen Dispersion oder einer Lösung, die bis zu 10 Gew.-% organisches Lösungsmittel enthält, an die Folie angetragen. Das Verfahren ist hinsichtlich der verwendbaren Polymere und der erzielbaren Schichtdicken für die heißsiegelbare, peelfähige Schicht eingeschränkt. Die maximal erreichbare Schichtdicke wird mit 0,5 µm angegeben. Die maximale Siegelnahtfestigkeit ist gering, sie beträgt 500 bis 600 g/25 mm² bzw. [(500 bis 600)/170] N/15 mm Folienbreite.

[0019] In der WO 02/059186 A1 wird ein Verfahren zur Herstellung peelfähiger Folien beschrieben, bei dem die heißsiegelbare, peelfähige Schicht ebenfalls in-line auf die Polyesterfolie aufgebracht wird. Angewendet wird in diesem Fall die sogenannte Schmelz-Beschichtung (melt-coating), wobei vorzugsweise die längsgestreckte Folie mit dem heißsiegelbaren, peelfähigen Polymer beschichtet wird. Das heißsiegelbare, peelfähige Polymer enthält Polyester auf Basis von aromatischen und aliphatischen Säuren, sowie auf Basis von aliphatischen Diolen. Die in den Beispielen offenbarten Copolymere haben Glasübergangstemperaturen von unter -10 °C; solche Copolyester sind zu weich, weshalb sie sich nicht in üblichen Walzenstreckverfahren orientieren lassen (Kleben an den Walzen). Die Dicke der heißsiegelbaren, peelfähigen Schicht beträgt weniger als 8 µm. In der WO 02/059186 A1 wird die an sich bekannte Schmelz-Beschichtung von der an sich bekannten Extrusions-Beschichtung technisch und über die Viskosität der Schmelze abgegrenzt. Nachteilig an dem Verfahren ist, dass nur vergleichsweise dünnflüssige Polymere (max. 50 Pa*sec) mit niedrigem Molekulargewicht verwendet werden können. Daraus resultieren nachteilige Peel-Eigenschaften der Folie. Außerdem ist bei diesem Verfahren die Beschichtungsgeschwindigkeit limitiert, wodurch der Herstellungsprozess unwirtschaftlich wird. Qualitätsmäßig zeigen sich Mängel bei der Optik der Folie, die z. B. als Beschichtungsstreifen sichtbar werden. Auch ist es bei diesem Verfahren schwierig, eine über die Bahnbreite der Folie gleichmäßige Dicke der Siegel-schicht zu erhalten, was wiederum zu einer ungleichmäßigen Peelcharakteristik führt.

[0020] Aufgabe der vorliegenden Erfindung war es, eine coextrudierte, heißsiegelbare und peelfähige, biaxial orientierte Polyesterfolie zur Verfügung zu stellen, die sich durch hervorragende Peeleigenschaften gegenüber Menüschnalen auszeichnet, insbesondere gegenüber der APET-Seite von Menüschnalen aus APET/CPET. Sie soll die Nachteile der Folien nach dem Stand der Technik nicht mehr aufweisen und sich insbesondere dadurch auszeichnen, dass

- sie gegenüber der APET-Seite von Menüschnalen aus APET/CPET eine leichte bis feste Peelbarkeit (easy peel bis strong peel) zeigt; die Peelkraft soll im Bereich von 1,7 bis 8 N je 15 mm, bevorzugt im Bereich von 2,0 bis 8 N je 15 mm und besonders bevorzugt im Bereich von 2,3 bis 8 N je 15 mm Folienstreifenbreite liegen;
- in der heißsiegelbaren und peelfähigen Schicht keine organischen Lösemittelrückstände enthalten sind;
- die heißsiegelbare und peelfähige Schicht gegenüber der APET-Seite von APET/CPET-Menüschnalen eine Mindestsiegeltemperatur von 150 °C, bevorzugt 140 °C, insbesondere 130 °C, aufweist und wobei die max. Siegeltemperatur im Allgemeinen 220 °C, bevorzugt 200 °C und besonders bevorzugt 190 °C beträgt;
- bei ihrer Herstellung Verfahren angewendet werden, bei denen von vornherein keine organischen Lösemittel verwendet werden;
- sich die Folie wirtschaftlich herstellen lässt; dies bedeutet beispielsweise auch, dass zur Herstellung der Folie in der Industrie übliche Streckverfahren eingesetzt werden können; weiterhin sollte die Folie bei heute üblichen Maschinengeschwindigkeiten bis zu 500 m/min herstellbar sein;
- eine gute Haftung (größer als 2 N/15 mm Folienbreite) zwischen den einzelnen Schichten der Folie für deren praktische Anwendung gewährleistet ist;
- die optischen Eigenschaften der Folie gut sind; dies bedeutet beispielsweise eine niedrige Trübung (kleiner als 25 %) und ein hoher Glanz (> 70 für die siegelfähige Seite und > 100 für die der siegelfähigen gegenüberliegende Seite; jeweils bei 20° Einstrahlwinkel) der Folie;
- bei der Herstellung der Folie gewährleistet ist, dass das Regenerat in einer Menge von bis zu 60 Gew.-% wieder der Extrusion zugeführt werden kann, ohne dass dabei die physikalischen (die Reißfestigkeit der Folie in beiden Richtungen sollte nicht um mehr als 10 % abnehmen), insbesondere aber die optischen Eigenschaften der Folie nennenswert negativ beeinflusst werden.

[0021] Außerdem soll dafür Sorge getragen werden, dass die Folie auf schnelllaufenden Maschinen verarbeitet werden kann. Andererseits sollten sich gleichzeitig die bekannten, Polyesterfolien auszeichnende Eigenschaften nicht verschlechtern. Hierzu gehören beispielsweise die mechanischen (der E-Modul der biaxial gestreckten Folien sollte in beiden Orientierungsrichtungen größer als 3000 N/mm², bevorzugt größer als 3500 N/mm² und besonders bevorzugt größer als 4000 N/mm² sein) und die thermischen Eigenschaften (der Schrumpf der biaxial gestreckten Folien sollte in beiden Orientierungsrichtungen nicht größer als 3 %, bevorzugt nicht größer als 2,8 % und besonders bevorzugt nicht größer als 2,5 % sein), das Wickelverhalten und die Verarbeitbarkeit der Folie, insbesondere bei der Bedruckung, Kaschierung oder bei der Beschichtung der Folie mit metallischen oder keramischen Materialien.

[0022] Unter heißsiegelbar wird hier die Eigenschaft einer coextrudierten, mehrschichtigen, mindestens eine Basisschicht (B) enthaltenden Polyester-Folie verstanden, die zumindest eine Deckschicht (= heißsiegelbare Deckschicht) enthält, die mittels Siegelbacken durch Anwendung von Wärme (140 bis 220 °C) und Druck (2 bis 5 bar) in einer bestimmten Zeit (0,2 bis 2 sec) mit sich selbst (Fin-Siegelung) bzw. mit einem Substrat aus thermoplastischem Kunststoff (= Lab-Siegelung, hier insbesondere die APET-Seite von APET/CPET-Menüschalen) verbunden werden kann, ohne dass dabei die Trägerschicht (= Basisschicht) selbst plastisch wird. Um dies zu erreichen, besitzt das Polymer der Siegelschicht im Allgemeinen einen deutlich niedrigeren Schmelzpunkt als das Polymer der Basisschicht. Wird als Polymer für die Basisschicht beispielsweise Polyethylenterephthalat mit einem Schmelzpunkt von 254 °C verwendet, so beträgt der Schmelzpunkt der heißsiegelbaren Schicht im Allgemeinen weniger als 230 °C, im vorliegenden Fall bevorzugt weniger als 210 °C und besonders bevorzugt weniger als 190 °C.

[0023] Unter peelfähig wird hier die Eigenschaft einer coextrudierten Polyester-Folie verstanden, die zumindest eine Schicht (= heißsiegelbare und peelfähige Deckschicht) enthält, die nach der Heißsiegelung auf ein Substrat (hier im Wesentlichen die APET-Seite einer APET/CPET-Schale) derart wieder von dem Substrat abgezogen werden kann, dass dabei die Folie weder ein- noch abreißt. Der Verbund aus heißsiegfähiger Folie und Substrat geht beim Abziehen der Folie von dem Substrat in der Naht zwischen der Heißsiegelschicht und der Substratoberfläche auf (vgl. auch Ahlhaus, O.E.: Verpackung mit Kunststoffen, Carl Hanser Verlag, S. 271, 1997, ISBN 3-446-17711-6). Beim Abziehen der auf einen Teststreifen des Substrates heißgesiegelten Folie in einem Zug-Dehnungs-Prüfgerät unter einem Schälwinkel von 180° entsprechend Figur 2 wird dann ein Reiß-Dehnverhalten der Folie gemäß Figur 3b erhalten. Bei Beginn des Abschälens der Folie von dem Substrat steigt die dazu erforderliche Kraft gemäß Figur 3b bis zu einem bestimmten Wert (z. B. 4 N/15 mm) an und bleibt dann über den gesamten Schälweg in etwa konstant, ist allerdings mit mehr oder weniger großen Schwankungen behaftet (ca. +/- 20 %).

[0024] Gelöst wird die Aufgabe durch die Bereitstellung einer coextrudierten, transparenten, biaxial orientierten Polyesterfolie, enthaltend eine Basisschicht (B) und eine heißsiegelbare und zumindest gegenüber APET peelfähige Deckschicht (A), wobei die heißsiegelbare und peelfähige Deckschicht (A) aus

a) 60- 97 Gew.-% Polyester und

b) 3-30 Gew.-% eines polyesterunverträglichen Polymers (= anti-PET-Polymer), bezogen auf die Masse der Deckschicht (A), besteht, wobei

c) der Polyester aus 25-95 Mol-% an Einheiten aufgebaut ist, die auf mindestens eine aromatische Dicarbonsäure, und 5-75 Mol-% an Einheiten, die auf mindestens eine aliphatische Dicarbonsäure zurückgehen, wobei die Summe der dicarbonsäureabgeleiteten Molprozentage 100 ergibt, und

d) die Schichtdicke der Deckschicht (A) d_A 0,7 bis 2,5 μm beträgt.

[0025] Das Material der Deckschicht (A) besteht also überwiegend aus einem Polyester und einem polyesterunverträglichen Polymer (anti-PET-Polymer). Der Polyester ist aufgebaut aus Einheiten, die von aromatischen und aliphatischen Dicarbonsäuren abgeleitet sind. Die auf die aromatischen Dicarbonsäuren zurückgehenden Einheiten sind in dem Polyester in einer Menge von 25-95 Mol-%, bevorzugt 40-90 Mol-%, besonders bevorzugt 50-88 Mol-%, enthalten. Die auf die aliphatischen Dicarbonsäuren zurückgehenden Einheiten sind in dem Polyester in einer Menge von 5-75 Mol-%, bevorzugt 10-60 Mol-%, besonders bevorzugt 12-50 Mol-%, enthalten, wobei die Mol-%-Angaben sich immer zu 100 % ergänzen. Die hierzu korrespondierenden Diol-Einheiten ergeben ebenfalls immer 100 Mol-%.

[0026] Bevorzugte aliphatische Dicarbonsäuren sind Pimelinsäure, Korksäure, Azelainsäure, Sebazinsäure, Glutarsäure und Adipinsäure. Insbesondere bevorzugt sind die Azelainsäure, die Sebazinsäure und die Adipinsäure.

[0027] Bevorzugte aromatische Dicarbonsäuren sind Terephthalsäure, Isophthalsäure und 2,6-Naphthalindicarbonsäure, insbesondere Terephthalsäure und Isophthalsäure.

[0028] Bevorzugte Diol sind Ethylenglykol, Butylenglykol und Neopentylglykol.

[0029] Im Allgemeinen beinhaltet der Polyester die folgenden Dicarboxylate und Alkylene, jeweils bezogen auf die Gesamtdicarboxylat- bzw. Gesamtalkylenmenge:

- 25 bis 95 Mol-%, bevorzugt 30 bis 90 Mol-% und besonders bevorzugt 40 bis 70 Mol-% Terephthalat,
- 0 bis 25 Mol-%, bevorzugt 5 bis 20 Mol-% und besonders bevorzugt 10 bis 20 Mol-% Isophthalat,

- 5 bis 75 Mol.-%, bevorzugt 8 bis 70 Mol.-% und besonders bevorzugt 11 bis 65 Mol.-% Azelat,
- 0 bis 50 Mol.-%, bevorzugt 0 bis 40 Mol.-% und besonders bevorzugt 0,2 bis 30 Mol.-% Sebazat,
- 0 bis 50 Mol.-%, bevorzugt 0 bis 40 Mol.-% und besonders bevorzugt 0 bis 30 Mol.-% Adipat;
- mehr als 30 Mol.-%, bevorzugt mehr als 40 Mol.-% und besonders bevorzugt mehr als 50 Mol.-% Ethylen oder Butylen.

[0030] 3-30 Gew.-%, bevorzugt 5-25 Gew.-% und besonders bevorzugt 7-20 Gew.-% des Deckschichtmaterials besteht aus einem Polymer, welches mit Polyester unverträglich ist (anti-PET-Polymer).

[0031] 0 bis zu 10 Gew.-% des Materials der Deckschicht (A) besteht aus Partikeln, Additiven, Hilfsmitteln und/oder sonstigen in der Polyesterfolientechnologie üblicherweise verwendeten Zusatzstoffen.

[0032] Es hat sich als zweckmäßig erwiesen, den Hauptpolyester der Deckschicht (A) aus zwei getrennten Polyestern I und II herzustellen, die dem Extruder für diese Schicht als Mischung zugeführt werden.

[0033] Die heißsiegelbare und peelfähige Deckschicht (A) zeichnet sich durch charakteristische Merkmale aus. Sie besitzt eine Siegelanspringtemperatur (= Mindestsiegeltemperatur) gegenüber der APET-Seite von APET/CPET-Menüschalen von nicht mehr als 150 °C, bevorzugt nicht mehr als 140 °C und besonders bevorzugt nicht mehr als 130 °C, und eine Siegelnahtfestigkeit gegenüber der APET-Seite von APET/CPET-Menüschalen von mindestens 1,7 N, bevorzugt mindestens 2,0 N, besonders bevorzugt mindestens 2,3 N (immer bezogen auf 15 mm Folienbreite). Die heißsiegelbare und peelfähige Deckschicht (A) hat gegenüber der APET-Seite von APET/CPET-Menüschalen eine max. Siegeltemperatur von im Allgemeinen 220 °C, bevorzugt 200 °C und besonders bevorzugt 190 °C, wobei im gesamten Siegelbereich eine gegenüber der APET-Seite von APET/CPET-Menüschalen peelfähige Folie erhalten wird. D. h. mit dieser Folie wird beim 180°-Zugversuch gemäß Figur 2 eine Kurve gemäß Figur 3b erhalten.

[0034] Für die bevorzugten, oben angegebenen Bereiche lassen sich die Peelergebnisse auch zahlenmäßig beschreiben. Entsprechend den vorliegenden experimentellen Untersuchungen können die Peelergebnisse einfach durch folgenden Zusammenhang zwischen der Siegeltemperatur (ϑ in °C) und der Peelkraft (in N/15 mm) miteinander korreliert werden:

$$0,02 \cdot \vartheta / ^\circ\text{C} - 0,8 \leq \text{Peelkraft } F / \text{N je } 15 \text{ mm} \leq 0,033 \cdot \vartheta / ^\circ\text{C} + 1,4$$

[0035] Dieser Zusammenhang ist graphisch zur Veranschaulichung in Figur 5 dargestellt.

[0036] Die Folie nach der vorliegenden Erfindung enthält eine Basisschicht (B) und mindestens eine erfindungsgemäße Deckschicht (A). In diesem Fall ist die Folie zweischichtig aufgebaut. In einer bevorzugten Ausführungsform ist die Folie drei- oder mehr als dreischichtig aufgebaut. Im Falle der besonders bevorzugten dreischichtigen Ausführungsform besteht sie dann aus der Basisschicht (B), der erfindungsgemäßen Deckschicht (A) und einer der Deckschicht (A) gegenüberliegenden Deckschicht (C). Bei einer vierschichtigen Ausführungsform enthält die Folie eine Zwischenschicht (D) zwischen der Basisschicht (B) und der Deckschicht (A) oder (C).

[0037] Die Basisschicht der Folie besteht zu mindestens zu 80 Gew.-% aus thermoplastischem Polyester. Dafür geeignet sind Polyester aus Ethylenglykol und Terephthalsäure (= Polyethylenterephthalat, PET), aus Ethylenglykol und Naphthalin-2,6-dicarbonsäure (= Polyethylen-2,6-naphthalat, PEN), aus 1,4-Bis-hydroxymethyl-cyclohexan und Terephthalsäure (= Poly-1,4-cyclohexandimethylenterephthalat, PCDT) sowie aus Ethylenglykol, Naphthalin-2,6-dicarbonsäure und Biphenyl-4,4'-dicarbonsäure (= Polyethylen-2,6-naphthalatbibenzoat, PENBB). Bevorzugt sind Ethyleneinheiten enthaltende Polyester, die - bezogen auf die Dicarboxylateinheiten - aus mindestens 90 Mol.-%, besonders bevorzugt mindestens 95 Mol.-%, Terephthalat- oder 2,6-Naphthalat-Einheiten bestehen. Die restlichen Monomereinheiten stammen aus anderen Dicarbonsäuren bzw. Diolen. In vorteilhafter Weise können für die Basisschicht (B) auch Copolymere oder Mischungen oder Blends aus den genannten Homo- und/oder Copolymeren verwendet werden. (Bei der Angabe der Mengen für die Dicarbonsäuren bildet die Gesamtmenge aller Dicarbonsäuren 100 Mol.-%. Analog bildet die Gesamtmenge aller Dirole auch 100 Mol.-%.)

[0038] Geeignete andere aromatische Dicarbonsäuren sind bevorzugt Benzoldicarbonsäuren, Naphthalindicarbonsäuren (beispielsweise Naphthalin-1,4- oder 1,6-dicarbonsäure), Biphenyl-x,x'-dicarbonsäuren (insbesondere Biphenyl-4,4'-dicarbonsäure), Diphenylacetylen-x,x'-dicarbonsäuren (insbesondere Diphenylacetylen-4,4'-dicarbonsäure) oder Stilben-x,x'-dicarbonsäuren. Von den cycloaliphatischen Dicarbonsäuren sind Cyclohexandicarbonsäuren (insbesondere Cyclohexan-1,4-dicarbonsäure) zu nennen. Von den aliphatischen Dicarbonsäuren sind die ($\text{C}_3\text{-C}_{19}$) Alkandisäuren besonders geeignet, wobei der Alkanteil geradkettig oder verzweigt sein kann.

[0039] Geeignete andere aliphatische Dirole sind beispielsweise Diethylenglykol, Triethylenglykol, aliphatische Glykole der allgemeinen Formel $\text{HO}-(\text{CH}_2)_n\text{-OH}$, wobei n eine ganze Zahl von 3 bis 6 darstellt (insbesondere Propan-1,3-diol, Butan-1,4-diol, Pentan-1,5-diol und Hexan-1,6-diol), oder verzweigte aliphatische Glykole mit bis zu 6 Kohlenstoff-Atomen, cycloaliphatische, gegebenenfalls heteroatomhaltige Dirole mit einem oder mehreren Ringen. Von den cycloaliphatischen Diolen sind Cyclohexandiole (insbesondere Cyclohexan-1,4-diol) zu nennen. Geeignete andere aromatische

Dirole entsprechen beispielsweise der Formel $\text{HO}-\text{C}_6\text{H}_4-\text{X}-\text{C}_6\text{H}_4-\text{OH}$, wobei X für $-\text{CH}_2-$, $-\text{C}(\text{CH}_3)_2-$, $-\text{C}(\text{CF}_3)_2-$, $-\text{O}-$, $-\text{S}-$ oder $-\text{SO}_2-$ steht. Daneben sind auch Bisphenole der Formel $\text{HO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{OH}$ gut geeignet.

[0040] Besonders vorteilhaft ist es, wenn in der Basisschicht (B) ein Polyester-Copolymer auf Basis von Terephthalat und geringen Mengen (< 5 Mol-%) Isophthalsäure oder auf Basis von Terephthalat und geringen Mengen (< 5 Mol-%) Naphthalin-2,6-dicarbonsäure verwendet wird. In diesem Fall sind die Herstellbarkeit der Folie und die optischen Eigenschaften der Folie besonders gut. Die Basisschicht (B) enthält dann im Wesentlichen ein Polyester Copolymeres, das überwiegend aus Terephthalsäure- und Isophthalsäure-Einheiten und/oder Terephthalsäure- und Naphthalin-2,6-dicarbonsäure-Einheiten und aus Ethylenglykol-Einheiten zusammengesetzt ist. Die besonders bevorzugten Copolyester, die die gewünschten Eigenschaften der Folie bereitstellen, sind solche, die aus Terephthalat- und Isophthalat-Einheiten und aus Ethylenglykol-Einheiten aufgebaut sind.

[0041] Die Herstellung der Polyester kann nach dem Umesterungsverfahren erfolgen. Dabei geht man von Dicarbonsäureestern und Diolen aus, die mit den üblichen Umesterungskatalysatoren, wie Zink-, Calcium-, Lithium- und Mangan-Salzen, umgesetzt werden. Die Zwischenprodukte werden dann in Gegenwart allgemein üblicher Polykondensationskatalysatoren, wie Antimontrioxid, Titanoxide oder Ester sowie Germanium-Verbindungen, polykondensiert. Die Herstellung kann ebenso gut nach dem Direktveresterungsverfahren in Gegenwart von Polykondensationskatalysatoren erfolgen. Dabei geht man direkt von den Dicarbonsäuren und den Diolen aus.

[0042] Die Folie nach der vorliegenden Erfindung ist zumindest zweischichtig aufgebaut. Sie besteht dann aus der Basisschicht (B) und der auf dieser durch Coextrusion aufgetragenen erfindungsgemäßen siegelbaren und peelfähigen Deckschicht (A).

[0043] Die durch Coextrusion auf die Basisschicht (B) aufgetragene siegelbare und peelfähige Deckschicht (A) ist überwiegend, d. h. zu mindestens ca. 60 Gew.-% aus Polyestern aufgebaut.

[0044] Erfindungsgemäß enthält die heißsiegelbare und peelfähige Deckschicht (A) Polyester auf Basis von aromatischen und aliphatischen Säuren und bevorzugt aliphatischen Diolen. Des Weiteren enthält die Deckschicht (A) ein zu Polyester unverträgliches Polymer (anti-PET-Polymer) in einer Konzentration von 3-30 Gew.-%.

[0045] Unter den Polyestern werden in der bevorzugten Ausführungsform Copolyester oder Blends aus Homo- und Copolyester oder Blends aus verschiedenen Copolyestern verstanden, die auf Basis von aromatischen und aliphatischen Dicarbonsäuren und aliphatischen Diolen aufgebaut sind.

[0046] Beispiele für die erfindungsgemäß einsetzbaren aromatischen Dicarbonsäuren sind die Terephthalsäure, die Isophthalsäure, die Phthalsäure und die 2,6-Naphthalindicarbonsäure.

[0047] Beispiele für die erfindungsgemäß einsetzbaren aliphatischen Dicarbonsäuren sind die Bernsteinsäure, die Glutarsäure, die Adipinsäure, die Pimelinsäure, die Korksäure, die Azelainsäure und die Sebazinsäure.

[0048] Beispiele für die erfindungsgemäß einsetzbaren aliphatischen Dirole sind Ethylenglykol, 1,3-Propandiol, 1,3-Butandiol, 1,4-Butandiol, 1,5-Pentandiol, 2,2-Dimethyl-1,3-Propandiol, Diethylenglykol, Triethylenglykol und 1,4-Cyclohexandimethanol.

[0049] Der Polyester für die Deckschicht (A) wird bevorzugt aus zwei Polyestern I und II hergestellt.

[0050] Der Anteil des Polyesters I, der aus einem oder mehreren aromatischen Dicarboxylaten und einem oder mehreren aliphatischen Alkylenen besteht, in der Deckschicht (A) beträgt 10 bis 60 Gew.-%. In der bevorzugten Ausführungsform beträgt der Anteil des Polyesters I 15 bis 55 Gew.-%, und in der besonders bevorzugten Ausführungsform beträgt er 20 bis 50 Gew.-%.

[0051] Im Allgemeinen basiert der Polyester I der erfindungsgemäßen Deckschicht (A) auf den folgenden Dicarboxylaten und Alkylenen, jeweils bezogen auf die Gesamtdicarboxylat- bzw. Gesamtalkylenmenge:

- 70 bis 100 Mol-%, bevorzugt 72 bis 95 Mol-% und besonders bevorzugt 74 bis 93 Mol-% Terephthalat,
- 0 bis 30 Mol-%, bevorzugt 5 bis 28 Mol-% und besonders bevorzugt 7 bis 26 Mol-% Isophthalat,
- mehr als 50 Mol-%, bevorzugt mehr als 65 Mol-% und besonders bevorzugt mehr als 80 Mol-% Ethyleneinheiten.

[0052] Eventuell vorhandene restliche Anteile stammen von anderen aromatischen Dicarbonsäuren und anderen aliphatischen Diolen, wie sie bereits zuvor für die Basisschicht (B) als Haupt- und Nebencarbonsäuren aufgelistet worden sind.

[0053] Ganz besonders bevorzugt sind solche Copolyester, bei denen der Anteil an Terephthalat-Einheiten 74 bis 88 Mol-%, der entsprechende Anteil an Isophthalat-Einheiten 12 bis 26 Mol-% (wobei die Dicarboxylatanteile sich zu 100 Mol-% ergänzen) und der Anteil an Ethyleneinheiten 100 Mol-% beträgt. D. h. es handelt sich um Polyethylen-terephthalat/isophthalat.

[0054] In einer weiteren bevorzugten Ausführungsform besteht der Polyester I aus einer Mischung, welche einen Copolyester, aufgebaut aus Terephthalat-, Isophthalat- und aus Ethylen-Einheiten und ein aromatisches Polyesterhomopolymeres, z. B. ein Polybutylenterephthalat, enthält.

[0055] Es wurde gefunden, dass für den Fall, wo der Anteil an Polyester I in der Deckschicht (A) weniger als 10 Gew.-% beträgt, die Herstellbarkeit der Folie über die Coextrusionstechnologie deutlich erschwert bzw. nicht mehr gewährleistet

ist. Die Tendenz der Folie, an bestimmten Maschinenteilen zu kleben, insbesondere an mitlaufenden, metallischen Walzen in der Längsstreckung und nach der Querstreckung, ist hier besonders hoch. Beträgt demgegenüber andererseits der Anteil an Polyester I in der Deckschicht (A) mehr als 60 Gew.-%, so wird das Peelverhalten der Folie stark beeinträchtigt. Das Siegelverhalten der Folie ändert sich in diesem Fall von "peelable" zu "weldable".

[0056] Entsprechend der vorliegenden Erfindung beträgt der Anteil von Polyester II in der Deckschicht (A) 20 bis 70 Gew.-%. In der bevorzugten Ausführungsform beträgt der Anteil von Polyester II 25 bis 65 Gew.-%, und in der besonders bevorzugten Ausführungsform beträgt er 30 bis 60 Gew.-%.

[0057] Bevorzugt besteht der Polyester II aus einem Copolymeren aus aliphatischen und aromatischen Säurekomponenten, bei welchem die aliphatischen Säurekomponenten 20 bis 90 Mol-%, bevorzugt 30 bis 70 Mol-% und besonders bevorzugt 35 bis 60 Mol-% betragen, bezogen auf die Gesamtsäuremenge des Polyesters II. Der zu 100 Mol-% fehlende Dicarboxylatanteil stammt von aromatischen Säuren, bevorzugt der Terephthalsäure und/oder der Isophthalsäure, sowie auf der glykolischen Seite von aliphatischen oder cycloaliphatischen oder aromatischen Diolen, wie sie bereits oben bezüglich der Basisschicht ausführlich beschrieben wurden.

[0058] Im Allgemeinen basiert der Polyester II der erfindungsgemäßen Deckschicht (A) zumindest auf den folgenden Dicarboxylaten und Alkylenen, jeweils bezogen auf die Gesamtdicarboxylat- bzw. Gesamtalkylenmenge:

- 20 bis 65 Mol-%, bevorzugt 30 bis 70 Mol-% und besonders bevorzugt 35 bis 60 Mol-% Azelat,
- 0 bis 50 Mol-%, bevorzugt 0 bis 45 Mol-% und besonders bevorzugt 0 bis 40 Mol-% Sebazat,
- 0 bis 50 Mol-%, bevorzugt 0 bis 45 Mol-% und besonders bevorzugt 0 bis 40 Mol-% Adipat,
- 10 bis 80 Mol-%, bevorzugt 20 bis 70 Mol-% und besonders bevorzugt 30 bis 60 Mol-% Terephthalat,
- 0 bis 30 Mol-%, bevorzugt 3 bis 25 Mol-% und besonders bevorzugt 5 bis 20 Mol-% Isophthalat,
- mehr als 30 Mol-%, bevorzugt mehr als 40 Mol-% und besonders bevorzugt mehr als 50 Mol-% Ethylen oder Butylen.

[0059] Eventuell vorhandene restliche Anteile stammen von anderen aromatischen Dicarbonsäuren und anderen aliphatischen Diolen, wie sie bereits zuvor für die Basisschicht (B) als Haupt- und Nebencarbonsäuren aufgelistet worden sind, oder auch von Hydroxycarbonsäuren wie Hydroxybenzoesäure o. ä..

[0060] Durch das Vorhandensein von mindestens 10 Mol-% aromatischer Dicarbonsäure wird gewährleistet, dass das Polymer II ohne Verklebungen z. B. im Coextruder oder in der Längsstreckung verarbeitbar ist.

[0061] Beträgt der Anteil an Polyester II in der Deckschicht (A) weniger als 20 Gew.-%, so wird das Peelverhalten der Folie stark beeinträchtigt. Das Siegelverhalten der Folie ändert sich in diesem Fall von "peelable" zu "weldable". Beträgt demgegenüber andererseits der Anteil an Polyester II in der Deckschicht (A) mehr als 70 Gew.-%, so wird die Herstellbarkeit der Folie über die Coextrusionstechnologie erschwert bzw. nicht mehr gewährleistet. Die Tendenz der Folie an bestimmten Maschinenteilen zu kleben, insbesondere an mitlaufenden, metallischen Walzen in der Längsstreckung und nach der Querstreckung, ist hier besonders hoch.

[0062] Bevorzugt enthält die Deckschicht (A) eine Mischung aus den Polyestern I und II. Gegenüber der Verwendung von nur einem Polyester mit vergleichbaren Komponenten und vergleichbaren Anteilen der Komponenten weist eine Mischung die folgenden Vorteile auf:

- Die Mischung der beiden Polyester I und II ist von den jeweiligen Glasübergangstemperaturen (T_g) gesehen leichter zu verarbeiten (zu extrudieren). Wie Untersuchungen gezeigt haben, neigt die Mischung aus einem Polymeren mit einem hohen T_g (Polyester I) und einem Polymeren mit einem niedrigen T_g (Polyester II) weniger zum Verkleben im Coextruder als ein einziges Polymer mit einem entsprechend gemischten T_g .
- Die Polymerherstellung ist einfacher, weil man in der Regel nicht beliebig viel Dosierstationen für die Ausgangsstoffe zur Verfügung hat.
- Außerdem können mit der Mischung praktisch gesehen die gewünschten Peeleigenschaften individueller eingestellt werden als bei Einsatz eines einzigen Polyesters.
- Auch die Zugabe von Partikeln (siehe unten) gestaltet sich bei Polyester I einfacher als bei Polyester II.

[0063] Zweckmäßigerweise beträgt die Glasübergangstemperatur von Polyester I mehr als 50 °C. Bevorzugt beträgt die Glasübergangstemperatur von Polyester I mehr als 55 °C und besonders bevorzugt mehr als 60 °C. Ist die Glasübergangstemperatur von Polyester I kleiner als 50 °C, kann die Folie nicht verfahrenssicher hergestellt werden. Die Klebeneigung der Deckschicht (A) z. B. gegenüber Walzen ist dabei so groß, dass mit häufigen Folienabrissen, insbesondere in der Längsstreckung, gerechnet werden muss. Die Folie kann sich dabei um die Walzen in der Längsstreckung wickeln, was zu beträchtlichen Schäden an der Maschine führen kann. Bei der Extrusion verklebt ein solcher Polyester leicht an den metallischen Wänden und führt damit zu Verstopfungen.

[0064] Zweckmäßigerweise beträgt die Glasübergangstemperatur von Polyester II weniger als 20 °C. Bevorzugt beträgt die Glasübergangstemperatur weniger als 15 °C und besonders bevorzugt weniger als 10 °C. Ist die Glasübergangstemperatur von Polyester II größer als 20 °C, so neigt die Folie beim Abziehen von der Menüschale vermehrt zum

Einreißen oder zum Abreißen, was unerwünscht ist.

[0065] Erfindungsgemäß enthält die heißsiegelbare und peelfähige Deckschicht (A) ein mit Polyester unverträgliches Polymer (anti-PET-Polymer) in einer bestimmten Konzentration. Entsprechend der vorliegenden Erfindung beträgt der Anteil des polyesterunverträglichen Polymeren (anti-PET-Polymer) 3 bis 30 Gew.-%, bezogen auf die Masse der Deckschicht (A). In einer bevorzugten Ausführungsform beträgt der Anteil des Polymeren 5 bis 25 Gew.-%, und in der besonders bevorzugten Ausführungsform beträgt er 7 bis 20 Gew.-%, ebenfalls bezogen auf die Masse der Deckschicht (A).

[0066] Beispiele für geeignete unverträgliche Polymere (anti-PET-Polymer) sind Polymere auf Basis von Ethylen (z. B. LLDPE, HDPE), Propylen (PP), Cycloolefinen (CO), Amiden (PA) oder Styrol (PS). In einer bevorzugten Ausführungsform wird als polyesterunverträgliches Polymer (anti-PET-Polymer) ein Copolymeres verwendet. Beispiele hierfür sind Copolymere auf Basis von Ethylen (C2/C3-, C2/C3/C4-Copolymere), Propylen (C2/C3-, C2/C3/C4-Copolymere), Butylen (C2/C3-, C2/C3/C4-Copolymere) oder auf Basis von Cycloolefinen (Norbornen/Ethylen-, Tetracyclododecen/Ethylen-Copolymere). In einer der besonders bevorzugten Ausführungsformen ist das mit Polyester unverträgliche Polymer (anti-PET-Polymer) ein Cycloolefincopolymer (COC). Solche Cycloolefincopolymere sind beispielsweise in der EP-A 1 068 949 oder in der JP 05-009319 allgemein beschrieben, auf die hier Bezug genommen wird.

[0067] Unter den Cycloolefincopolymeren sind insbesondere diejenigen bevorzugt, die polymerisierte Einheiten polycyclischer Olefine mit Norbornengrundstruktur, besonders bevorzugt Norbornen oder Tetracyclododecen, enthalten. Besonders bevorzugt sind Cycloolefincopolymere (COC), die polymerisierte Einheiten acyclischer Olefine, insbesondere Ethylen, enthalten. Ganz besonders bevorzugt sind Norbornen/Ethylen- und Tetracyclododecen/Ethylen-Copolymere, welche 5 bis 80 Gew.-% Ethylen-Einheiten, vorzugsweise 10 bis 60 Gew.-% Ethylen-Einheiten enthalten (bezogen auf die Masse des Copolymeren).

[0068] Die Cycloolefinpolymere weisen im Allgemeinen Glasübergangstemperaturen zwischen -20 und 400 °C auf. Für die Erfindung sind solche Cycloolefincopolymerisate (COC) geeignet, die eine Glasübergangstemperatur von kleiner als 160 °C, bevorzugt kleiner als 120 °C und besonders bevorzugt kleiner als 80 °C aufweisen. Vorzugsweise sollte die Glasübergangstemperatur oberhalb von 50 °C liegen, bevorzugt oberhalb von 55 °C, insbesondere oberhalb von 60 °C. Die Viskositätszahl (Dekalin, 135 °C, DIN 53 728) liegt zweckmäßigerweise zwischen 0,1 und 200 ml/g, bevorzugt zwischen 50 und 150 ml/g. Folien, die ein COC mit einer Glasübergangstemperatur von kleiner als 80 °C enthalten, zeichnen sich gegenüber solchen, die ein COC mit einer Glasübergangstemperatur von größer 80 °C enthalten, durch verbesserte optische Eigenschaften, insbesondere durch eine niedrigere Trübung aus.

[0069] Die Herstellung der Cycloolefincopolymere (COC) geschieht durch eine heterogene oder homogene Katalyse mit metallorganischen Verbindungen und ist in einer Vielzahl von Dokumenten beschrieben. Geeignete Katalysatorsysteme, basierend auf Mischkatalysatoren aus Titan- bzw. Vanadiumverbindungen in Verbindung mit Aluminiumorganen, werden in der DD 109 224, DD 237 070 und der EP-A-0 156 464 beschrieben.

[0070] EP-A-0 283 164, EP-A-0 407 870, EP-A-0 485 893 und EP-A-0 503 422 beschreiben die Herstellung von Cycloolefincopolymeren (COC) mit Katalysatoren, basierend auf löslichen Metallocenkomplexen. Auf Cycloolefincopolymere, hergestellt mit Katalysatoren, die auf löslichen Metallocenkomplexen basieren, wird besonders bevorzugt zurückgegriffen. Solche COCs sind käuflich erhältlich; z. B. Topas® (Ticona, Frankfurt).

[0071] Beträgt der Anteil des polyesterunverträglichen Polymeren (anti-PET-Polymer) weniger als 3 Gew.-%, bezogen auf das Gewicht der Deckschicht (A), so ist ein positiver Einfluss des Polymeren auf das Abziehverhalten der Folie von der Menüschaale nicht gegeben. Beim Abziehen der Folie von der Menüschaale neigt diese nach wie vor zum Einreißen oder zum Abreißen. Insbesondere bei höheren Siegeltemperaturen (> 160 °C) kommt dieser Effekt durch die Zugabe von polyesterunverträglichem Polymer (anti-PET-Polymer) besonders deutlich zum Tragen. Erfindungsgemäß hergestellte Folien reißen beim Abziehen von der Menüschaale auch dann nicht ein oder ab. Andererseits sollte der Anteil von polyesterunverträglichem Polymer (anti-PET-Polymer) 30 Gew.-% nicht überschreiten, da die Trübung der Folie sonst zu hoch wird.

[0072] Zur Verbesserung der Handhabung der Folie, der Verarbeitbarkeit der Folie, insbesondere aber auch zur Verbesserung des Abziehverhaltens der Folie von der Menüschaale ist es von Vorteil, die heißsiegelbare und peelfähige Deckschicht (A) weiter zu modifizieren.

[0073] Dies geschieht am Besten mit Hilfe von geeigneten Antiblockmitteln (Partikel), die der Siegelschicht gegebenfalls zugegeben werden, und zwar in Mengen, dass sich das Abziehverhalten der Folie von der Menüschaale weiter verbessert, ein Verblocken der Folie verhindert und das Verarbeitungsverhalten der Folie optimiert wird.

[0074] Es hat sich als günstig erwiesen, dass zumindest die Deckschicht (A) Partikel in einer bestimmten Größe, in einer bestimmten Konzentration und in einer bestimmten Verteilung beinhaltet. Daneben können auch Mischungen von zwei und mehreren verschiedenen Partikelsystemen oder Mischungen von Partikelsystemen in gleicher chemischer Zusammensetzung, aber unterschiedlicher Partikelgröße der Deckschicht (A) zugegeben werden.

[0075] Übliche Antiblockmittel (auch als "Pigmente" oder "Partikel" bezeichnet) sind anorganische und/oder organische Partikel, beispielsweise Calciumcarbonat, amorphe Kieselsäure, Talk, Magnesiumcarbonat, Bariumcarbonat, Calciumsulfat, Bariumsulfat, Lithiumphosphat, Calciumphosphat, Magnesiumphosphat, Aluminiumoxid, Lithiumfluorid, Calcium-,

Barium-, Zink- oder Mangan-Salze der eingesetzten Dicarbonsäuren, Ruß, Titandioxid, Kaolin oder vernetzte Polystyrol- oder Acrylat-Partikel. Die Partikel können der Schicht in den jeweils vorteilhaften Konzentrationen, z. B. als glykologische Dispersion während der Polykondensation oder über Masterbatche bei der Extrusion zugegeben werden.

[0076] Erfindungsgemäß bevorzugte Partikel sind synthetisch hergestellte, amorphe SiO_2 -Partikel in kolloidaler Form. Diese Partikel werden hervorragend in die Polymermatrix eingebunden und erzeugen nur wenige Vakuolen (Hohlräume). Vakuolen entstehen an den Partikeln bei der biaxialen Orientierung, verursachen im Allgemeinen Trübung und sind daher für die vorliegende Erfindung wenig geeignet. Zur (synthetischen) Herstellung der SiO_2 -Partikel (auch Silicagel genannt) werden zunächst Schwefelsäure und Natriumsilikat unter kontrollierten Bedingungen zur Bildung von Hydrosol miteinander gemischt. Dieses formt sich schließlich zu einer harten, durchsichtigen Masse, die als Hydrogel bekannt ist. Nach Absonderung des als Nebenprodukt anfallenden Natriumsulfats durch ein Waschverfahren kann es getrocknet und weiterverarbeitet werden. Durch Kontrolle des Waschwasser-pH-Wertes und der Trocknungsbedingungen können die wichtigen physikalischen Parameter, wie z. B. Porenvolumen, Porengröße und die Größe der Oberfläche des anfallenden Silikagels variiert werden. Die gewünschte Partikelgröße (z. B. den d_{50} -Wert) und die gewünschte Partikelgrößenverteilung (z. B. die SPAN98) erhält man durch geeignete Mahlung des Silikagels (z. B. mechanisch oder hydro-mechanisch). Solcher Partikel können z. B. über Grace, Fuji, Degussa oder Ineos bezogen werden.

[0077] Es hat sich als besonders vorteilhaft erwiesen, Teilchen mit einem mittleren Partikeldurchmesser d_{50} von 2,0 bis 8 μm , bevorzugt von 2,5 bis 7 μm und besonders bevorzugt von 3,0 bis 6 μm , zu verwenden. Bei der Verwendung von Teilchen mit einem Durchmesser, der unterhalb 2,0 μm liegt, ist ein positiver Einfluss der Partikel auf das Abziehverhalten der Folie von der Menüschale nicht gegeben. In diesem Fall neigt die Folie beim Abziehen von der Menüschale wiederum zum Ein- oder Weiterreißen, was natürlich unerwünscht ist. Teilchen mit einem Durchmesser größer als 8 μm verursachen in der Regel Filterprobleme.

[0078] In einer bevorzugten Ausführungsform ist in der heißsiegelbaren und peelfähigen Deckschicht (A) der Durchmesser der Partikel größer als die Dicke dieser Schicht. Es hat sich als günstig erwiesen, ein Durchmesser/Schichtdicken-Verhältnis von mindestens 1,2, bevorzugt mindestens 1,3 und besonders bevorzugt mindestens 1,4 zu wählen. In diesen Fällen ist ein besonders positiver Einfluss der Partikel auf das Abziehverhalten der Folie von der Menüschale gegeben.

[0079] Zur Bereitstellung der gewünschten Peeleigenschaften hat es sich als günstig erwiesen, wenn die heißsiegelbare und peelfähige Deckschicht (A) Partikel in einer Konzentration von 0,5 bis 10 Gew.-% enthält. Bevorzugt beträgt die Konzentration der Partikel 0,7 bis 8,0 Gew.-% und besonders bevorzugt 1,0 bis 6,0 Gew.-%. Enthält die Deckschicht (A) der Folie dagegen Partikel, bei dem diese in einer Konzentration von weniger als 0,5 Gew.-% vorliegen, so ist ein positiver Einfluss auf das Abziehverhalten der Folie von der Menüschale nicht mehr gegeben. Enthält dagegen die Deckschicht (A) der Folie Partikel, bei dem diese in einer Konzentration von mehr als 10 Gew.-% vorliegen, so wird die Trübung der Folie zu groß.

[0080] Es hat sich als besonders vorteilhaft erwiesen, in der heißsiegelbaren und peelfähigen Deckschicht (A) Partikel zu verwenden, deren Verteilung für den Partikeldurchmesser eine Streuung aufweist, die durch einen SPAN98 von $\leq 2,0$ beschrieben wird (Definition des SPAN98, siehe Messvorschrift). Bevorzugt ist ein SPAN98 von $\leq 1,9$, und besonders bevorzugt ist ein SPAN98 von $\leq 1,8$. Enthält die Deckschicht (A) der Folie dagegen Partikel, deren SPAN98 größer als 2,0 ist, so werden die optischen Eigenschaften und die Siegeleigenschaften der Folie schlechter.

[0081] Weiterhin hat es sich als vorteilhaft erwiesen, die Rauigkeit der heißsiegelbaren und peelfähigen Deckschicht (A) so einzustellen, dass ihr R_a -Wert größer als 60 nm ist. Bevorzugt ist die Rauigkeit R_a größer als 80 nm, und besonders bevorzugt ist sie größer als 100 nm; die Obergrenze der Rauigkeit sollte 400 nm, bevorzugt 350 nm, insbesondere 300 nm, nicht überschreiten. Dies kann durch die Auswahl der Partikeldurchmesser, deren Konzentration und die Variation der Schichtdicke gesteuert werden.

[0082] Um das Verarbeitungsverhalten der Folie nach der vorliegenden Erfindung weiterhin zu verbessern, ist es von Vorteil, in die Basisschicht (B) bei einem zweischichtigen Folienaufbau (AB) bzw. in die nicht siegelfähige Deckschicht (C) bei einem dreischichtigen Folienaufbau (ABC) ebenfalls Partikel einzuarbeiten, wobei folgende Bedingungen eingehalten werden sollten:

a) Die Partikel sollten einen mittleren Partikeldurchmesser d_{50} (= Median) von 1,5 bis 6 μm aufweisen. Es hat sich dabei als besonders zweckmäßig erwiesen, Teilchen mit einem mittleren Partikeldurchmesser d_{50} von 2,0 bis 5 μm und besonders bevorzugt von 2,5 bis 4 μm zu verwenden.

b) Die Partikel sollten eine Streuung aufweisen, die durch einen SPAN98 von $\leq 2,0$ beschrieben wird. Bevorzugt ist der SPAN98 $\leq 1,9$, und besonders bevorzugt ist der SPAN98 $\leq 1,8$.

c) Die Partikel sollten in einer Konzentration von 0,1 bis 0,5 Gew.-% vorhanden sein. Bevorzugt beträgt die Konzentration der Partikel 0,12 bis 0,4 Gew.-% und besonders bevorzugt 0,15 bis 0,3 Gew.-%.

[0083] Zur Erzielung der vorgenannten Eigenschaften, insbesondere der optischen Eigenschaften der siegelbaren

und peelfähigen Folie, hat es sich insbesondere bei einer dreischichtigen Folie mit ABC-Aufbau als zweckmäßig erwiesen, die Menge an Partikeln in der Basisschicht (B) niedriger einzustellen als in Deckschicht (A). Bei der dreischichtigen Folie vom genannten Typ soll zweckmäßiger Weise in der Basisschicht (B) die Menge der Partikel zwischen 0 und 2,0 Gew.-% liegen, vorzugsweise zwischen 0 und 1,5 Gew.-%, insbesondere zwischen 0 und 1,0 Gew.-%. Als besonders zweckmäßig hat es sich erwiesen, in die Basisschicht nur Partikel einzuarbeiten, wie sie über das arteigene Regenerat (Rezyklat) in die Folie gelangen. Die optischen Eigenschaften der Folie, insbesondere die Trübung der Folie, sind dann besonders gut.

[0084] Zwischen der Basisschicht und den Deckschichten kann sich gegebenenfalls noch eine Zwischenschicht befinden. Diese kann wiederum aus den für die Basisschicht beschriebenen Polymeren bestehen. In einer besonders bevorzugten Ausführungsform besteht die Zwischenschicht aus den für die Basisschicht verwendeten Polyestern. Die Zwischenschicht kann auch die unten beschriebenen üblichen Additive enthalten. Die Dicke der Zwischenschicht ist im Allgemeinen größer als 0,3 μm und liegt vorzugsweise im Bereich von 0,5 bis 15 μm , insbesondere im Bereich von 1,0 bis 10 μm , besonders bevorzugt im Bereich von 1,0 bis 5 μm .

[0085] Bei der zweischichtigen und der besonders vorteilhaften dreischichtigen Ausführungsform der erfindungsgemäßen Folie liegt die Dicke der Deckschicht (A) im Bereich von 0,7 und 2,5 μm , bevorzugt im Bereich von 0,8 und 2,2 μm und besonders bevorzugt im Bereich von 0,8 und 1,9 μm . Beträgt die Dicke der Deckschicht (A) mehr als 2,5 μm , so wächst die Peelkraft deutlich an und liegt nicht mehr im erfindungsgemäßen Bereich. Darüber hinaus wird das Peelverhalten der Folie beeinträchtigt. Beträgt die Dicke der Deckschicht (A) dagegen weniger 0,5 μm , so ist die Folie nicht mehr heißsiegelbar.

[0086] Die Dicke der anderen, nicht siegelbaren Deckschicht (C) kann gleich der Deckschicht (A) sein oder von dieser verschieden; ihre Dicke liegt im Allgemeinen zwischen 0,5 und 5 μm .

[0087] Die Gesamtdicke der erfindungsgemäßen Polyesterfolie kann innerhalb bestimmter Grenzen variieren. Sie beträgt 3 bis 200 μm , insbesondere 4 bis 150 μm , vorzugsweise 5 bis 100 μm , wobei die Schicht (B) einen Anteil von vorzugsweise 45 bis 97 % an der Gesamtdicke hat.

[0088] Die Basisschicht und die anderen Schichten können zusätzlich übliche Additive wie Stabilisatoren (UV, Hydrolyse), flammhemmende Stoffe oder Füller enthalten. Sie werden zweckmäßig dem Polymer bzw. der Polymermischung bereits vor dem Aufschmelzen zugesetzt.

[0089] Gegenstand der vorliegenden Erfindung ist auch ein Verfahren zur Herstellung der Folie. Zur Herstellung der erfindungsgemäßen heißsiegelbaren und peelfähigen Deckschicht (A) werden zweckmäßigerweise die jeweiligen Polymere (Polyester I, Polyester II, polyesterunverträgliches Polymer [anti-PET-Polymer], ggf. weitere Polymere [= z. B. Masterbatch(e) für Partikel]) direkt dem Extruder für die Deckschicht (A) zugeführt. Die Materialien lassen sich bei etwa 200 bis 280 °C extrudieren. Aus verfahrenstechnischer Sicht (Durchmischung der verschiedenen Komponenten) hat es sich dabei als besonders günstig erwiesen, wenn die Extrusion der Polymere für die Deckschicht (A) mit einem Zweischneckenextruder mit Entgasungsmöglichkeit(en) durchgeführt wird.

[0090] Die Polymere für die Basisschicht (B) und für die eventuell vorhandene weitere Deckschicht (C) und gegebenenfalls die Zwischenschicht werden zweckmäßig über weitere Extruder dem (Coextrusions-) System zugeführt. Die Schmelzen werden in einer Mehrschichtdüse zu flachen Schmelzeffilmen ausgeformt und übereinander geschichtet. Anschließend wird der Mehrschichtfilm mit Hilfe einer Kühlwalze und gegebenenfalls weiteren Walzen abgezogen und verfestigt.

[0091] Die biaxiale Streckung der Folie wird im Allgemeinen sequenziell durchgeführt. Eine simultane Streckung der Folie ist auch möglich, ist aber nicht notwendig. Bei der sequenziellen Streckung wird vorzugsweise erst in Längsrichtung (d. h. in Maschinenrichtung) und anschließend in Querrichtung (d. h. senkrecht zur Maschinenrichtung) gestreckt. Das Strecken in Längsrichtung lässt sich mit Hilfe zweier entsprechend dem angestrebten Streckverhältnis verschieden schnell rotierender Walzen durchführen. Zum Querstrecken benutzt man im Allgemeinen einen entsprechenden Kluppenrahmen.

[0092] Die Temperatur, bei der die Streckung durchgeführt wird, kann in einem relativ großen Bereich variieren und richtet sich nach den gewünschten Eigenschaften der Folie. Im Allgemeinen wird die Streckung in Längsrichtung (machine direction orientation = MDO) in einem Temperaturbereich von 60 bis 130 °C (Aufheiztemperaturen 60 bis 130 °C) und in Querrichtung (transverse direction orientation = TDO) in einem Temperaturbereich von 90 °C (Beginn der Streckung) bis 140 °C (Ende der Streckung) durchgeführt. Das Längsstreckverhältnis liegt im Bereich von 2,0:1 bis 5,5:1, bevorzugt von 2,3:1 bis 5,0:1. Das Querstreckverhältnis liegt allgemein im Bereich von 2,4:1 bis 5,0:1, bevorzugt von 2,6:1 bis 4,5:1.

[0093] Der bevorzugte Temperaturbereich, bei der die biaxiale Streckung durchgeführt wird, beträgt bei der Längsstreckung (MDO) 60 bis 120 °C. Die Aufheiztemperaturen der Folie in der Längsstreckung liegen dabei in einem Bereich von 60 bis 115 °C. Bei der Querstreckung (TDO) liegen die Temperaturen der Folie in einem Bereich von 90 °C (Beginn der Streckung) bis 140 °C (Ende der Streckung). Das Längsstreckverhältnis liegt bei diesem bevorzugten Temperaturbereich im Bereich von 2,0:1 bis 5,0:1, bevorzugt von 2,3:1 bis 4,8:1. Das Querstreckverhältnis liegt allgemein im Bereich von 2,4:1 bis 5,0:1, bevorzugt von 2,6:1 bis 4,5:1.

[0094] Der besonders bevorzugte Temperaturbereich, bei der die biaxiale Streckung durchgeführt wird, beträgt bei

der Längsstreckung (MDO) 60 bis 110 °C. Die Aufheiztemperaturen der Folie in der Längsstreckung liegen dabei in einem Bereich von 60 bis 105 °C. Bei der Querstreckung (TDO) liegen die Temperaturen der Folie in einem Bereich von 90 °C (Beginn der Streckung) bis 140 °C (Ende der Streckung). Das Längsstreckverhältnis liegt bei diesem bevorzugten Temperaturbereich im Bereich von 2,0:1 bis 4,8:1, bevorzugt von 2,3:1 bis 4,6:1. Das Querstreckverhältnis liegt

allgemein im Bereich von 2,4:1 bis 5,0:1, bevorzugt von 2,6:1 bis 4,5:1.
[0095] Mit den bevorzugten und insbesondere mit den besonders bevorzugten Temperaturen in der MDO wird dem klebrigen Verhalten von Deckschicht (A) auf Walzen (metallische, keramische oder besonders beschichtete Walzenoberflächen) besonders gut Rechnung getragen.

[0096] Vor der Querstreckung kann man eine oder beide Oberfläche(n) der Folie nach den an sich bekannten Verfahren in-Line beschichten. Die In-Line-Beschichtung kann beispielsweise zu einer verbesserten Haftung zwischen einer Metallschicht oder einer Druckfarbe und der Folie, zu einer Verbesserung des antistatischen Verhaltens, des Verarbeitungsverhaltens oder auch zur weiteren Verbesserung von Barriereigenschaften der Folie führen. Letzteres wird beispielsweise durch Auftragung von Barrierebeschichtungen wie EVOH, PVOH o. ä. erhalten. Vorzugsweise werden solche Schichten dann auf die nicht siegelbare Oberfläche, z. B. die Oberfläche (C) der Folie, aufgetragen.

[0097] Bei der nachfolgenden Thermofixierung wird die Folie über eine Zeitdauer von etwa 0,1 bis 10 s bei einer Temperatur von 150 bis 250 °C gehalten. Anschließend wird die Folie in üblicher Weise aufgewickelt.

[0098] Der Glanz der Folienoberfläche (B) im Falle einer zweischichtigen Folie bzw. der Glanz der Folienoberfläche (C) bei einer dreischichtigen Folie ist größer als 100 (gemessen nach DIN 67530 in Anlehnung an ASTM-D 523-78 und ISO 2813 mit Einstrahlwinkel 20°). In einer bevorzugten Ausführungsform beträgt der Glanz dieser Seiten mehr als 110 und in einer besonders bevorzugten Ausführungsform mehr als 120. Diese Folienoberflächen eignen sich daher insbesondere für eine weitere funktionelle Beschichtung, für die Bedruckung oder für die Metallisierung.

[0099] Die Trübung der Folie ist kleiner als 25. In einer bevorzugten Ausführungsform beträgt die Trübung der Folie weniger als 20 und in einer besonders bevorzugten Ausführungsform weniger als 15.

[0100] Ein weiterer Vorteil der Erfindung besteht darin, dass die Herstellungskosten der erfindungsgemäßen Folie nicht wesentlich über denen einer Folie aus Standardpolyester liegen. Daneben ist bei der Herstellung der Folie gewährleistet, dass Verschnittmaterial, das bei der Folienherstellung im Betrieb immanent anfällt, als Regenerat in einer Menge von bis zu 60 Gew.-%, bevorzugt 5 bis 50 Gew.-%, jeweils bezogen auf das Gesamtgewicht der Folie, wieder für die Folienherstellung verwendet werden kann, ohne dass dabei die physikalischen Eigenschaften der Folie nennenswert negativ beeinflusst werden.

[0101] Die erfindungsgemäße Folie eignet sich hervorragend zum Verpacken von Nahrungs- und Genussmitteln, insbesondere zur Verpackung von Nahrungs- und Genussmitteln in Menüschalen, bei denen peelfähige Polyesterfolien zum Öffnen der Verpackung verwendet werden.

[0102] Die nachstehende Tabelle (Tabelle 1) fasst die wichtigsten erfindungsgemäßen Folieneigenschaften noch einmal zusammen.

Tabelle 1

Deckschicht (A)	Erfindungsgemäßer Bereich	Bevorzugt	Besonders bevorzugt	Einheit	Messmethode
Anteil Einheiten im erfindungsgemäßen Polyester, aufgebaut aus aromatischen Dicarbonsäuren	25 bis 95	40 bis 90	50 bis 88	Mol.-%	
Anteil Einheiten im erfindungsgemäßen Polyester, aufgebaut aus aliphatischen Dicarbonsäuren	5 bis 75	10 bis 60	12 bis 50	Mol.-%	
Anti-PET-Polymer	3 bis 30	5 bis 25	7 bis 20	Gew.-%	
Polyester I	10 bis 60	15 bis 55	20 bis 50	Gew.-%	
polyester II	20 bis 70	25 bis 65	30 bis 60	Gew.-%	
Partikeldurchmesser d_{50}	2,0 bis 8	2,5 bis 7	3,0 bis 6	μm	
Füllstoffkonzentration	0,5 bis 10	0,7 bis 8,0	1,0 bis 6,0	%	
Dicke der Deckschicht A	0,7 bis 2,5	0,8 bis 2,2	0,8 bis 1,9	μm	
Partikeldurchmesser/Schichtdicken-Verhältnis	$\geq 1,2$	$\geq 1,3$	$\geq 1,4$		
Eigenschaften					
Dicke der Folie	3 bis 200	4 bis 150	5 bis 100	μm	
Mindestsiegeltemperatur von DS (A) gegen APET/CPET-Menüschalen	150	140	130	$^{\circ}\text{C}$	
Siegelhaftfestigkeit von DS (A) gegen APET/CPET-Menüschalen	1,7 bis 8	2,0 bis 8	2,3 bis 8	N/15 mm	
Glanz der Deckschichten A und C	> 70 und > 100	> 75 und > 110	> 80 und > 120		DIN 67530
Trübung der Folie	< 25	< 20	< 15	%	ASTM-D 1003-52
DS: Deckschicht, $\geq$: größer/gleich					

[0103] Zur Charakterisierung der Rohstoffe und der Folien wurden im Rahmen der vorliegenden Erfindung die folgenden Messmethoden benutzt:

Messung des mittleren Durchmessers d_{50}

[0104] Die Bestimmung des mittleren Durchmessers d_{50} wurde mittels Laserauf einem Malvern Master Sizer (Malvern Instruments Ltd., UK) mittels Laserscannung durchgeführt (andere Messgeräte sind z. B. Horiba LA 500 oder Sympatec Helos, welche das gleiche Messprinzip verwenden). Die Proben wurden dazu in eine Küvette mit Wasser gegeben und diese dann in das Messgerät gestellt. Mittels Laser wird die Dispersion abgerastert und aus dem Signal durch Vergleich mit einer Eichkurve die Partikelgrößenverteilung bestimmt. Die Partikelgrößenverteilung ist durch zwei Parameter gekennzeichnet, den Medianwert d_{50} (= Lagemaß für den Mittelwert) und das Streumaß, der sog. SPAN98 (= Maß für die Streuung des Partikeldurchmessers). Der Messvorgang ist automatisch und beinhaltet auch die mathematische Bestimmung des d_{50} -Wertes. Der d_{50} -Wert wird dabei definitionsgemäß aus der (relativen) Summenkurve der Partikelgrößenverteilung bestimmt: Der Schnittpunkt des 50%-Ordinatenwertes mit der Summenkurve liefert auf der Abszissenachse den gewünschten d_{50} -Wert (auch Median genannt).

Messung der SPAN98

[0105] Die Bestimmung des Streumaßes, der SPAN98, wurde mit dem gleichen Messgerät durchgeführt wie oben bei der Bestimmung des mittleren Durchmessers d_{50} beschrieben. Der SPAN98 ist dabei wie folgt definiert:

$$SPAN98 = \frac{d_{98} - d_{10}}{d_{50}}$$

[0106] Der Ermittlung von d_{98} und d_{10} wird wiederum die (relative) Summenkurve der Partikelgrößenverteilung (s. o. "Messung des mittleren Durchmessers d_{50} ") zu Grunde gelegt. Der Schnittpunkt des 98%-Ordinatenwertes mit der Summenkurve liefert auf der Abszissenachse sofort den gewünschten d_{98} -Wert, und der Schnittpunkt des 10%-Ordinatenwertes der Summenkurve mit der Kurve liefert auf der Abszissenachse den gewünschten d_{10} -Wert.

SV-Wert

[0107] Der SV-Wert des Polymers wurde durch die Messung der relativen Viskosität (η_{rel}) einer 1%-igen Lösung in Dichloressigsäure in einem Ubbelohde-Viskosimeter bei 25° C bestimmt. Der SV-Wert ist wie folgt definiert:

$$SV = (\eta_{rel} - 1) \cdot 1000.$$

Glasübergangstemperaturen T_g

[0108] Die Glasübergangstemperatur T_g wurde anhand von Folienproben mit Hilfe der DSC (Differential Scanning Calorimetry) bestimmt. Verwendet wurde ein DSC 1090 der Fa. Perkin-Elmer. Die Aufheizgeschwindigkeit betrug 20 K/min und die Einwaage ca. 12 mg. Um die thermische Vorgeschichte zu eliminieren, wurden die Proben zunächst auf 300 °C aufgeheizt, 5 Minuten gehalten und dann anschließend mit flüssigem Stickstoff abgeschreckt. Aus dem Thermogramm wurde die Temperatur für den Glasübergang T_g als die Temperatur bei halber Stufenhöhe entnommen.

Siegelnahtfestigkeit

[0109] Zur Bestimmung der Siegelnahtfestigkeit wird ein Folienstreifen (100 mm lang x 15 mm breit) auf die APET-Seite eines entsprechenden Streifens der APET/CPET-Menüschale gelegt und bei der eingestellten Temperatur von = 140 °C, einer Siegelzeit von 0,5 s und einem Siegeldruck von 3 bar (Siegelgerät HSG/ET der Firma Brugger, DE, beidseitig beheizte Siegelbacke) gesiegelt. Entsprechend Figur 2 werden die gesiegelten Streifen in die Zugprüfmaschine (z. B. Zwick, DE) eingespannt und die 180°-Siegelnahtfestigkeit, d. h. die zur Auftrennung der Prüfstreifen benötigte Kraft, mit einer Abzugsgeschwindigkeit von 200 mm/min bestimmt. Die Siegelnahtfestigkeit wird in N pro 15 mm Folienstreifen angegeben (z. B. 3 N/15 mm).

Bestimmung der Mindestsiegeltemperatur

[0110] Mit dem Siegelgerät HSG/ET der Firma Brugger werden, wie zuvor bei der Messung der Siegelnahtfestigkeit beschrieben, heißgesiegelte Proben (Siegelnaht 15 mm x 100 mm) hergestellt, wobei die Folie bei unterschiedlichen Temperaturen mit Hilfe zweier beheizter Siegelbacken bei einem Siegeldruck von 3 bar und einer Siegeldauer von 0,5 s gesiegelt wird. Die 180°-Siegelnahtfestigkeit wurde wie bei der Bestimmung der Siegelnahtfestigkeit gemessen. Die Mindestsiegeltemperatur ist die Temperatur, bei der eine Siegelnahtfestigkeit von mindestens 1,7 N/15 mm erreicht wird.

Rauigkeit

[0111] Die Rauigkeit R_a der Folie wurde nach DIN 4768 bei einem Cut-off von 0,25 mm bestimmt. Es wurde dabei nicht auf einer Glasplatte, sondern im Ring gemessen. Bei der Ringmethode wird die Folie in einen Ring eingespannt, so dass keine der beiden Oberflächen eine dritte Oberfläche (z. B. Glas) berührt.

Trübung

[0112] Die Trübung nach Hölz wurde nach ASTM-D 1003-52 bestimmt.

Glanz

[0113] Der Glanz der Folie wurde nach DIN 67530 bestimmt. Gemessen wurde der Reflektorwert als optische Kenngröße für die Oberfläche einer Folie. Angelehnt an die Normen ASTM-D 523-78 und ISO 2813 wurde der Einstrahlwinkel mit 20° eingestellt. Ein Lichtstrahl trifft unter dem eingestellten Einstrahlwinkel auf die ebene Prüffläche und wird von dieser reflektiert bzw. gestreut. Die auf den photoelektronischen Empfänger auffallenden Lichtstrahlen werden als proportionale elektrische Größe angezeigt. Der Messwert ist dimensionslos und muss mit dem Einstrahlwinkel angegeben werden.

Reißfestigkeit

[0114] Die Reißfestigkeit der Folie wurde nach DIN 53455 gemessen. Die Prüfgeschwindigkeit ist 1 %/min; 23 °C; 50 % r. F.

E-Modul

[0115] Der E-Modul der Folie wurde nach DIN 53457 gemessen. Die Prüfgeschwindigkeit ist 1 %/min; 23 °C; 50 % r. F.

Schrumpf

[0116] Der Glanz der Folie wurde nach DIN 40634 gemessen. Die Prüfbedingungen sind 150 °C, 15 min.

[0117] Im Folgenden wird die Erfindung anhand von Beispielen näher erläutert.

Beispiel 1

[0118] Chips aus Polyethylenterephthalat wurden dem Extruder für die Basisschicht (B) zugeführt. Ebenfalls wurden Chips aus Polyethylenterephthalat und Partikel dem Extruder (Zweischneckenextruder) für die nicht siegelfähige Deckschicht (C) zugeführt. Entsprechend den in unten stehender Tabelle aufgeführten Verfahrensbedingungen wurden die Rohstoffe in den beiden jeweiligen Extrudern aufgeschmolzen und homogenisiert.

[0119] Daneben wurde für die heißsiegelbare und peelfähige Deckschicht (A) eine Mischung bestehend aus Polyester I, Polyester II und antiPET-Polymer hergestellt. In Tabelle 2 sind die jeweiligen Anteile der in beiden Polyestern I und II enthaltenen Dicarbonsäuren und Glykole in Mol-% und die jeweiligen Anteile der in der Mischung enthaltenen Komponenten in Gew.-% angegeben. Die Mischung wurde dem Zweischneckenextruder mit Entgasung für die siegelbare und peelfähige Deckschicht (A) zugeführt. Entsprechend den in unten stehender Tabelle angeführten Verfahrensbedingungen wurden die Rohstoffe in dem Zweischneckenextruder aufgeschmolzen und homogenisiert.

[0120] Dann wurden durch Coextrusion in einer Dreischichtdüse die drei Schmelzeströme übereinander geschichtet und über die Düsenlippe ausgestoßen. Der resultierende Schmelzefilm wurde abgekühlt und anschließend über eine stufenweise Orientierung in Längs- und Querrichtung eine transparente, dreischichtige Folie mit ABC-Aufbau in einer Gesamtdicke von 25 µm hergestellt. Die Dicken der beiden Deckschichten betragen jeweils 1 µm (vgl. auch Tabelle 2).

Deckschicht (A), Mischung aus:

[0121]

5	40 Gew.-%	Polyester I (= Copolymeres aus 78 Mol-% Ethylenterephthalat, 22 Mol-% Ethylenisophthalat) mit einem SV-Wert von 850. Die Glasübergangstemperatur von Polyester I beträgt ca. 75 °C. Polyester I enthält darüber hinaus 5,0 Gew.-% [®] Sylsia 430 (synthetisches SiO ₂ , Fuji, Japan) mit einem Partikeldurchmesser von d ₅₀ = 3,4 µm und einem SPAN98 von 1,7. Das Verhältnis von Partikeldurchmesser d ₅₀ zu Deckschichtdicke d _(A) beträgt 3,4:1 (vgl. Tabelle 2)
10	40 Gew.-%	Polyester II (= Copolymeres enthaltend 40 Mol-% Ethylenazelat, 50 Mol-% Ethylenterephthalat, 10 Mol-% Ethylenisophthalat) mit einem SV-Wert von 1000. Die Glasübergangstemperatur von Polyester II beträgt ca. 0 °C.
	20 Gew.-%	anti-PET-Polymer (= COC, [®] Topas 8007, Ticona, Frankfurt, mit einer T _g von ca. 75 °C)
15		

Basisschicht (B):

[0122]

20	100 Gew.-%	Polyethylenterephthalat mit einem SV-Wert von 800
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Deckschicht (C), Mischung aus:

[0123]

25	85 Gew.-%	Polyethylenterephthalat mit einem SV-Wert von 800
	15 Gew.-%	Masterbatch aus 99 Gew.-% Polyethylenterephthalat (SV-Wert von 800) und 1,0 Gew.-% Sylobloc 44 H (synthetisches SiO ₂ , Grace, Worms), d ₅₀ = 2,5 µm, SPAN98 = 1,9
30		

[0124] Die Herstellungsbedingungen in den einzelnen Verfahrensschritten waren:

	Extrusion	Temperaturen	A-Schicht:	230 °C
35			B-Schicht:	280 °C
			C-Schicht:	280 °C
		Temperatur der Abzugswalze		20 °C
	Längsstreckung	Aufheiztemperatur		70-100 °C
		Strecktemperatur		105 °C
40		Längsstreckverhältnis		4,0
	Querstreckung	Aufheiztemperatur		100 °C
		Strecktemperatur		135 °C
		Querstreckverhältnis		4,0
45	Fixierung	Temperatur		230 °C
		Dauer		3s

[0125] In Tabelle 3 sind die Eigenschaften der Folie dargestellt. Laut Messungen (Spalte 2), beträgt die Mindestsiegeltemperatur der Folie gegenüber der APET-Seite von APET/CPET-Menüschalen 142 °C. Die Folie wurde bei 140, 160, 180 und 200 °C gegen die APET-Seite von APET/CPET-Menüschalen gesiegelt (Siegedruck 4 bar, Siegelzeit 0,5 s). Anschließend wurden Streifen des Verbundes aus erfindungsgemäßer Folie und APET/CPET-Menüschale mittels Spannungs-Dehnungstester entsprechend der vorgenannten Messvorschrift (vgl. Figur 2) auseinander gezogen. Für alle Siegeltemperaturen zeigte sich das gewünschte Abschälen der Folien von der Menüschale gemäß Figur 3b. Die gemessenen Siegelnahtfestigkeiten sind in Spalte 3 gelistet. Für alle Siegeltemperaturen wurden peelfähige Folien erhalten. Die Siegelnahtfestigkeiten liegen im mittleren Bereich, d. h., dass sich die Folien ohne große Kraftanstrengung von der Menüschale abziehen lassen (= easy peel). Weiterhin hatte die Folie die geforderten guten optischen Eigenschaften, zeigte das gewünschte Handling und das gewünschte Verarbeitungsverhalten.

Beispiel 2

[0126] Im Vergleich zu Beispiel 1 wurde die Deckschichtdicke der siegelfähigen Schicht (A) von 1,0 auf 2,0 μm bei sonst identischem Folienaufbau und sonst identischer Herstellungsweise angehoben. Die Mindestsiegeltemperatur der Folie gegenüber der APET-Seite von APET/CPET-Menüschalen beträgt jetzt 128 °C. Für alle Siegeltemperaturen zeigte sich das gewünschte Abschälen der Folien von der Menüschale gemäß Figur 3b. Die gemessenen Siegelnahtfestigkeiten sind in Spalte 3 gelistet. Für alle Siegeltemperaturen wurden wiederum peelfähige Folien erhalten. Die Siegelnahtfestigkeiten der erfindungsgemäßen Folien sind etwas höher als im Beispiel 1. Sie liegen aber immer noch im mittleren Bereich, so dass sich die Folie ohne große Kraftanstrengung von der Menüschale abziehen lässt. Es wurde eine etwas geringere Trübung der Folie gemessen; das Handling und das Verarbeitungsverhalten der Folie waren wie in Beispiel 1.

Beispiel 3

[0127] Im Vergleich zu Beispiel 1 wurde bei sonst identischem Folienaufbau die Zusammensetzung der Mischung für die siegelfähige Deckschicht (A) geändert. Die Zusammensetzung der einzelnen Komponenten blieb im Vergleich zu Beispiel 1 unverändert. Die Mischung besteht jetzt aus den folgenden Rohstoffanteilen:

- Polyester I = 40 Gew.-%,
- Polyester II = 50 Gew.-% und
- Anti-PET-Polymer = 10 Gew.-%

Auf Grund des höheren Anteils von Polyester II in der Mischung wurden die Verfahrensparameter in der Längsstreckung modifiziert. Die neuen Bedingungen für die Längsstreckung sind in unten stehender Tabelle aufgelistet.

Längsstreckung	Aufheiztemperatur	70-95 °C
	Strecktemperatur	100 °C
	Längsstreckverhältnis	3,8

[0128] Die Mindestsiegeltemperatur der Folie gegenüber der APET-Seite von APET/CPET-Menüschalen beträgt jetzt 134 °C. Für alle Siegeltemperaturen zeigte sich das gewünschte Abschälen der Folien von der Menüschale gemäß Figur 3b. Die gemessenen Siegelnahtfestigkeiten sind in Spalte 3 gelistet. Für alle Siegeltemperaturen wurden wiederum peelfähige Folien erhalten. Die Siegelnahtfestigkeiten der erfindungsgemäßen Folien sind höher als im Beispiel 1. Sie liegen in einem mittleren Bereich, so dass sich die Folie ohne wesentliche Kraftanstrengung von der Menüschale abziehen lässt. Das Handling und das Verarbeitungsverhalten der Folie waren wie in Beispiel 1.

Beispiel 4

[0129] Im Vergleich zu Beispiel 3 wurde die Deckschichtdicke der siegelfähigen Schicht (A) von 1,0 auf 2,0 μm bei sonst identischem Folienaufbau und sonst identischer Herstellungsweise angehoben. Die Mindestsiegeltemperatur der Folie gegenüber der APET-Seite von APET/CPET-Menüschalen beträgt jetzt 128 °C. Für alle Siegeltemperaturen zeigte sich das gewünschte Abschälen der Folien von der Menüschale gemäß Figur 3b. Die gemessenen Siegelnahtfestigkeiten sind in Spalte 3 gelistet. Für alle Siegeltemperaturen wurden wiederum peelfähige Folien erhalten. Die Siegelnahtfestigkeiten der erfindungsgemäßen Folien sind etwas höher als im Beispiel 3. Sie liegen aber immer noch in einem mittleren bis festen Bereich, so dass sich die Folie ohne allzu große Kraftanstrengung von der Menüschale abziehen lässt. Es wurde eine etwas geringere Trübung der Folie gemessen; das Handling und das Verarbeitungsverhalten der Folie waren wie in Beispiel 1.

Beispiel 5

[0130] Im Vergleich zu den vorgenannten Beispielen wurde bei sonst identischem Folienaufbau die Zusammensetzung der Mischung für die siegelfähige Deckschicht (A) geändert. Die Zusammensetzung der einzelnen Komponenten blieb im Vergleich zu Beispiel 1 unverändert. Die Mischung besteht jetzt aus den folgenden Rohstoffen:

- Polyester I = 30 Gew.-%,
- Polyester II = 60 Gew.-% und
- Anti-PET-Polymer = 10 Gew.-%.

Auf Grund des höheren Anteils von Polyester II im Blend wurden die Verfahrensparameter in der Längsstreckung wiederum leicht modifiziert. Die neuen Bedingungen für die Längsstreckung sind in unten stehender Tabelle aufgelistet.

Längsstreckung	Aufheiztemperatur	70-90 °C
	Strecktemperatur	95 °C
	Längsstreckverhältnis	3,6

[0131] Die Mindestsiegeltemperatur der Folie gegenüber der APET-Seite von APET/CPET-Menüschalen beträgt jetzt 132 °C. Für alle Siegeltemperaturen zeigte sich das gewünschte Abschälen der Folien von der Menüschale gemäß Figur 3b. Die gemessenen Siegelnahtfestigkeiten sind in Spalte 3 gelistet. Für alle Siegeltemperaturen wurden wiederum peelfähige Folien erhalten. Die Siegelnahtfestigkeiten der erfindungsgemäßen Folien sind vergleichbar zu denen im Beispiel 1. Das Handling und das Verarbeitungsverhalten der Folie waren wie in Beispiel 1.

Beispiel 6

[0132] Im Vergleich zu Beispiel 5 wurde die Deckschichtdicke der siegelfähigen Schicht (A) von 1,0 auf 2,0 µm bei sonst identischem Folienaufbau und sonst identischer Herstellungsweise angehoben. Die Mindestsiegeltemperatur der Folie gegenüber der APET-Seite von APET/CPET-Menüschalen beträgt jetzt 128 °C. Für alle Siegeltemperaturen zeigte sich das gewünschte Abschälen der Folien von der Menüschale gemäß Figur 3b. Die gemessenen Siegelnahtfestigkeiten sind in Spalte 3 gelistet. Für alle Siegeltemperaturen wurden wiederum peelfähige Folien erhalten. Die Siegelnahtfestigkeiten der erfindungsgemäßen Folien sind höher als im Beispiel 5. Sie liegen in einem mittleren bis höheren Bereich, so dass sich die Folie mit Kraftanstrengung von der Menüschale abziehen lässt. Das Handling und das Verarbeitungsverhalten der Folie waren wie in Beispiel 1.

Beispiel 7

[0133] Im Vergleich zu Beispiel 5 wurde bei sonst identischem Folienaufbau die Zusammensetzung von Polyester II für die siegelfähige Deckschicht (A) geändert. Die Zusammensetzung der einzelnen Komponenten in der Mischung blieb im Vergleich zu Beispiel 5 unverändert. Die verwendete Mischung in Deckschicht (A) besteht jetzt aus folgenden Rohstoffanteilen:

30 Gew.-%	Polyester I, identisch zu Beispiel 1
60 Gew.-%	Polyester II, ®Vitel1912, (Polyester, Bostik-Findley, USA; enthält die Dicarbonsäure-Bestandteile Azelainsäure, Sebazinsäure, Terephthalsäure, Isophthalsäure und weitere Dicarbonsäuren etwa im Molverhältnis 40/1/45/10/4 und als Diolkomponente mindestens 60 Mol-% Ethylenglykol). Die Glasübergangstemperatur von Polyester II beträgt ca. -1 °C.
10 Gew.-%	COC (®Topas 8007, Ticona, Frankfurt; ein Ethylen/Norbornen-COC mit einer T _g von ca. 75 °C)

[0134] Die Verfahrensparameter in der Längsstreckung entsprachen denjenigen in Beispiel 5. Die Mindestsiegeltemperatur der erfindungsgemäß hergestellten Folie gegenüber der APET-Seite von APET/CPET-Menüschalen beträgt jetzt 130 °C. Für alle Siegeltemperaturen zeigte sich das gewünschte Abschälen der Folien von der Menüschale gemäß Figur 3b. Die gemessenen Siegelnahtfestigkeiten sind in Spalte 3 gelistet. Für alle Siegeltemperaturen wurden wiederum peelfähige Folien erhalten. Die Siegelnahtfestigkeiten der erfindungsgemäßen Folien sind höher als in Beispiel 1. Sie liegen in einem mittleren Bereich, so dass sich die Folie ohne wesentliche Kraftanstrengung von der Menüschale abziehen lässt. Das Handling und das Verarbeitungsverhalten der Folie waren wie in Beispiel 1.

Vergleichsbeispiel 1

[0135] Im Vergleich zu Beispiel 1 wurde die Zusammensetzung der siegelfähigen Schicht (A) geändert. In der Deckschicht (A) wurde nur der auf Basis von aromatischen Säuren aufgebaute Polyester I verwendet:

100,0 Gew.-%	Polyester I (= Copolymeres aus 78 Mol-% Ethylterephthalat und 22 Mol-% Ethylenisophthalat) mit einem SV-Wert von 850. Die Glasübergangstemperatur von Polyester I beträgt ca. 75 °C. Polyester I enthält darüber hinaus 5,0 % ®Sylysia 430.
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[0136] Die Herstellungsbedingungen in den einzelnen Verfahrensschritten wurden in der Längsstreckung der Glasü-

bergangstemperatur des Deckschichtrohstoffes angepasst:

Längsstreckung	Aufheiztemperatur	70-115 °C
	Strecktemperatur	120 °C
	Längsstreckverhältnis	4,0

[0137] In Tabelle 3 sind die Eigenschaften der Folie dargestellt. Obwohl die Folie hochpigmentiert ist und die Pigmente Schwachstellen in der Siegelschicht darstellen, wurde für keine der angegebenen Siegeltemperaturen eine peelfähige Folie erhalten. Beim Abziehen der Folie von der Menüschale riss die Folie direkt ein und zeigte ein Diagramm gemäß Figur 3a. Die Folie zeigte "weldable" Verhalten und ist damit für die Lösung der genannten Aufgabe ungeeignet.

Vergleichsbeispiel 2

[0138] Es wurde das Beispiel 5 aus der EP-A 0 035 835 nachgearbeitet. In Tabelle 3 sind die Eigenschaften der Folie dargestellt. Es wurde für keine der angegebenen Siegeltemperaturen eine peelfähige Folie erhalten. Beim Abziehen der Folie von der Menüschale riss die Folie direkt ein und zeigte ein Diagramm gemäß Figur 3a. Die Folie zeigte "weldable" Verhalten und ist damit für die Lösung der genannten Aufgabe ungeeignet.

Vergleichsbeispiel 3

[0139] Es wurde das Beispiel 1 aus der EP-A 0 379190 nachgearbeitet. In Tabelle 3 sind die Eigenschaften der Folie dargestellt. Es wurde für keine der angegebenen Siegeltemperaturen eine peelfähige Folie erhalten. Beim Abziehen der Folie von der Menüschale riss die Folie direkt ein und zeigte ein Diagramm gemäß Figur 3a. Die Folie zeigte "weldable" Verhalten und ist damit für die Lösung der genannten Aufgabe ungeeignet.

Vergleichsbeispiel 4

[0140] Es wurde das Beispiel 22 aus der EP-A 0 379190 nachgearbeitet. In Tabelle 3 sind die Eigenschaften der Folie dargestellt. Es wurde für keine der angegebenen Siegeltemperaturen eine peelfähige Folie erhalten. Beim Abziehen der Folie von der Menüschale riss die Folie direkt ein und zeigte ein Diagramm gemäß Figur 3a. Die Folie zeigte "weldable" Verhalten und ist damit für die Lösung der genannten Aufgabe ungeeignet.

Tabelle 2

	Zusammensetzung Polyester I				Zusammensetzung Polyester II								Antip ET- Poly mer	Verhältnis PI/PII/ AntiPET- Polymer	Glastem- peraturen PI/PII/ AntiPET- Polymer	Folien- aufbau	Folien- dicke	Deckschicht- Dicken		Partikel	Verhältnis d ₅₀ /d ₁₀		
	Mol.-%				Mol.-%													(A)	(C)			Durchmes- ser	Konzen- tration
	TS	IS	EG	NG	AzS	SzS	AdS	TS	IS	EG	BD	WS											
Beispiele	1	78	22	100			40	50	10	100			100	40/40/20	75/0/75	ABC	25	1	1	3.4	1.8	2.00	3.4
	2	78	22	100			40	50	10	100			100	40/40/20	75/0/75	ABC	25	2	1	3.4	1.8	2.00	1.7
	3	78	22	100			40	50	10	100			100	40/50/10	75/0/75	ABC	25	1	1	3.4	1.8	2.00	3.4
	4	78	22	100			40	50	10	100			100	40/50/10	75/0/75	ABC	25	2	1	3.4	1.8	2.00	1.7
	5	78	22	100			40	50	10	100			100	30/60/10	75/0/75	ABC	25	1	1	3.4	1.8	1.50	3.4
	6	78	22	100			40	50	10	100			100	30/60/10	75/0/75	ABC	25	2	1	3.4	1.8	1.50	1.7
	7	78	22	100			40	1	45	10	>60	4	100	30/60/10	75/-1/75	ABC	25	1	1	3.4	1.8	1.50	3.4
V-Beispiele	1	78	22	100			-	-	-	-	-	-	-	100/0/0/	75	ABC	25	1	1	3.4	1.8	5	3.4
	2	82	18	100			-	-	-	-	-	-	-	100/0/0/	75	AB	20	2.98	-	1,5+5	-	0.3	1.68
	3	-	-	-			10	90	100	100			-	0/100/0/	ca. 50	AB	17.2	4.1	-	-	-	-	-
	4	100	-	84.6	15	-	31.5	2.4	65	1.1	95.4	4.6	-	50/50/0/	ca. 20	AB	11.5	2.5	-	2	-	0.25	0.8

TS: Terephthalat, IS: Isophthalat, EG: Ethylen, BD: Butan, NG: Neopentyl
AzS: Azelaat, SzS: Sebazaat, AdS: Adipat, WS: weitere Dicarbonsäuren und Glykole

Tabelle 3

	Mindestsiegeltemperatur °C	Siegelhaftfestigkeit gegenüber APET/CPET-Menüschalen				Schältest (=Peelverhalten)	Trübung %	Glanz		Rauhigkeiten		
		140°C	160°C	180°C	200°C			A-Seite	C-Seite	A-Seite	C-Seite	
		N/15mm								µm		
Beispiele	1	142	1,7	3,6	5,8	6,4	++++	24	75	130	259	60
	2	128	4,8	4,2	6	8	++++	19	80	130	278	60
	3	134	3,5	5,8	6,5	6,9	++++	17	72	130	224	60
	4	128	5,5	7,4	7	7,2	++++	11	88	130	207	60
	5	132	3,1	3,8	4,6	6	++++	15	82	130	190	60
	6	128	4,8	6,4	7	7,4	++++	10	96	130	206	60
	7	130	3,3	4,7	4,8	5,5	++++	14	85	130	212	60
V-Beispiele	1	105	1,7	3,5	5	8	-	23	55	130	310	60
	2	109	2	4,2	5,5	8,1	-	13	110	190	69	25
	3	112	1,5	2	4	6	-	4	150	190	33	20
	4	110	2	3	4	5	-	1,5	130	190	120	22
Schältest:		Bei allen Siegeltemperaturen wird Folie von der Menüschale "gepeelt", ohne dass dabei die Folie ein- oder weiterreißt. Einwandfreies, sattes, sauberes Peelen der Folie von Menüschale, auch im oberen Temperaturbereich bei hoher Siegelhaftfestigkeit.										
		Bei allen Siegeltemperaturen reißt Folie beim Abziehen von der Menüschale ein.										

Patentansprüche

1. Coextrudierte, transparente, biaxial orientierte Polyesterfolie, enthaltend eine Basisschicht (B) und eine heißsiegelbare und zumindest gegenüber APET peelfähige Deckschicht (A), wobei die heißsiegelbare und peelfähige Deckschicht (A) aus

- a) 60- 97 Gew.-% Polyester und
b) 3-30 Gew.-% einem polyesterunverträglichem Polymer (= anti-PET-Polymer),

bezogen auf die Masse der Deckschicht (A),
besteht, wobei

c) der Polyester aus 25-95 Mol-% an Einheiten aufgebaut ist, die auf mindestens eine aromatische Dicarbonsäure und 5-75 Mol-% an Einheiten, die auf mindestens eine aliphatische Dicarbonsäure zurückgehen, wobei die Summe der dicarbonsäureabgeleiteten Molprozent 100 ergibt und

d) die Schichtdicke der Deckschicht (A) d_A 0,7 bis 2,5 μm beträgt, und das anti-PET-Polymer ein Cycloolefin-copolymer (COC) ist.

2. Siegelbare und peelfähige Polyesterfolie nach Anspruch 1, **dadurch gekennzeichnet, dass** die aliphatischen Dicarbonsäuren ausgewählt sind aus einer oder mehreren der folgenden Substanzen: Pimelinsäure, Korksäure, Azelainsäure, Sebazinsäure, Glutarsäure und Adipinsäure.

3. Siegelbare und peelfähige Polyesterfolie nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** die aromatischen Dicarbonsäuren ausgewählt sind aus einer oder mehreren der folgenden Substanzen: Terephthalsäure, Isophthalsäure und 2,6-Naphthalindicarbonsäure.

4. Siegelbare und peelfähige Polyesterfolie nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** der Polyester der Deckschicht (A):

25 bis 95 Mol-% Terephthalat,
0 bis 25 Mol-% Isophthalat,
5 bis 75 Mol-% Azelat,
0 bis 50 Mol-% Sebazat,
0 bis 50 Mol-% Adipat,
mehr als 30 Mol-% Ethylen,

jeweils bezogen auf die Gesamtdicarboxylat- bzw. Gesamtalkylenmenge, enthält.

5. Siegelbare und peelfähige Polyesterfolie nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** die heißsiegelbare und peelfähige Deckschicht (A) eine Siegelanspringtemperatur (= Mindestsiegeltemperatur) gegenüber der APET-Seite von APET/CPET-Menüschalen von nicht mehr als 150 °C aufweist.

6. Siegelbare und peelfähige Polyesterfolie nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** die heißsiegelbare und peelfähige Deckschicht (A) eine Siegelnahtfestigkeit gegenüber der APET-Seite von APET/CPET-Menüschalen von mindestens 1,7 N aufweist.

7. Siegelbare und peelfähige Polyesterfolie nach einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet, dass** die heißsiegelbare und peelfähige Deckschicht (A) gegenüber der APET-Seite von APET/CPET-Menüschalen eine max. Siegeltemperatur von 220 °C aufweist.

8. Siegelbare und peelfähige Polyesterfolie nach einem der Ansprüche 1 bis 7, **dadurch gekennzeichnet, dass** die Siegeltemperatur (ϑ in °C) und die Peelkraft (in N/15 mm) über folgende Gleichung korreliert sind:

$$0,02 \cdot \vartheta / ^\circ\text{C} - 0,8 \leq \text{Peelkraft } F / \text{N je } 15 \text{ mm} \leq 0,033 \cdot \vartheta / ^\circ\text{C} + 1,4.$$

9. Siegelbare und peelfähige Polyesterfolie nach Anspruch 1, **dadurch gekennzeichnet, dass** das anti-PET-Polymer

ausgewählt wird aus einer oder mehreren der folgenden Substanzen: Copolymere auf Basis von Norbornen/Ethylen und Tetracyclododecen/Ethylen.

10. Siegelbare und peelfähige Polyesterfolie nach einem der Ansprüche 1 bis 9, **dadurch gekennzeichnet, dass** der Polyester für die Deckschicht (A) aus zwei Polyestern I und II hergestellt wird.

11. Siegelbare und peelfähige Polyesterfolie nach Anspruch 10, **dadurch gekennzeichnet, dass** der Anteil des Polyesters I in der Deckschicht (A) 10 bis 60 Gew.-% beträgt.

12. Siegelbare und peelfähige Polyesterfolie nach Anspruch 11, **dadurch gekennzeichnet, dass** der Polyester I aus einem oder mehreren aromatischen Dicarboxylaten und einem oder mehreren aliphatischen Alkylenen besteht.

13. Siegelbare und peelfähige Polyesterfolie nach Anspruch 10, **dadurch gekennzeichnet, dass** der Anteil von Polyester II in der Deckschicht (A) 20 bis 70 Gew.-% beträgt.

14. Siegelbare und peelfähige Polyesterfolie nach Anspruch 13, **dadurch gekennzeichnet, dass** der Polyester II aus einem oder mehreren aromatischen Dicarboxylaten sowie einem oder mehreren aliphatischen Dicarboxylaten und einem oder mehreren aliphatischen Alkylenen besteht.

15. Siegelbare und peelfähige Polyesterfolie nach einem der Ansprüche 10 bis 14, **dadurch gekennzeichnet, dass** die Glasübergangstemperatur von Polyester I mehr als 50 °C beträgt.

16. Siegelbare und peelfähige Polyesterfolie nach einem der Ansprüche 10 bis 15, **dadurch gekennzeichnet, dass** die Glasübergangstemperatur von Polyester II weniger als 20 °C beträgt.

17. Siegelbare und peelfähige Polyesterfolie nach einem der Ansprüche 1 bis 16, **dadurch gekennzeichnet, dass** die Verteilung der Partikeldurchmesser der Partikel eine Streuung aufweist, die durch einen SPAN98 von $\leq 2,0$ beschrieben wird.

18. Siegelbare und peelfähige Polyesterfolie nach einem der Ansprüche 1 bis 17, **dadurch gekennzeichnet, dass** die Folie zweischichtig ist und einen AB-Aufbau hat.

19. Siegelbare und peelfähige Polyesterfolie nach einem der Ansprüche 1 bis 17, **dadurch gekennzeichnet, dass** die Folie dreischichtig ist und einen ABC-Aufbau hat.

20. Verfahren zur Herstellung einer siegelbaren und peelfähigen Polyesterfolie nach Anspruch 1, bei dem die Polymere für die Basisschicht (B) und die Deckschicht (A), die aus einem Polyester aufgebaut ist, der aus

- 25-95 Mol-% an Einheiten aufgebaut ist, die auf mindestens eine aromatische Dicarbonsäure und
- 5-75 Mol-% an Einheiten, die auf mindestens eine aliphatische Dicarbonsäure zurückgehen,

besteht, und ein Cycloolefincopolymer als anti-PET Polymer enthält, und gegebenenfalls die Deckschicht (C) getrennten Extrudern zugeführt werden, die Schmelzen dann in einer Mehrschichtdüse zu flachen Schmelzefilmen ausgeformt und übereinander geschichtet werden, anschließend der Mehrschichtfilm mit Hilfe einer Kühlwalze und gegebenenfalls weiteren Walzen abgezogen, verfestigt und danach biaxial streckorientiert und hitzefixiert wird, wobei die biaxiale Streckung aufeinanderfolgend durchgeführt wird, wobei zuerst längs (in Maschinenrichtung) und dann quer (senkrecht zur Maschinenrichtung) gestreckt wird, dass die Längsstreckung bei einer Temperatur im Bereich von 60 bis 130 °C und die Querstreckung im Bereich von 90 bis 140 °C durchgeführt wird und dass das Längsstreckverhältnis im Bereich von 2,0:1 bis 5,5:1 und das Querstreckverhältnis im Bereich von 2,4:1 bis 5,0:1 eingestellt wird.

21. Verfahren nach Anspruch 20, bei dem die Längsstreckung bei einer Temperatur im Bereich von 60 bis 120 °C und die Querstreckung im Bereich von 90 bis 140 °C durchgeführt wird und dass das Längsstreckverhältnis im Bereich von 2,0:1 bis 5,0:1 und das Querstreckverhältnis im Bereich von 2,4:1 bis 5,0:1 liegt.

22. Verfahren nach Anspruch 20, bei dem die Längsstreckung bei einer Temperatur im Bereich von 60 bis 110 °C und die Querstreckung im Bereich von 90 bis 140 °C durchgeführt wird und dass das Längsstreckverhältnis im Bereich von 2,0:1 bis 4,8:1 und das Querstreckverhältnis im Bereich von 2,4:1 bis 5,0:1 eingestellt wird.

23. Verwendung einer siegelfähigen Polyesterfolie nach einem der Ansprüche 1 bis 19 als Deckelfolie für die Abdeckung von Menüschalen aus APET/CPET.

5 Claims

1. A coextruded, transparent, biaxially oriented polyester film comprising a base layer (B) and a heatsealable top layer (A) which is peelable at least from APET, the heatsealable and peelable top layer (A) consisting of

- a. 60-97 % by weight of polyester and
b. 3-30 % by weight of a polyester-incompatible polymer (= anti-PET polymer)

based on the mass of the top layer (A),
and

- c. the polyester being composed of 25-95 mol% of units which derive from at least one aromatic dicarboxylic acid and 5-75 mol% of units which derive from at least one aliphatic dicarboxylic acid, the sum of the dicarboxylic acid-derived molar percentages being 100, and
d. the layer thickness of the top layer (A) d_A being from 0.7 to 2.5 μm , and the anti-PET polymer being a cycloolefin copolymer (COC).

2. The sealable and peelable polyester film as claimed in claim 1, wherein the aliphatic dicarboxylic acids are selected from one or more of the following substances: pimelic acid, suberic acid, azelaic acid, sebacic acid, glutaric acid and adipic acid.

3. The sealable and peelable polyester film as claimed in claim 1 or 2, wherein the aromatic dicarboxylic acids are selected from one or more of the following substances: terephthalic acid, isophthalic acid and 2,6-naphthalenedicarboxylic acid.

4. The sealable and peelable polyester film as claimed in one of claims 1 to 3, wherein the polyester of the top layer (A) comprises:

from 25 to 95 mol% of terephthalate,
from 0 to 25 mol% of isophthalate,
from 5 to 75 mol% of azelate,
from 0 to 50 mol% of sebacate,
from 0 to 50 mol% of adipate,
more than 30 mol% of ethylene,

based in each case on the total amount of dicarboxylate or the total amount of alkylene.

5. The sealable and peelable polyester film as claimed in one of claims 1 to 4, wherein the heatsealable and peelable top layer (A) has a sealing commencement temperature (= minimum sealing temperature) with respect to the APET side of APET/CPET trays of not more than 150 °C.

6. The sealable and peelable polyester film as claimed in one of claims 1 to 5, wherein the heatsealable and peelable top layer (A) has a seal seam strength with respect to the APET side of APET/CPET trays of at least 1.7 N.

7. The sealable and peelable polyester film as claimed in one of claims 1 to 6, wherein the heatsealable and peelable top layer (A) with respect to the APET side of APET/CPET trays has a max. sealing temperature of 220 °C.

8. The sealable and peelable polyester film as claimed in one of claims 1 to 7, wherein the sealing temperature (in °C) and the peeling force (in N/15 mm) are correlated via the following equation:

$$0.02 \cdot \theta / ^\circ\text{C} - 0.8 \leq \text{peeling force } F/N \text{ per } 15 \text{ mm} \leq 0.033 \cdot \theta / ^\circ\text{C} \\ 1.4.$$

9. The sealable and peelable polyester film as claimed in claim 1, wherein the anti-PET polymer is selected from one or more of the following substances: copolymers based on norbornene/ethylene and tetracyclododecene/ethylene.
10. The sealable and peelable polyester film as claimed in one of claims 1 to 9, wherein the polyester for the top layer (A) is produced from two polyesters I and II.
11. The sealable and peelable polyester film as claimed in claim 10, wherein the proportion of the polyester I in the top layer (A) is from 10 to 60 % by weight.
12. The sealable and peelable polyester film as claimed in claim 11, wherein the polyester I consists of one or more aromatic dicarboxylates and one or more aliphatic alkenes.
13. The sealable and peelable polyester film as claimed in claim 10, wherein the proportion of polyester II in the top layer (A) is from 20 to 70 % by weight.
14. The sealable and peelable polyester film as claimed in claim 13, wherein the polyester II consists of one or more aromatic dicarboxylates and also one or more aliphatic dicarboxylates and one or more aliphatic alkenes.
15. The sealable and peelable polyester film as claimed in one of claims 10 to 14, wherein the glass transition temperature of polyester I is more than 50 °C.
16. The sealable and peelable polyester film as claimed in one of claims 10 to 15, wherein the glass transition temperature of polyester II is less than 20 °C.
17. The sealable and peelable polyester film as claimed in one of claims 1 to 16, wherein the distribution of the particle diameters of the particles has a degree of scatter which is described by a SPAN98 of ≤ 2.0 .
18. The sealable and peelable polyester film as claimed in one of claims 1 to 17, wherein the film has two layers and an AB structure.
19. The sealable and peelable polyester film as claimed in one of claims 1 to 17, wherein the film has three layers and an ABC structure.
20. A process for producing a sealable and peelable polyester film as claimed in claim 1, in which the polymers for the base layer (B) and the top layer (A) which is composed of a polyester which consists of
 - a) 25-95 mol% of units which derive from at least one aromatic dicarboxylic acid and
 - b) 5-75 mol% of units which derive from at least one aliphatic dicarboxylic acid,
 and contains a cycloolefin copolymer as anti-PET polymer, and, where appropriate, the top layer (C) are fed to separate extruders, the melts are then shaped and layered on top of one another in a multilayer die to give flat melt films, then the multilayer film is drawn off with the aid of a chill roll and optionally further rolls, solidified and then biaxially stretch-oriented and heat-set, the biaxial stretching being carried out in succession, first longitudinally (in machine direction) and then transversely (at right angles to machine direction) that the longitudinal stretching is carried out at a temperature in the range from 60 to 130 °C and the transverse stretching in the range from 90 to 140 °C, and that the longitudinal stretching ratio is set within the range from 2.0:1 to 5.5:1 and the transverse stretching ratio within the range from 2.4:1 to 5.0:1.
21. The process as claimed in claim 20, in which the longitudinal stretching is carried out at a temperature in the range from 60 to 120 °C and the transverse stretching in the range from 90 to 140 °C and that the longitudinal stretching ratio is in the range from 2.0:1 to 5.0:1 and the transverse stretching in the range from 2.4:1 to 5.0:1.
22. The process as claimed in claim 20, in which the longitudinal stretching is carried out at a temperature in the range from 60 to 110 °C and the transverse stretching in the range from 90 to 140 °C and that the longitudinal stretching ratio is set within the range from 2.0:1 to 4.8:1 and the transverse stretching within the range from 2.4:1 to 5.0:1.
23. The use of a sealable polyester film as claimed in one of claims 1 to 19 as a lid film for covering APET/CPET trays.

Revendications

1. Film de polyester co-extrudé, transparent, orienté de façon biaxiale, contenant une couche de base (B) et une couche de recouvrement (A) thermoscellable et pelable au moins par rapport à l'APET, dans lequel la couche de recouvrement thermoscellable et pelable (A) consiste en

- a) 60 à 97 % en poids de polyester et
b) 3 à 30 % en poids d'un polymère non compatible avec le polyester (= polymère anti-PET),

par rapport à la masse de la couche de recouvrement (A), dans lequel

- c) le polyester est constitué de 25 à 95 % en mole de motifs qui proviennent d'au moins un acide dicarboxylique aromatique et 5 à 75 % en mole de motifs qui proviennent d'au moins un acide dicarboxylique aliphatique, dans lequel la somme des pourcentages en mole dérivés de l'acide dicarboxylique donne 100 et

- d) l'épaisseur de couche de la couche de recouvrement (A) d_A est de 0,7 à 2,5 μm , et le polymère anti-PET est un copolymère de cyclo-oléfine (COC).

2. Film de polyester thermoscellable et pelable selon la revendication 1, **caractérisé en ce que** les acides dicarboxyliques aliphatiques sont choisis parmi une ou plusieurs des substances suivantes : acide pimélique, acide subérique, acide azélaïque, acide sébacique, acide glutarique et acide adipique.

3. Film de polyester thermoscellable et pelable selon la revendication 1 ou 2, **caractérisé en ce que** les acides dicarboxyliques aromatiques sont choisis parmi une ou plusieurs des substances suivantes : acide téréphtalique, acide isophtalique et acide 2,6-naphtaline-dicarboxylique.

4. Film de polyester thermoscellable et pelable selon l'une des revendications 1 à 3, **caractérisé en ce que** le polyester de la couche de recouvrement (A) contient :

- 25 à 95 % en mole de téréphtalate,
0 à 25 % en mole d'isophtalate,
5 à 75 % en mole d'azélate,
0 à 50 % en mole de sébacate,
0 à 50 % en mole d'adipate,
plus de 30 % en mole d'éthylène,

respectivement par rapport à la quantité totale de dicarboxylate ou d'alkylène.

5. Film de polyester thermoscellable et pelable selon l'une des revendications 1 à 4, **caractérisé en ce que** la couche de recouvrement thermoscellable et pelable (A) présente une température d'amorçage du thermosoudage (= température de thermosoudage minimale) par rapport au côté d'APET des barquettes alimentaires en APET/CPET non supérieure à 150 °C.

6. Film de polyester thermoscellable et pelable selon l'une des revendications 1 à 5, **caractérisé en ce que** la couche de recouvrement thermoscellable et pelable (A) présente une résistance de soudage par rapport au côté d'APET des barquettes alimentaires en APET/CPET d'au moins 1,7 N.

7. Film de polyester thermoscellable et pelable selon l'une des revendications 1 à 6, **caractérisé en ce que** la couche de recouvrement thermoscellable et pelable (A) présente par rapport au côté d'APET des barquettes alimentaires en APET/CPET, une température maximale de thermoscellage de 220 °C.

8. Film de polyester thermoscellable et pelable selon l'une des revendications 1 à 7, **caractérisé en ce que** la température de thermoscellage (ϑ en °C) et la force de pelage (en N/15 mm) sont corrélées selon l'équation suivante :

$$0,02 \cdot \vartheta / ^\circ\text{C} - 0,8 \leq \text{force de pelage } F / \text{N pour } 15 \text{ mm} \leq 0,033 \cdot \vartheta / ^\circ\text{C} + 1,4.$$

9. Film de polyester thermoscellable et pelable selon la revendication 1, **caractérisé en ce que** le polymère anti-PET est choisi parmi une ou plusieurs des substances suivantes : copolymères à base de norbornène/éthylène et de tétracyclododécène/éthylène.

5 10. Film de polyester thermoscellable et pelable selon l'une des revendications 1 à 9, **caractérisé en ce que** le polyester pour la couche de recouvrement (A) est produit à partir de deux polyesters I et II.

11. Film de polyester thermoscellable et pelable selon la revendication 10, **caractérisé en ce que** la proportion de polyester I dans la couche de recouvrement (A) est de 10 à 60 % en poids.

10 12. Film de polyester thermoscellable et pelable selon la revendication 11, **caractérisé en ce que** le polyester I consiste en un ou plusieurs dicarboxylates aromatiques et un ou plusieurs alkylènes aliphatiques.

13. Film de polyester thermoscellable et pelable selon la revendication 10, **caractérisé en ce que** la proportion de polyester II dans la couche de recouvrement (A) est de 20 à 70 % en poids.

14. Film de polyester thermoscellable et pelable selon la revendication 13, **caractérisé en ce que** le polyester II consiste en un ou plusieurs dicarboxylates aromatiques ainsi qu'en un ou plusieurs dicarboxylates aliphatiques et un ou plusieurs alkylènes aliphatiques.

20 15. Film de polyester thermoscellable et pelable selon l'une des revendications 10 à 14, **caractérisé en ce que** la température de transition vitreuse du polyester I est supérieure à 50 °C.

25 16. Film de polyester thermoscellable et pelable selon l'une des revendications 10 à 15, **caractérisé en ce que** la température de transition vitreuse du polyester II est inférieure à 20 °C.

17. Film de polyester thermoscellable et pelable selon l'une des revendications 1 à 16, **caractérisé en ce que** la répartition du diamètre particulaire des particules présente une dispersion qui est décrite par un SPAN98 de $\leq 2,0$.

30 18. Film de polyester thermoscellable et pelable selon l'une des revendications 1 à 17, **caractérisé en ce que** le film a deux couches et une structure AB.

35 19. Film de polyester thermoscellable et pelable selon l'une des revendications 1 à 17, **caractérisé en ce que** le film a trois couches et une structure ABC.

20. Procédé de fabrication d'un film de polyester thermoscellable et pelable selon la revendication 1, dans lequel le polymère pour la couche de base (B) et la couche de recouvrement (A), qui est constituée d'un polyester, est constitué de

- 40 - 25 à 95 % en mole de motifs qui proviennent d'au moins un acide dicarboxylique aromatique et de
- 5 à 75 % en mole de motifs qui proviennent d'au moins un acide dicarboxylique aliphatique

45 et contient un copolymère de cyclo-oléfine comme polymère anti-PET, et éventuellement la couche de recouvrement (C) est acheminée à des extrudeuses séparées, les masses fondues sont ensuite moulées en film fondu plat dans une buse à couches multiples et sont stratifiées l'une sur l'autre, ensuite, le film multicouche est étiré à l'aide d'un cylindre de refroidissement et éventuellement d'autres rouleaux, est fixé et ensuite, est orienté biaxialement par étirement et thermofixé, dans lequel l'étirement biaxial est réalisé consécutivement, dans lequel l'étirement est tout d'abord longitudinal (dans le sens de la machine) puis perpendiculaire (perpendiculaire au sens de la machine), en ce que l'étirement longitudinal est réalisé à une température dans la plage de 60 à 130 °C et l'étirement perpendiculaire est réalisé dans la plage de 90 à 140 °C et en ce que le rapport d'étirement longitudinal est ajusté dans la

50 plage de 2,0 : 1 à 5,5 : 1 et le rapport d'étirement perpendiculaire est ajusté dans la plage de 2,4 : 1 à 5,0 : 1.

21. Procédé selon la revendication 20, dans lequel l'étirement longitudinal est réalisé à une température dans la plage de 60 à 120 °C et l'étirement perpendiculaire est réalisé dans la plage de 90 à 140 °C et en ce que le rapport d'étirement longitudinal se situe dans la plage de 2,0 : 1 à 5,0 : 1 et le rapport d'étirement perpendiculaire se situe dans la plage de 2,4 : 1 à 5,0 : 1.

22. Procédé selon la revendication 20, dans lequel l'étirement longitudinal est réalisé à une température dans la plage

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de 60 à 110 °C et l'étirement perpendiculaire est réalisé dans la plage de 90 à 140 °C et en ce que le rapport d'étirement longitudinal se situe dans la plage de 2,0 : 1 à 4,8 : 1 et le rapport d'étirement perpendiculaire se situe dans la plage de 2,4 : 1 à 5,0 : 1.

- 5 **23.** Utilisation d'un film de polyester thermoscellable selon l'une des revendications 1 à 19, comme film servant de couvercle pour le recouvrement de barquettes alimentaires en APET/CPET.

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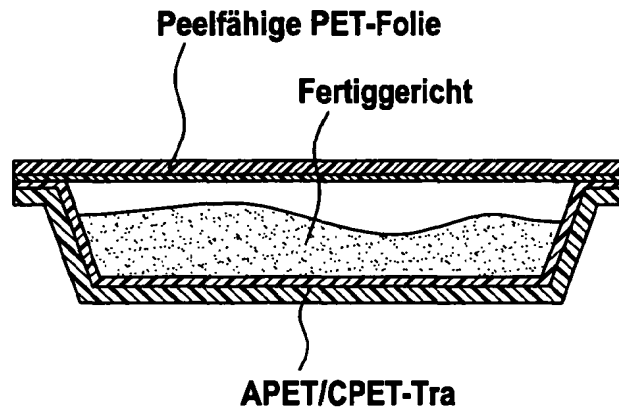


Fig. 1 Menseschale (Tray) aus APET/CPET mit Fertiggericht und von Menseschale abziehbarer (peelfähiger) Folie

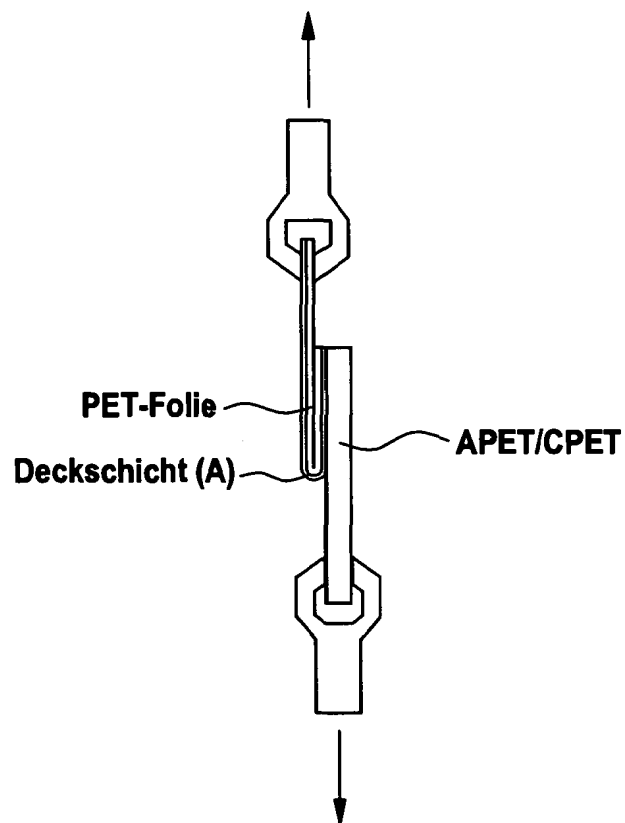


Fig. 2 Anordnung von "peelfähiger" Folie und Streifen einer APET/CPE-Menseschale im Zug-Dehnungs-Messgerät

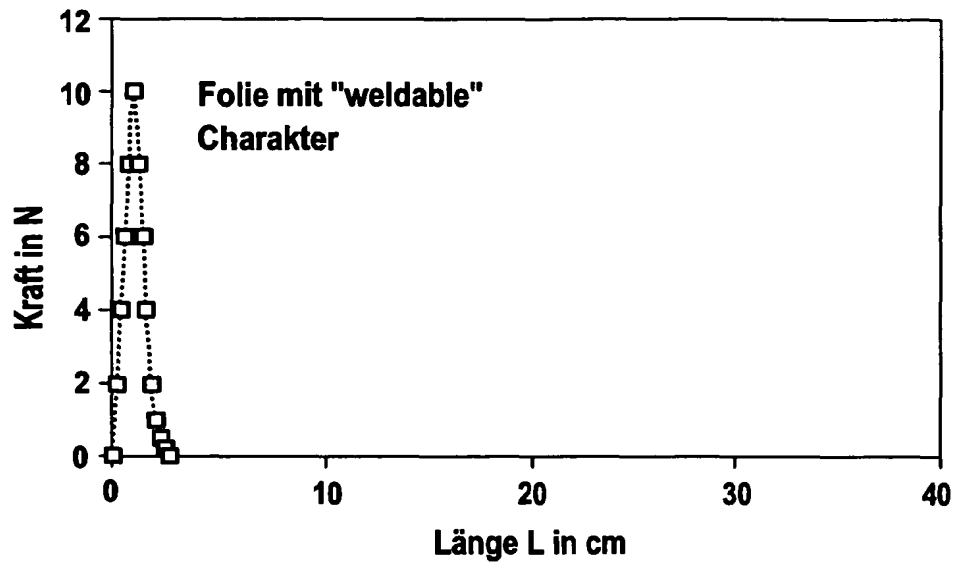


Fig. 3a Reiss-Dehnungsdiagramm einer Folie mit "weldable" Verhalten

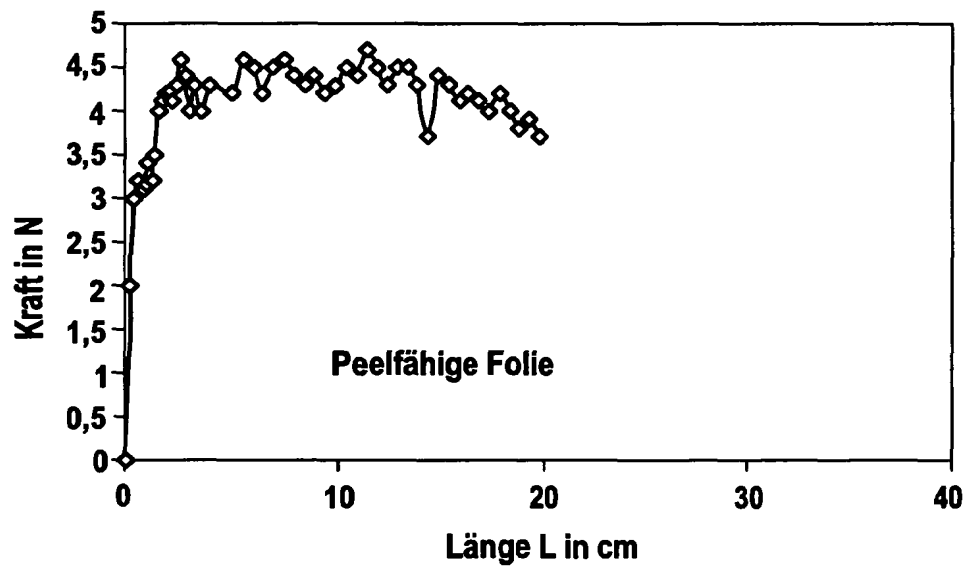


Fig. 3b Reiss-Dehnungsdiagramm einer Folie mit "peelable" Verhalten

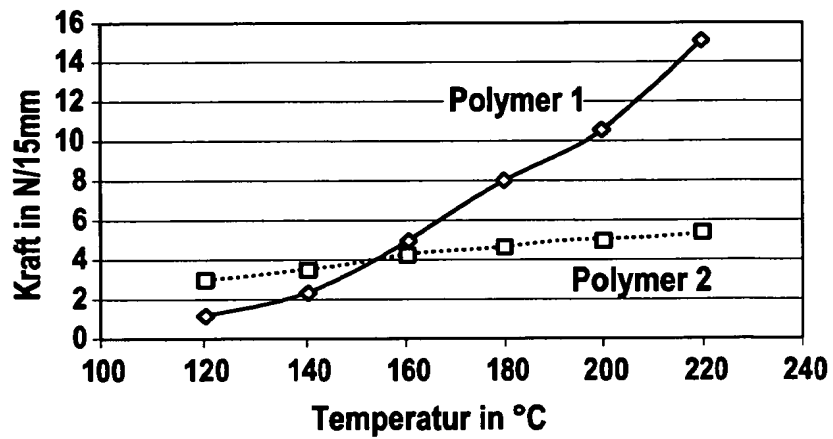


Fig. 4 Reiss-Dehnungsverhalten einer Folie mit "weldable" und "peelable" Verhalten

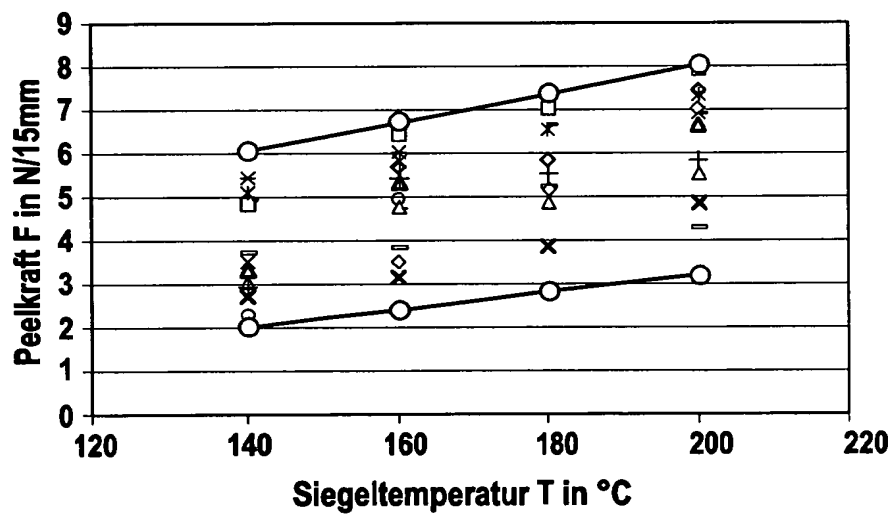


Fig. 5 Zusammenhang zwischen Siegeltemperatur in °C und Peelkraft in N/15mm

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- **AHLHAUS, O.E.** Verpackung mit Kunststoffen. Carl Hanser Verlag, 1997, 271 [0023]

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(54) **MULTILAYER FILM COMPRISING AN AMORPHOUS POLYMER**

MEHRSSCHICHTFOLIE ENTHALTEND AMORPHES POLYMER

FILM A COUCHES MULTIPLES CONTENANT UN POLYMERE AMORPHE

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DescriptionBackground of the Invention

5 **[0001]** The present invention relates to packaging materials of a type employing flexible, polymeric films. More specifically, the invention pertains to multilayer packaging films used in applications requiring a high degree of dimensional stability, i.e., both low shrinkage and low stretch, at elevated temperatures, and also a relatively low oxygen transmission rate.

10 **[0002]** Packaging applications requiring dimensionally stable films at high temperatures, e.g., up to about 150 °C and sometimes as high as about 180°C, include vertical form-fill-seal (VFFS) packaging for "hot fill" products, such as soups, sauces, jellies, beverages, and other liquified foods. As is well known, in VFFS packaging, a flowable product is introduced through a central, vertical fill tube and into a formed tubular film that has been heat-sealed transversely at its lower end and also longitudinally. Heat-sealing temperatures typically range from about 90 to about 150 °C, and often reach or exceed 180 °C as packaging equipment operators attempt to make strong heat-seals, e.g., those that will seal through

15 hot-fill product that inadvertently contaminates the seal area of the film.
[0003] After being filled, the package, in the form of a pouch, is completed by transversely heat-sealing the upper end of the tubular segment and simultaneously severing the pouch from the tubular film above it, usually by applying sufficient heat to melt through the tube above the newly formed upper heat-seal. If the film from which the package is made does not have sufficient dimensional stability, the package becomes distorted both from the heated product and from heat-sealing. Not only does package distortion ruin the aesthetic qualities of the package, e.g., by distorting any printed information or other labeling on the package, but it can cause the package to become misaligned in the packaging machinery, often resulting in ruined packages and costly downtime in production as misaligned packages become wedged between pieces of the machinery or when heat-sealing/severing equipment inadvertently contacts and melts through the walls of the package instead of sealing and severing at the periphery of the misaligned package as intended.

20 **[0004]** Similar considerations apply in VFFS and horizontal form/fill/seal (HFFS) packaging of flowable particulate products, e.g., shredded cheese, frozen chicken wings and nuggets, etc. Although such products are generally not filled while in a heated state, transverse and longitudinal heat-sealing and heat-severing alone are sufficient to cause package distortion, thereby making a film which is dimensionally stable at elevated temperatures highly desirable for such packaging applications.

30 **[0005]** Another packaging application for which high-temperature dimensional film stability would be desirable is when films are used as lidding materials for flexible packages, such as thermoformed pockets in which, e.g., hot dogs, lunch meats, etc., are contained; semi-rigid vacuum and/or gas-flushed packages for meat and poultry contained in a foam or other semi-rigid type tray; and rigid packages, e.g., for yogurt, custard and other dairy products contained in a rigid cup-like container. When lidding films are applied to such packages, heat is generally used to seal the film to the thermoformed container, tray, or cup in which the product is contained. As with the foregoing form-fill-seal packaging operations, high heat-seal temperatures are often employed in order to form strong heat-seals that will seal through particles or globs of food that contaminate the heat-seal area. Without sufficient dimensional stability, the lidding films can either stretch or shrink during the lidding process, resulting in incompletely sealed packages and distorted printed images on the films.

40 **[0006]** A further process necessitating dimensional stability at elevated temperatures is printing. Maintenance of color-to-color registration on the printing press is important, as is overall consistency of the "repeat length" of each printed image. Drying tunnel temperatures commonly reach temperatures of 49°C or more. It is therefore preferred that the film have sufficient resistance to stretching, necking and other types of deformation at these temperatures so that registration is not lost, and that the repeat length of the images are consistently maintained on downstream packaging equipment, where it may again face elevated temperatures as noted above. When a film is printed, any deformation that occurs during the packaging process is particularly troublesome, in that the printed image becomes visibly distorted. Thus, maintaining dimensional stability under high-temperature packaging is especially important when the film is printed.

45 **[0007]** Another requirement of films used in many of the aforementioned packaging applications is a low transmission rate of oxygen in order to preserve and extend the shelf life of packaged food products. For many food products, the oxygen transmission rate (OTR) must be on the order of 40 cc/m² per 24 hours at 101325 Pa, (1 atmosphere) or less.

50 **[0008]** In order to achieve the above properties, many conventional packaging films used for such applications have been laminates, i.e., two or more film components that are adhesively bonded together, e.g., biaxially-oriented and heat-set polypropylene, polyester, or polyamide films that are adhesively laminated to a heat-sealable film where one of the laminated film components contains a low OTR material such as polyvinylidene chloride. However, adhesive lamination is expensive, due to the relatively high cost of the adhesives and the extra production steps required to produce the laminate, and the reliability of such adhesives is sometimes suspect, e.g., solvents from printing inks can reduce the bond-strength of the adhesives, leading to delamination. Further, certain types of adhesives contain low-molecular weight components that can migrate through films and contact the packaged food products.

[0009] Instead of using a laminate, it would be preferred to use a film that is fully coextruded, i.e., formed by extruding two or more polymeric materials through a single die with two or more orifices arranged so that the extrudates merge and weld together into a multilayer structure.

[0010] A proposed coextruded film having high-temperature dimensional stability and a low OTR includes a core layer of ethylene/vinyl alcohol copolymer (EVOH), a layer of amorphous polyamide to provide relatively high modulus at high temperatures, and a heat-sealing layer. While this film was able to address some of the problems detailed above, it was found that it did not provide a sufficiently wide temperature-processing window to make high quality packages from such film. That is, the glass transition temperature of the amorphous polyamide and the melting point of the heat-sealing layer were found to be too close to one another to provide a desired combination of good heat-sealability and dimensional stability at elevated temperatures.

[0011] US6379812 discloses multilayer films comprising a layer of amorphous polyamide as well as an external heat-seal layer.

[0012] Accordingly, there continues to be a need in the art for a coextruded, low-OTR multilayer film having a combination of high-temperature dimensional stability and low-temperature heat-sealability.

Summary of the Invention

[0013] That need is met by the present invention which provides a multilayer film, comprising,

- a. a first layer comprising an amorphous polymer that exhibits a glass transition temperature; and
- b. a second layer forming an exterior layer of the multilayer film and comprising a sealant material capable of forming a heat-seal, the sealant material comprising a polymer that exhibits a melting point.

[0014] The glass transition temperature of the amorphous polymer is greater than the melting point of the sealant material by at least about 45 degrees centigrade.

Brief Description of the Drawing

[0015]

FIG. 1 is a cross-sectional view of a multilayer film in accordance with the invention.

Detailed Description of the Invention

[0016] FIG. 1 depicts one embodiment of a multilayer film in accordance with the present invention. In the instant depiction, multilayer film 10 includes nine layers. As is readily understood by those of ordinary skill in the art of film manufacture, a greater or lesser number of layers may be included, depending on the specific attributes that are desired in such a film to suit the intended end-use application. As used herein, the term "multilayer film" refers to a thermoplastic material, generally in sheet or web form, having one or more layers formed from polymeric or other materials which are bonded together by any conventional or suitable method, including one or more of the following methods: coextrusion, extrusion coating, lamination, vapor deposition coating, solvent coating, emulsion coating, or suspension coating, but preferably by coextrusion.

[0017] Multilayer film 10 includes a first layer 12, comprising an amorphous polymer that exhibits a glass transition temperature, and a second layer 14, which forms an exterior layer of multilayer film 10 as shown and which comprises a sealant material capable of forming a heat-seal. First layer 12 may be an interior or exterior layer, but is preferably an interior layer, and preferably includes at least one layer positioned between the first layer and the exterior layers of the film that serves as a moisture vapor barrier, such as, e.g., a layer comprising polyolefin.

[0018] As used herein, the term "amorphous polymer" refers to those polymers that are substantially lacking in crystallinity as shown by the lack of an endotherm crystalline melting peak in a Differential Scanning Calorimeter (DSC) test in accordance with ASTM D-3417. Amorphous polymers generally lack a regular three-dimensional arrangement of molecules or molecule sub-units that extend over distances which are large relative to atomic dimensions. However, regularity of structure may exist on a local scale as minor, semi-crystalline phases. See, "Amorphous Polymers," Encyclopedia of Polymer Science and Engineering, 2nd Ed., pp. 789-842 (J. Wiley & Sons, Inc. 1985).

[0019] As used herein, the term "glass transition temperature," sometimes abbreviated herein as "T_g", refers to the approximate midpoint of the temperature range over which an amorphous polymer undergoes a reversible change from a hard, glassy, or brittle condition to a flexible or elastomeric condition, and may be determined in accordance with ISO 3146-C or ASTM D-3418.

[0020] The amorphous polymer in first layer 12 preferably has a glass transition temperature of at least about 140 °C,

such as at least about 145, 150, 155, 160, 165, 170, 175, or 180 °C. First layer 12 preferably comprises less than about 50 % of the total thickness of film 10, such as less than about 45, 40, 35, 30, or 25 % of the total thickness of film 10. If desired, other layers in addition to layer 12 may have such amorphous polymer therein, either as a major or minor component. Generally, the amorphous polymer is preferably a minor component of the total constituency of film 10. Thus, film 10 preferably contains at least about 40 wt.%, such as at least about 45, 50, 55, 60, 65, 70 or 75 wt.%, of materials having a T_g of less than 125 °C.

[0021] An example of an amorphous polymer that may be used in first layer 12 is an amorphous polyamide. Generally, amorphous polyamides can be characterized as high molecular-weight polymers in which amide linkages occur, and which contain aromatic segments with various proportions of aliphatic segments. For example, some amorphous polyamides are copolyamides of an aliphatic diamine and an aromatic isophthalic and/or terephthalic diacid.

[0022] Suitable amorphous polyamides may include those amorphous polymers that are prepared from the following diamines: hexamethylenediamine, 2-methylpentamethylenediamine (MPMD), 2,2,4-trimethylhexamethylenediamine (TMD), 2,4,4-trimethylhexamethylenediamine (IND), bis(4-aminocyclohexyl)methane, 2,2-bis(4-aminocyclohexyl)isopropylidene, 1,4-diaminocyclohexane, 1,3-diaminocyclohexane, meta-xylylenediamine (MXD), 1,5-diaminopentane, 1,4-diaminobutane, 1,3-diaminopropane, 2-ethyldiaminobutane, 1,4-diaminomethylcyclohexane, 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane (MACM), 3-aminomethyl-3,5,5-trimethylcyclohexylamine (IPD), bis(4-aminocyclohexyl)methane (PACM), 2,2-bis(p-aminocyclohexyl) propane (PACP), 1,6-diamino-2,2,4-trimethylhexane (ND), p-xylylenediamine (PXD), m-phenylenediamine, p-phenylenediamine, and alkyl substituted m-phenylenediamine and p-phenylenediamine.

[0023] Examples of amorphous polyamides that can be used also include those amorphous polymers prepared from the following dicarboxylic acids: isophthalic acid (I), terephthalic acid (T), 1,3-phenylenedoxydiacetic acid, 1,4-cyclohexanedicarboxylic acid, 2,6-naphthalene dicarboxylic acid (N), 1,1,3-trimethyl-3-phenylindan-4,5 dicarboxylic acid, alkyl substituted iso- and terephthalic acid, adipic acid, sebacic acid, octadecanedioic, dodecanedioic acid (DDA), brassylic acid, tetradecanedioic acid, butane dicarboxylic acid, and the like.

[0024] The diamines and dicarboxylic acids mentioned above can be combined as desired. For example, an aliphatic diamine can generally be combined with an aromatic dicarboxylic acid as noted above, or an aromatic diamine can be combined with an aliphatic dicarboxylic acid. Amorphous polyamides prepared from aromatic diamines and aromatic diacids, or those prepared from aliphatic diamines and aliphatic diacids, may also be suitable. Preferred amorphous polyamides are those in which either the diamine or the dicarboxylic acid moiety is aromatic, and the other moiety is aliphatic. The aliphatic groups of these polyamides preferably contain between 4 and 12 carbon atoms in a chain or an aliphatic cyclic ring system having up to 15 carbon atoms. The aromatic groups of the polyamides preferably have mono or bicyclic aromatic rings which may contain aliphatic substituents of up to about 6 carbon atoms. If desired, more than one diamine may be combined with one diacid, more than one diacid may be combined with one diamine, and more than one diacid and more than one diamine may be combined. The amorphous polyamides may also contain as comonomers amounts of lactam species such as caprolactam or lauryl lactam, 3,6-bis(aminomethyl)norbornane (AMNB) and diphenylmethane-4-4'-diisocyanate (MDI).

[0025] It is not necessary that the above-recited polyamide forming monomers be used per se in the polymerization reaction. The actual materials used in the polymerization reaction may be the recited monomers or polyamide-forming derivatives of these monomers, such as the acid chloride, ammonium salt, ester, half-ester, and the like.

[0026] Specific examples of suitable amorphous polyamides include: polyamide 6I/6T, polyamide 6I/MACMT, polyamide 6I/MACMI, polyamide 6I/MACMI/MACMT, polyamide 6/MACMI/MXD, polyamide 6I/6T/MACMI, polyamide 12/MACMI, polyamide 12/MACMT, polyamide 12/MACMI, polyamide 12/IPDI/PACMI, polyamide 12/PACMI, polyamide TMDT, polyamide 6I/6T/IPD, polyamide 6I/6T/PACMI/PACMT, polyamide 6I/6, polyamide MACMVMACMX, polyamide XT/MA.CMT, polyamide PACM12, polyamide 6/AMNB and polyamide MDI6/MDI9. Such amorphous polyamides are commercially available from a number of manufactures, such as from EMS-Chemie under the designation Grilamid and Grivory; from Degussa under the designation Trogamid; from ELF Atochem under the designation Cristamid; from Mitsubishi Kasei under the designation Novamid; from Bayer AG under the designation Durethan; and from DuPont under the designation Selar or Zytel.

[0027] Further information regarding the foregoing amorphous polyamides may be found in the "Nylon Plastics Handbook" by M. I. Kohan, particularly at pgs. 3-8 and 377-387, the disclosure of which is hereby incorporated by reference herein.

[0028] If desired, first layer 12 may comprise a blend of at least two amorphous polyamides. When amorphous polyamides are to be employed as the amorphous polymer in first layer 12, it is preferred that layer 12 consists essentially of amorphous polyamide, whether one or more amorphous polyamides are used in such layer. Optionally, however, the amorphous polyamide may be blended with a crystalline material, e.g., crystalline polyamide.

[0029] Alternative materials that may be used as the amorphous polymer in first layer 12 are polymers that are referred to as "high-performance polymers," which have been developed for structural applications or for use in mechanical and electrical components with long-term heat-resistance requirements at temperatures greater than 150 °C. Such polymers include polycarbonate (PC), cyclic olefin copolymers (e.g., ethylene/norbornene copolymer), polysulfone (PSU), poly-

ethersulfone (PES), polyarylsulfone (PAS), styrene maleic anhydride copolymer (SMA), polyetherimide (PEI), polyphenylene oxide (PPO), PPO/polystyrene (PS) alloys, polyphenylene ether (PPE), and polyarylate. Suitable polycarbonates are available from Dow Chemicals under the designation Calibre® and from Bayer Corporation under the designation APEC®. Suitable PPO/PS alloys and polyphenylene oxides are available from General Electric Corporation under the designation Noryl® and PPO®, respectively. Suitable polyphenylene ethers are available from Degussa under the designation Vestoran®. Suitable PEI is available from General Electric Corporation under the designation Ultem®. Suitable styrene maleic anhydride copolymers are available from Nova Chemicals under the designation Dylark®. Suitable cyclic olefin copolymers are available from Zeon under the designation Zeonor® and from Ticona under the designation Topas®. Suitable polysulfones are available from Solvay under the designation Udel® or from BASF under the designation Ultrason®. Suitable polyethersulfones are available from Amoco Polymers under the designation Radel®. Suitable polyarylates are from Amoco Polymers under the designation Ardek®.

[0030] Multilayer film 10 preferably has a storage modulus of at least 100 pounds/linear inch of width at temperatures up to 140 °C. For a film having a thickness of 2.5 mils (0.0025 inch), a storage modulus of at least 17.5 kN/m (100 pounds/linear inch) equates to a storage modulus of at least 276 MPa (40,000 pounds/in²)(storage modulus is based on the cross-sectional area of the film, and may be determined in accordance with ASTM D-5026-95a). Such a storage modulus provides the films of the present invention with excellent high-temperature dimensional stability, and may be achieved by including an amorphous polymer in first layer 12, e.g., having a T_g of at least about 140 °C. More preferably, film 10 maintains a storage modulus of at least 175 N/cm (100 pounds/linear inch) at temperatures up to 145 °C and beyond, such as 150, 155, 160, or 165 °C. Regardless of the thickness of film 10, it preferably maintains a storage modulus of at least about 138 MPa (20,000 psi), such as at least about 207 MPa (30 000 psi), 241 MPa (35 000 psi), 276 MPa (40 000 psi), or 310 MPa (45 000psi), at temperatures up to 130 °C, such as up to 135, 140, 145, 150, 155, 160, or 165 °C. Preferably, however, the film is not overly stiff or brittle at room temperatures. Thus, the film preferably has a storage modulus of less than about 5171 MPa, (750,000 psi), such as less than 4137 MPa (600,000 psi), 3447 MPa (500,000 psi), 2758 MPa (400,000 psi), 2068 MPa (300,000 psi), 1379 MPa (200,000 psi), or 1034 MPa (150,000 psi) at temperatures of about 23°C (73°F).

[0031] As noted above, second layer 14 forms an exterior layer of multilayer film 10 and comprises a sealant material capable of forming a heat-seal. The sealant material is preferably a type of polymer that exhibits a melting point.

[0032] As used herein, the phrase "exterior layer" refers to any layer of a multilayer film having only one of its principal surfaces directly adhered to another layer of that film. In a multilayer film, there are two exterior layers, each of which has a principal surface adhered to only one other layer of the film. The other principal surface of each of the two exterior layers forms the two principal outer surfaces of the film. The layers disposed between the two exterior layers are "interior layers," i.e., those that have both of their principal surfaces directly adhered to another layer of the film.

[0033] As used herein, the term "heat-seal" refers to the union of two films by bringing the films into contact, or at least close proximity, with one another and then applying sufficient heat and pressure to a predetermined area (or areas) of the films to cause the contacting surfaces of the films in the predetermined area to become molten and intermix with one another, thereby forming an essentially inseparable bond between the two films in the predetermined area when the heat and pressure are removed therefrom and the area is allowed to cool.

[0034] As used herein, the term "melting point," sometimes abbreviated herein as " T_m ", refers to an endotherm crystalline melting peak as determined by Differential Scanning Calorimetry (DSC) in accordance with ASTM D-3417.

[0035] The sealant material in second layer 14 preferably has a melting point of less than about 130 °C, such as less than about 120, 110, 100, 90, 80, or 70 °C. The sealant material preferably comprises at least about 20 wt.% of second layer 14, based on the total weight of layer 14, such as at least about 40, 60, 80, 90, or 95 wt.%. Examples of suitable polymers for the sealant material include ionomers (e.g., SURLYN from DuPont), heterogeneous (Ziegler-Natta catalyzed) ethylene/alpha-olefin copolymer such as linear low density polyethylene, homogeneous (single-site, metallocene-catalyzed) ethylene/alpha-olefin copolymer, ethylene/unsaturated ester copolymer (e.g., ethylene/vinyl acetate copolymer, ethylene/methyl acrylate copolymer, ethylene/butyl acrylate copolymer, etc.), ethylene/unsaturated acid copolymer (e.g., ethylene/acrylic acid copolymer, ethylene/methacrylic acid copolymer, etc.), ethylene/propylene copolymer, and polybutylene homopolymer or copolymer.

[0036] In accordance with the present invention, the glass transition temperature of the amorphous polymer in first layer 12 is greater than the melting point of the sealant material in second layer 14 by at least about 45 degrees centigrade, i.e., the T_g of the amorphous polymer minus the T_m of the sealant material (" ΔT ") is greater than or equal to about 45 °C. The inventors found that when the ΔT between the T_g of the amorphous polymer and the T_m of the sealant material is greater than or equal to about 45 °C, the film possesses a sufficiently wide temperature-processing window to make high-quality packages from such film on a large-scale, commercial basis in a wide variety of packaging processes.

[0037] That is, with a ΔT of 45 °C or more, it is now more readily possible to employ processing temperatures that are above the T_m of the sealant material in order to form strong heat-seals and, at the same time, remain below the T_g of the amorphous polymer in order to maintain the dimensional stability of the film and package throughout the packaging process. In this manner, the same film can be used in various types of packaging operations (some of which have been

discussed hereinabove), which invariably employ different heat-seal temperatures and otherwise subject the film to different levels of temperature and mechanical stress. The wide processing window provided by a ΔT of 45 °C or more in accordance with the present invention allows the film to be used in these different packaging processes without the costly necessity of tailoring a number of different films to suit each process. A more preferred ΔT is at least 55 °C, such as 65, 75, 85 or 90 °C.

[0038] Multilayer film 10 preferably further includes a third, interior layer 16 adhered to surface 18 of first layer 12. Third layer 16 preferably comprises at least one member selected from polyamide homopolymer or copolymer (e.g., one having greater than 50 mole percent polyamide 6 or polyamide 66), acid-modified polyolefins, anhydride-modified polyolefins, ethylene/acrylic acid copolymer, and ethylene/methacrylic acid copolymer.

[0039] A fourth, interior layer 20 is preferably also included, and may be adhered to surface 22 of third layer 16. The composition of fourth layer 20 may be selected such that layer 20 functions as an oxygen barrier layer, and preferably has an oxygen transmission rate (OTR) of less than or equal to 30 cc of oxygen per square meter of film per 24 hour period at 1 atmosphere and at a temperature of 23°C (73°F) (at 0% relative humidity). In this manner, the entire film 10 will have such OTR. More preferably, layer 20, and therefore film 10, has an OTR of less than 25 cc/m² per 24 hours at 101325 Pa (1 atm.), and more preferably less than 20, more preferably still less than 15, even more preferably less than 10, such as less than 8, less than 7, or less than 6 cc/m² per 24 hours at 101325 Pa (1 atm.) (23°C (73°F) and 0% RH). Examples of suitable materials for fourth layer 20 include ethylene/vinyl alcohol copolymer (EVOH), polyamide MXD6, polyamide MXD6/MXDI, polyvinylidene chloride (PVDC), and polyacrylonitrile (PAN), including copolymers of PVDC and PAN. EVOH is preferred.

[0040] When the fourth layer 20 comprises ethylene/vinyl alcohol copolymer, polyamide MXD6, or polyamide MXD6/MXDI, the third layer 16 preferably comprises at least one member selected from polyamide homopolymer or copolymer having greater than 50 mole percent polyamide 6, polyamide homopolymer or copolymer having greater than 50 mole percent polyamide 66, acid-modified polyolefins, and anhydride-modified polyolefins. Preferred polyamides in accordance with the foregoing include polyamide 6, polyamide 66, polyamide 6/66, polyamide 6/69, polyamide 6/12, polyamide 66/610, and polyamide 66/69. Preferred examples of acid-modified polyolefins include ethylene/acrylic acid copolymer and ethylene/methacrylic acid copolymer. Preferred anhydride-modified polyolefins include anhydride-grafted ethylene/1-butene copolymer, anhydride-grafted ethylene/1-hexene copolymer, anhydride-grafted ethylene/1-octene copolymer, anhydride-grafted ethylene/vinyl acetate copolymer, and anhydride-grafted polypropylene.

[0041] As used herein, the term "anhydride-modified" refers to any form of anhydride functionality, such as the anhydride of maleic acid, fumaric acid, etc., whether grafted onto a polymer, copolymerized with a polymer, or blended with one or more polymers, and is also inclusive of derivatives of such functionalities, such as acids, esters, and metal salts derived therefrom.

[0042] When fourth layer 20 comprises polyvinylidene chloride or polyacrylonitrile, third layer 16 preferably comprises an ethylene copolymer or terpolymer having between 5 and 30 mole % ester mer units. Such ester mer units may include, for example, methacrylate, n-butyl acrylate, iso-butyl acrylate, ethyl acrylate, vinyl acetate (e.g., ethylene/methacrylate copolymer, etc.). An example of a suitable terpolymer may comprise 80% ethylene, 10% iso-butyl acrylate, and 10% methacrylic acid.

[0043] Multilayer film 10 may further comprise a fifth layer 26 to form a second exterior layer of the multilayer film in opposing relation to second layer 14. This fifth exterior layer 26 preferably comprises a material having a surface energy of at least 3.6 Pa (36 dynes/cm²). Such a surface energy allows an image to be printed on outer surface 28 of fifth layer 26. Suitable materials for fifth layer 26 include at least one material selected from polyamides, polyesters, polycarbonates, polyurethanes, and polyacrylates. Polyolefin surfaces having been modified by corona, plasma, flame treatment or acid etching such that the surface energy exceeds 3.6 Pa (36 dynes/cm²) are also suitable for printing. Fifth layer 26 also preferably provides heat- and abuse-resistance to the film. If a crystalline material is used, such material preferably has a melting point of at least about 100 °C, such as at least about 110, 120, 130°C, etc. If an amorphous material is used, such material preferably has a T_g of at least about 100 °C, such as at least about 110, 120, 130°C, etc. A crystalline polyamide such as polyamide 6 is preferred.

[0044] Multilayer film 10 may further comprise a sixth, interior layer 30 adhered to surface 32 of fourth layer 20. The sixth layer 30 may be formed from the same material(s) as third layer 16, and thus may comprise at least one member selected from polyamide homopolymer or copolymer having greater than 50 mole percent polyamide 6, polyamide homopolymer or copolymer having greater than 50 mole percent polyamide 66, acid-modified polyolefins, anhydride-modified polyolefins, ethylene/acrylic acid copolymer, ethylene/methacrylic acid copolymer, and ethylene copolymer or terpolymer having between 5 and 30 mole % ester mer units. Preferred materials include at least one member selected from polyamide 6, polyamide 66, and polyamide 6/66.

[0045] Multilayer film 10 may further comprise a seventh, interior layer 34 positioned generally between the second and sixth layers 14,30, e.g., adjacent second layer 14 as shown. It is preferred to include seventh layer 34 to balance any tendency of film 10 to curl. For example, the film may have a tendency to curl if fifth layer 26 contracts to a greater or lesser degree than the other layers of the film upon cooling. This may occur, for instance, when fifth layer 26 is a

crystalline or semi-crystalline material, such as a semi-crystalline polyamide. In such case, it may contract to a greater degree upon cooling than the other film layers and, being an exterior layer, exerts a curling force on the film such that the film tends to curl towards the fifth layer. This tendency can be offset by including in seventh layer 34 a material that balances the curl of the film such as, e.g., high density polyethylene, low density polyethylene, linear low density polyethylene, polypropylene, polyamide, cyclic olefin copolymer, or polyester.

[0046] Polymeric adhesive layers, commonly referred to as "tie" layers, may be included in multilayer film 10 wherever necessary or desired. Thus, a first polymeric adhesive layer 36 may be included between first layer 12 and fifth layer 26 and a second polymeric adhesive layer 38 may be included between sixth layer 30 and seventh layer 34. Layers 36 and 38 may comprise any suitable polymeric adhesive, such as an olefin polymer or copolymer having an anhydride functionality grafted thereon and/or copolymerized therewith and/or blended therewith. Examples of suitable polymeric adhesives include the following anhydride-grafted polymers: ethylene/1-butene copolymer, ethylene/1-hexene copolymer, ethylene/1-octene copolymer, ethylene/vinyl acetate copolymer, polypropylene, polyhydroxyether of bisphenol-A, styrene butadiene block copolymer, and low density polyethylene.

[0047] Multilayer film 10 may be made by any suitable film-making process, e.g., cast or blown through either an annular or flat die, and is preferably fully coextruded. As used herein, the term "coextruded" refers to the process of extruding two or more materials through a single die with two or more orifices arranged so that the extrudates merge and weld together into a laminar structure before chilling and solidifying, e.g., via water, chilled metal roll, or air quenching. Multilayer film 10 preferably has less than 5% shrink in at least one direction at 150°C. Thus, it is preferred that the film is not oriented after coextrusion or, if it is, that it be heat-set to remove substantially all of the shrink capability from the film.

[0048] Multilayer film 10 may have any desired thickness, e.g., ranging from about 13 to about 1270 μm (0.5 to about 50 mils). More preferably, the thickness ranges from 13 to 1016 μm (0.5 - 40 mils), such as between 13-762 μm (0.5 - 30 mils), 13-508 μm (0.5 - 20 mils), or 25-381 μm (1 - 15 mils), including sub-ranges such as 25-254 μm (1- 10 mils), 25-127 μm (1 - 5 mils), or 38-102 μm (1.5 - 4) mils. Each layer of the film, including those described hereinabove as well as other layer that may be included in film 10, may have any desired thickness ranging, e.g., from 5 to 70 % of the total thickness of film 10, including all sub-ranges therebetween, e.g., greater than 5, 10, 15, 20, 30 or 40 %, or less than 70, 60, 50, or 40 %.

[0049] Each of the layers of multilayer film 10 are preferably adhered to one another at a bond strength of at least 0.88 N/cm (0.5 lb_f/inch) (ASTM F 904) and, more preferably, at a bond strength of at least 1.23 N/cm (0.7 lb_f/inch).

[0050] Multilayer film 10 preferably has at least about 40 wt.% polyolefin, based on the total weight of the film, such as at least about 45, 50, 55, 60, 65, 70, or 75 wt.% polyolefin.

[0051] If desired or necessary, any desired lubricating agents or other processing aids may be included in any of the layers. Such processing aids may include, e.g., graphite, molybdenum disulphide, PEFT, polyethylene and other hydrocarbons, calcium stearate, metallic stearates, fatty acid amides and esters, polyolefin waxes, polyamides, fluoropolymers, silicones, boron nitride, etc.

[0052] Film 10 may be pigmented or clear. If clear, the film preferably has a haze of less than about 20%, such as less than about 15 or 10 % (ASTM D-1003).

[0053] Multilayer film 10 may advantageously be used to make any desired package, particularly those employing heat-seals as described above in the Background section hereof.

[0054] The invention will now be further described in the following examples.

EXAMPLES

[0055] The materials used in the examples are identified below:

1. **PA6-1:** CAPRON B100WP; a polyamide 6 resin having a melt flow index of 2.6 g/10 min (ASTM D-1238 (235/1.0)), a density of 1.135 g/cc (ASTM D-792) and a melting point of 220 °C; purchased from Honeywell of Hopewell, VA.

2. **aPA-1:** GRIVORY G21; an amorphous polyamide 6I/6T resin with a glass transition temperature (T_g) of 125 °C (ASTM D-3418) and a density of 1.18 g/cc (ASTM D-792); obtained from EMS of Sumter, SC.

3. **aPA-2:** GRILAMID TR55; an amorphous polyamide 12/MACMT resin with a glass transition temperature (T_g) of 155 °C (ASTM D-3418) and a density of 1.06 g/cc (ASTM D-792); obtained from EMS of Sumter, SC.

4. **aPA-3:** GRIVORY FE5749; an amorphous polyamide 6I/6T/MACMI resin with a glass transition temperature (T_g) of 158 °C (ASTM D-3418) and a density of 1.15 g/cc (ISO 1183); obtained from EMS of Sumter, SC.

5. **aPA-4:** GRIVORY FE5750; an amorphous polyamide 6I/6T/MACMI/MACMT resin with a glass transition temperature (T_g) of 181 °C (ISO 3146-C) and a density of 1.15 g/cc (ISO 1183); obtained from EMS of Sumter, SC.

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6. **PA6-2:** ULTRAMID KR-4407; a polyamide 6 resin having a density of 1.14 g/cc (ASTM D-3418) and a melting point of 220 °C (ASTM D-3418), containing less than 1% combined talc and silicon oil; purchased from BASF of Mount Olive, NJ.

5 7. **MB1:** GRILON XE 3361; a polyamide-6 masterbatch containing 5% talcum (magnesium silicate), 5% calcium carbonate, and 5% n,n'-ethylene bis stearamide with a density of 1.140 g/cc (ASTM D-792) and a melting point of 220 °C; purchased from EMS of Sumter, SC

10 8. **MB2:** CLARIANT 1080864S; a polyamide-6 masterbatch containing 20% diatomaceous earth and 10% erucamide with a density of 1.20 g/cc (ASTM D-792) and a melting point of 220 °C; purchased from Clariant of Minneapolis, MN.

15 9. **MB3:** FSU 255E: a low density polyethylene based masterbatch containing 25.0% diatomaceous earth silica and 5.0% erucamide with a melt index of 8.0 g/10 min (ASTM D-1238) and a density of 1.08 g/cc (ASTM D-792); obtained from A. Schulman of Cleveland, OH.

20 10. **MB4:** Compol 5B10S1: an ethylene-methacrylic acid based masterbatch containing 5 wt. % antiblock and 10 wt. % slip agent with a melt index of 2.5 g/10 min (ASTM D-1238 - condition "E") and a density of 0.96 g/cc (ASTM D-792); obtained from DuPont of Wilmington, DE.

25 11. **EV0H:** SOARANOL ET3803; an ethylene/vinyl alcohol copolymer having 38% ethylene, a melt index of 3.2 g/10 min (ASTM D-1238) and a density of 1.17 g/cc (ASTM D-792); obtained from Nippon Goshei, supplied by Soarus of Arlington Heights, IL.

30 12. **TIE-1:** PX 3236; an anhydride-grafted linear low density polyethylene having a melt index of 2.0 g/10 min (ASTM D-1238) and a density of 0.921 g/cc (ASTM D-792); purchased from Equistar Chemicals of Chicago, IL.

35 13. **TIE-2:** PX 2049; an anhydride-grafted high density polyethylene having a melt index of 4.7 g/10 min (ASTM D-1238) and a density of 0.955 g/cc (ASTM D-792); obtained from Equistar Chemicals of Chicago, IL.

40 14. **HDPE:** FORTIFLEX T60-500-119; a high density polyethylene with a melt index of 6.2 g/10 min (ASTM D-1238) and a density of 0.961 (ASTM D-792); obtained from Solvay Polymers of Houston, TX.

45 15. **LLDPE-1:** EXACT 3024: a homogeneous ethylene/butene-1 copolymer, produced by single site metallocene catalysis, with a melt index of 4.5 g/10 min (ASTM D-1238), a melting point (T_m) of 98 °C (DSC per ExxonMobil Method) and a density of 0.905 g/cc (Density per ExxonMobil Method); purchased from Exxon Mobil of Houston, TX.

50 16. **LLDPE-2:** AFFINITY KC 8852: a homogeneous ethylene/octene copolymer, produced via INSITE™ Technology, with a melt index 3.0 g/10 min of (ASTM D-1238), a melting point (T_m) of 68 °C (DSC per Dow Method) and a density of 0.875 g/cc (ASTM D-792); purchased from Dow Chemicals of Chicago, IL.

55 17. **LLDPE-3:** SURLYN 9020: an ethylene/methacrylic acid copolymer, partially neutralized with zinc ions (commonly referred to as an "ionomer"), with a melt index of 1.0 g/10 min (ASTM D-1238), a melting point (T_m) of 81 °C (Differential Thermal Analysis per DuPont method) and a density of 0.96 g/cc (ASTM D-792); purchased from DuPont of Wilmington, DE.

18. **LLDPE-4:** EXCEED 4518PA; an ethylene hexene-1 copolymer, produced by single site catalysis, with a melt index of 4.5 g/10 min (ASTM D-1238) and a density of 0.918 g/cc (ASTM D-1505); purchased from Exxon Mobil of Houston, TX.

50 19. **LLDPE-5:** TAFMER P-0480; an ethylene propylene copolymer (80% ethylene/20% propylene), with a melt index of 1.8 g/10 min (ASTM D-1238) and a density of 0.87 g/cc (ASTM D-792) purchased from Mitsui Chemicals of Newark, NJ.

55 20. **LDPE:** ESCORENE LD200.48; a low density polyethylene with a melt index of 7.5 g/10 min (Melt index per ExxonMobil Method) and a density of 0.917 g/cc (Density per ExxonMobil Method); obtained from Exxon Mobil of Houston, TX.

Example 1 (Comparative)

[0056] With reference to FIG. 1, a comparative multilayer film was made and had the following nine-layer structure with a total film thickness of 63.5 μm (2.5 mils):

Layer 14: 96% LLDPE-1 + 4% MB3 (12% of total thickness of layers 1-9) [Seal Layer];

Layer 34: HDPE (18% of total thickness of layers 1-9);

Layer 38: TIE-1 (10% of total thickness of layers 1-9);

Layer 30: PA6-1 (6.5% of total thickness of layers 1-9);

Layer 20: EVOH (6% of total thickness of layers 1-9);

Layer 16: PA6-1 (6.5% of total thickness of layers 1-9);

Layer 12: aPA-1 (18% of total thickness of layers 1-9);

Layer 36: TIE-1 (10% of total thickness of layers 1-9); and

Layer 26: 96% PA6-2 + 2% MB1 + 2% MB2 (13% of total thickness of layers 1-9).

[0057] The film was fully coextruded and produced by a cast coextrusion process using an annular die, followed by a water quench upon exiting the die.

Example 2

[0058] With reference to FIG. 1, a multilayer film in accordance with the present invention was made by the process described above for Comparative Example 1, and had the following nine-layer structure with a total film thickness 63.5 μm (2.5 mils):

Layer 14: 92% LLDPE-3 + 8% MB4 (12% of total thickness of layers 1-9) [Seal Layer];

Layer 34: 55% LLDPE-4 + 35%LLDPE-5 +10%LDPE (12% of total thickness of layers 1-9);

Layer 38: TIE-2 (16% of total thickness of layers 1-9);

Layer 30: PA6-1 (6.5% of total thickness of layers 1-9);

Layer 20: EVOH (6% of total thickness of layers 1-9);

Layer 16: PA6-1 (6.5% of total thickness of layers 1-9);

Layer 12: aPA-2 (18% of total thickness of layers 1-9);

Layer 36: TIE-1 (10% of total thickness of layers 1-9); and

Layer 26: 96% PA6-2 + 2% MB1 + 2% MB2 (13% of total thickness of layers 1-9).

Example 3

[0059] Again with reference to FIG. 1, a multilayer film in accordance with the present invention was made as described in Comparative Example 1 and had the following nine-layer structure with a total film thickness 63.5 μm (2.5 mils):

Layer 14: 93% LLDPE-2 + 7% MB3 (15% of total thickness of layers 1-9) [Seal Layer];

Layer 34: HDPE (15% of total thickness of layers 1-9);

Layer 38: TIE-1 (10% of total thickness of layers 1-9);
 Layer 30: PA6-1 (6.5% of total thickness of layers 1-9);
 5 Layer 20: EVOH (6% of total thickness of layers 1-9);
 Layer 16: PA6-1 (6.5% of total thickness of layers 1-9);
 Layer 12: aPA-2 (18% of total thickness of layers 1-9);
 10 Layer 36: TIE-1 (10% of total thickness of layers 1-9); and
 Layer 26: 96% PA6-2 + 2% MB1 + 2% MB2 (13% of total thickness of layers 1-9).

15 Example 4

[0060] Also with reference to FIG. 1, a multilayer film in accordance with the present invention was made as described in Comparative Example 1 and had the following nine-layer structure with a total film thickness 63.5 μm (2.5 mils):

20 Layer 14: 93% LLDPE-2 + 7% MB3 (15% of total thickness of layers 1-9) [Seal Layer];
 Layer 34: HDPE (15% of total thickness of layers 1-9);
 Layer 38: TIE-1 (10% of total thickness of layers 1-9);
 25 Layer 30: PA6-1 (6.5% of total thickness of layers 1-9);
 Layer 20: EVOH (6% of total thickness of layers 1-9);
 30 Layer 16: PA6-1 (6.5% of total thickness of layers 1-9);
 Layer 12: aPA-3 (18% of total thickness of layers 1-9);
 Layer 36: TIE-1 (10% of total thickness of layers 1-9); and
 35 Layer 26: 96% PA6-2 + 2% MB1 + 2% MB2 (13% of total thickness of layers 1-9).

Example 5

40 **[0061]** With further reference to FIG. 1, a multilayer film in accordance with the present invention was made as described in Comparative Example 1 and had the following nine-layer structure with a total film thickness 63.5 μm (2.5 mils):

Layer 14: 93% LLDPE-2 + 7% MB3 (15% of total thickness of layers 1-9) [Seal Layer];
 45 Layer 34: HDPE (18% of total thickness of layers 1-9);
 Layer 38: TIE-1 (10% of total thickness of layers 1-9);
 Layer 30: PA6-1 (6.5% of total thickness of layers 1-9);
 50 Layer 20: EVOH (6% of total thickness of layers 1-9);
 Layer 16: PA6-1 (6.5% of total thickness of layers 1-9);
 55 Layer 12: aPA-4 (18% of total thickness of layers 1-9);
 Layer 36: TIE-1 (10% of total thickness of layers 1-9); and

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Layer 26: 96% PA6-2 + 2% MB1 + 2% MB2 (13% of total thickness of layers 1-9).

Example 6

[0062] The films of Examples 1-5 were subjected to the following tests:

1) Storage Modulus: tested in both the machine direction (MD) and transverse direction (TD) in accordance with ASTM D-5026-95a; expressed in MPa and psi (pounds/in²) of the cross-sectional area of the film and reported as the average of the values measured for the MD and TD.

2) Tensile Strength and Elongation: tested in both the machine direction (MD) and transverse direction (TD) in accordance with ASTM D-882; tensile strength is expressed in MPa and psi (pounds/in²) and elongation is expressed in %.

3) Young's Modulus: tested in both the machine direction (MD) and transverse direction (TD) in accordance with ASTM D-882; expressed in MPa and psi (pounds/in²).

4) Haze: tested in accordance with ASTM D-1003; expressed in %.

5) Clarity: tested in accordance with ASTM D-1746; expressed in %. The results are summarized in Table 1.

TABLE 1

Test	Comp. Example 1	Example 2	Example 3	Example 4	Example 5
Tensile Strength at yield measured at 73° F MD/TD (MPa) [psi x 1000]	31.7/31.0 [4.6/4.5]	31.0/29.6 [4.5/4.3]	31.0/29.6 [4.5/4.3]	31.7/33.1 [4.6/4.8]	34.5/33.8 [5.0/4.9]
Elongation at yield measured at 23°C (73 °F) MD/TD (%)	7.5/7.4	9.3/9.3	8.6/8.4	7.8/7.5	8.1/7.7
Young's Modulus measured at 23°C (73°F) MD/TD (MPa) [psi x 1000]	877/910 [127/132]	689/758 [100/110]	841/800 [122/116]	882/945 [128/137]	1000/1014 [145/157]
Storage Modulus at 150 °C (MPa) [psi]	80.56 [11,684]	325.67 [47,235]	314.68 [45,640]	444.42 [64,458]	427.23 [61,964]
Haze (%)	7.8	10.9	9.1	9.4	9.6
Clarity (%)	3.7	25.4	3.8	4.3	15.0

[0063] As indicated, the films of Examples 2-5 were similar to that of Comparative Example 1 in terms of optics and mechanical properties at lower temperatures. Significantly, however, the films of Examples 2-5 maintained high storage modulus, i.e., greater than 310 MPa (45,000 psi), temperatures up to and exceeding 150 °C. Such films therefore have excellent dimensional stability at high temperatures, such as those that are experienced during various packaging operations as discussed hereinabove. This is contrast to the film of Comparative Example 1, which exhibited a storage modulus of less than 82.7 MPa (12,000 psi) at 150 °C.

Example 7

[0064] In this example, the films of Examples 1-5 were sealed to a thermoformed pocket after placing a plastic block in the pocket as described below and evacuating the space between the film and pocket so that the block was vacuum-packaged inside of the resultant package. A Multivac R7000 vacuum packaging machine was used to make the packages. The films of Examples 1-5 were employed as top webs and joined via heat-sealing to a bottom web having thermoformed pockets therein. A block was placed in each pocket and sandwiched between the top and bottom webs in an evacuation/sealing chamber, a component of the R7000 packaging machine. In the chamber, air was evacuated such that a 10 mbar vacuum was produced. A heated seal-head then forced the top and bottom webs together for 1.0 second to produce a heat-seal between the two webs around the periphery of the pocket, thereby enclosing the block between the two webs. Various sealing temperatures ranging from about 85 °C to about 155 °C were used in order to test the ability of the films to both resist deformation and produce a heat-seal at such temperatures. Each resultant package was severed from the top and bottom webs to produce individual packages for inspection and testing as described below.

[0065] For the films of Comparative Example 1 and Examples 3-5, the bottom web to which such films were sealed had the following 9-layer structure:

Layer 1: 94% LLDPE-A + 6% MB3 (8% of total thickness of layers 1-9) [Heat Seal Layer];
 Layer 2: 90% LLDPE-B + 10% LLDPE-C (17% of total thickness of layers 1-9);
 Layer 3: TIE-A (8% of total thickness of layers 1-9);
 Layer 4: PA6-A (13% of total thickness of layers 1-9);
 Layer 5: EVOH (10% of total thickness of layers 1-9);
 Layer 6: PA6-A (13% of total thickness of layers 1-9);
 Layer 7: TIE-B (7% of total thickness of layers 1-9);
 Layer 8: PP-1 (14% of total thickness of layers 1-9); and
 Layer 9: PP-2 (10% of total thickness of layers 1-9);

wherein,

LLDPE-A = a copolymer of ethylene and octene-1 having a density of 0.900 g/cc, a melt index of 6.0 g/10 min. and an octene percentage of 13%;

LLDPE-B = an ethylene/hexene-1 copolymer with a density of 0.918 g/cc and a melt index of 4.5 g/10 min.;

LLDPE-C = a linear low density polyethylene with a density of 0.915 g/cc;

Tie-A = an anhydride-grafted, butene-based LLDPE;

Tie-B = a maleic anhydride-grafted polypropylene;

PA6-A = a polycaprolactam (nylon-6) with a melting point of 220 degrees C;

EVOH = Same as other examples;

PP-1 = an ethylene/propylene copolymer with a density of 0.902 g/cc and an ethylene content of 2.8 wt. %; and

PP-2 = a propylene homopolymer a density of 0.900 g/cc.

[0066] "Layer 1" of the bottom web was sealed to "Layer 14" of the films of Examples 1 and 2-5 (both heat-seal layers are compatible in that both comprise a majority amount of LLDPE). With respect to the film of Example 2, the bottom web to which it was sealed was similar to the above-described bottom web, except that the heat-seal layer ("Layer 1") comprised a majority amount of an ionomer with a melting point of 96 °C to provide compatibility with the heat-seal layer of the film of Example 2 ("Layer 14"), which also comprised an ionomer.

[0067] In order to assess the ability of the films to resist deformation under stress and high temperatures, an "ink cracking" evaluation was performed on each film as follows. Prior to making the vacuum packages on the Multivac R7000 packaging machine as described above, the non-heat-seal surface of each film (i.e., the surface of "Layer 26") was first corona treated after extrusion [watt density of 2.0 kW and line speed of 61m/min (200 ft/min.)] and then again on a flexographic printing press [2.5 to 3.0 kW at a line speed of approximately 38m/min (125ft/min)]. The film was printed with a large coverage of white (model # P001) and black (model # P019) solvent-based inks from AXL. Flexographic printing plates having eyebars at 896 mm over 3 repeats were used. The inks were dried at tunnel temperatures ranging from about 49-54°C (120-130 °F). All printed areas, including eyebars, were overcoated with Sun GAIFB0440206 EB OPV from Sun Chemical. This electron-beam-curable over-print varnish was then electron-beam cured at a dose of 2 mR at 70 kV. The film was then slit to 405mm in order to be tested on the Multivac R7000.

[0068] As noted above, each of the vacuum packages contained therein a plastic block. Each block [(L=17.8cm (7.5"), W=7.6cm (3.5"), H=5.1cm (2.0"))] contained a total of 10 holes that were evenly spaced in two rows on the surface of the block. The diameter of the holes varied from 10 to 19 mm, and all had a depth of 40 mm deep (hole diameters in first row = 10, 11, 12, 13 and 14 mm; hole diameters in second row = 15, 16, 17, 18 and 19 mm). A total of 4 packages

were made with each of the films of Examples 1-5.

[0069] The performance of the films was evaluated for sealing temperatures (as applied on the vacuum packaging machine) ranging from 100 °C to 150 °C. The blocks were removed from the completed packages and the areas of the non-forming web corresponding to the hole locations on the test blocks were then inspected for ink cracking. During the vacuum packaging and heat-sealing process, a pressure differential across the films was produced, resulting in a net downward force that tended to push the films into the holes on the blocks. The ability of the film to resist such deformation at the applied sealing temperature is a measure of the film's ability to resist other types of deformation at similar temperatures, e.g., as may be experienced by the film during various packaging operations as described hereinabove. If the ink/varnish overcoat was found to be cracked in the area that was next to a hole during vacuum packaging, this indicated that excessive deformation occurred. The results are summarized in Table 2, and are expressed as the percentage of hole locations on the film that exhibited signs of ink cracking for each seal temperature (averaged from the 4 packages made at each seal temperature for each of the films of Examples 1-5).

[0070] Also set forth in Table 2 are the storage modulus values measured for each film at each of the applied seal temperatures.

TABLE 2

Example	ΔT (T_g of aPA minus T_m of Seal Layer (°C))	Sealing Temp. on Multivac R7000 (°C)	Storage Modulus (MPa) [psi]	% Holes with Ink Cracks
1 (Comp.) [aPA-1 ($T_g=125$ °C); LLDPE-1 ($T_m = 98$ °C)]	27	100	571.55 [82,897]	Not
		115	510.74 [74,077]	Sealed
		130	275.07 [39,896]	48
		150	80.56 [11,684]	78
2 [aPA-2 ($T_g=155$ °C); LLDPE-3 ($T_m = 81$ °C)]	74	100	472.16 [68,481]	3
		115	428.73 [62,182]	20
		130	383.97 [55,690]	43
		150	325.67 [47,235]	64
3 [aPA-2 ($T_g=155$ °C); LLDPE-2 ($T_m = 68$ °C)]	87	100	432.38 [62,712]	0
		115	391.13 [56,728]	18
		130	371.65 [53,903]	44
		150	314.68 [45,640]	71
4 [aPA-3 ($T_g=158$ °C); LLDPE-2 ($T_m = 68$ °C)]	90	100	603.89 [87,587]	1
		115	557.14 [80,806]	21
		130	530.83 [76,990]	48
		150	444.42 [64,458]	91
5 [aPA-4 ($T_g=181$ °C; LLDPE-2($T_m = 68$ °C)	113	100	530.52 [76,946]	0
		115	490.03 [71,073]	1
		130	460.95 [66,855]	15
		140	443.75 [64,361]	31
		150	427.23 [61,964]	49

[0071] As is apparent by the results shown in Table 2, the films of Examples 2-5, having a ΔT of at least 45 °C, exhibit less ink cracking at each sealing temperature than the films of Comparative Example 1, with a ΔT of only 27 °C. This provides a strong indication that the films of the invention exhibited less deformation at high temperatures than films having a ΔT of less than 45 °C.

[0072] Also, the films of Examples 2-5 maintained a storage modulus of greater than 45,000 psi even as the seal temperatures were increased to 150 °C. In contrast, the storage modulus of the film of Comparative Example 1 decreased sharply as the sealing temperature increased above 130 °C. Consistent with this finding, the mechanical properties of the film of Example 1 have also been observed to drop steeply as the temperature of the film approached and exceeded about 130 °C. Machineability issues such as poor print registration and excess web stretching were typically associated with this drop in mechanical properties. For example, the film of Comp. Example 1 was found to exhibit recurrent print

registration issues when a seal temperature of 150°C was employed. On the other hand, the films of Example 3 did not miss print registration at seal temperatures up to 165°C.

Example 8

[0073] In addition to greater dimensional stability at elevated temperatures as demonstrated in Example 7, films having a ΔT of at least 45 °C (T_g of the amorphous polyamide minus T_m of seal layer) in accordance with the present invention also provide the ability to seal at a lower temperature, relative to the T_g of the amorphous layer, than films having a lower ΔT . In this example, the seal strengths of Comparative Example 1 and Examples 3-5 were compared at various seal temperatures. For each test, the films of Examples 1 and 3-5 were sealed to the bottom web as described above (employing "LLDPE-A" as the heat seal layer). Seal strength was measured on an Instron's Model 5543 machine at a fast pulling rate as specified in ASTM D-882. All seals were produced on the Multivac R7000 machine using a 1 second dwell time and a pressure of approximately 320 kPa (3.2 bars). The seal strength values reported in Table 3 are an average of 4 readings at each seal temperature (2 readings in the machine direction, 2 readings in the transverse direction).

TABLE 3

Example	Seal Temp. (°C)									
	85	95	100	105	115	125	130	135	150	155
Seal Strength of Comp. Ex. 1 (N/cm) [pounds/linear inch]	0 [0]	0 [0]	-	4.7 [2.7]	27.5 [15.7]	28.0 [16.0]	-	25.6 [14.6]	-	27.3 [15.6]
Seal Strength of Ex. 3 (N/cm) [pounds/linear inch]	0 [0]	11.0 [6.3]	-	21.5 [12.3]	27.3 [15.6]	27.1 [15.5]	-	28.4 [16.2]	-	27.1 [15.5]
Seal Strength of Ex. 4 (N/cm) [pounds/linear inch]	-	-	10.5 [6.0]	-	25.4 [14.5]	-	25.2 [14.4]	-	26.4 [15.1]	-
Seal Strength of Ex. 5 (N/cm) [pounds/linear inch]	-	-	15.4 [8.8]	-	25.4 [14.5]	-	25.2 [14.4]	-	25.2 [14.4]	-

[0074] In general, a seal strength of at least 5 pounds/linear inch is required for commercial applications, and this was achieved for the films of Examples 3-5 at seal temperatures of 100 °C or less. In contrast, the film of Comparative Example 1 was unable to achieve a seal strength of at least 5 pounds/linear inch until a seal temp. of between 105 and 115 °C was reached. This is consistent with the data set forth above in Example 7, wherein the film of Comp. Ex. 1 could not form a seal sufficient to create a vacuum package at a seal temp. of 100 °C. However, as also seen above in Example

7, at seal temps of 115 °C and above, the ink-crack performance of the films of Comp. Ex. 1 were inferior to the ink-crack performance of the films in accordance with the present invention. Accordingly, films having a ΔT of at least 45 °C provide greater resistance to thermal deformation at higher temperatures but also allow lower seal temperatures to be used, thereby providing a broader processing window than similar films with a ΔT of less than 45 °C.

[0075] The seal strength performance of the films of Example 2 were similarly tested, except that the bottom web to which such films were sealed had a seal layer comprising an ionomeric material in order to be compatible with the ionomeric sealant in the seal layer of the film of Example 2. Ionomeric sealants exhibit different seal-strength characteristics than ethylene/alpha-olefin copolymer sealants as used in Examples 1 and 3-5. Thus, the seal-strength data is not directly comparable with that for Examples 1 and 3-5. For example, the film of Example 2 required a seal temp. of 135 °C to provide a seal-strength above 5 pounds/linear inch, which did not increase above 6 pounds/linear inch even at a seal temp. of 155 °C. However, because such film had a ΔT of 74 °C, the film still maintained good dimensional stability even at such elevated sealing temperatures (see Example 7).

[0076] While the invention has been described with reference to illustrative examples, those skilled in the art will understand that various modifications may be made to the invention as described without departing from the scope of the claims which follow.

Claims

1. A multilayer film, comprising:

- a. a first layer comprising an amorphous polymer that exhibits a glass transition temperature; and
- b. a second layer forming an exterior layer of said multilayer film and comprising a sealant material capable of forming a heat-seal, said sealant material comprising a polymer that exhibits a melting point,

wherein, the glass transition temperature of said amorphous polymer is greater than the melting point of said sealant material by at least 45 °C.

2. The multilayer film of claim 1, wherein said amorphous polymer in said first layer has a glass transition temperature of at least 140 °C.

3. The multilayer film of claim 1, wherein said amorphous polymer in said first layer comprises an amorphous polyamide.

4. The multilayer film of claim 3, wherein said amorphous polyamide comprises at least one member selected from polyamide 6I/6T, polyamide 6I/MACMT, polyamide 6I/MACMI, polyamide 6I/MACMI/MACMT, polyamide 6/MACMI/MXDI, polyamide 6I/6T/MACMI, polyamide 6I/6T/MACMI/MACMT, polyamide 12/MACMT, polyamide 12/MACMI, polyamide 12/IPDI/PACMI, polyamide 12/PACMI, polyamide TMDT, polyamide 6I/6T/IPD, polyamide 6I/6T/PACMI/PACMT, polyamide 6I/6, polyamide MACMI/MACMX, polyamide XT/MACMT, polyamide 6/AMNBT, polyamide PACM 12, and polyamide MDI6/MDI9.

5. The multilayer film of claim 3, wherein said first layer comprises a blend of at least two amorphous polyamides.

6. The multilayer film of claim 1, wherein said amorphous polymer in said first layer comprises at least one member selected from polycarbonate, cyclic olefin copolymer, polysulfone, polyethersulfone, polyarylsulfone, styrene maleic anhydride copolymer, polyetherimide, polyphenylene oxide, polyphenylene oxide/polystyrene alloys, polyphenylene ether and polyarylate.

7. The multilayer film of claim 1, wherein said sealant material in said second layer has a melting point of less than 110 °C.

8. The multilayer film of claim 1, wherein said sealant material in said second layer comprises at least one member selected from ionomers, heterogeneous ethylene/alpha-olefin copolymer, homogeneous ethylene/alpha-olefin copolymer, ethylene/unsaturated ester copolymer, ethylene/unsaturated acid copolymer, ethylene/propylene copolymer, and polybutylene homopolymer or copolymer.

9. The multilayer film of claim 1, further comprising a third layer adhered to a surface of said first layer.

10. The multilayer film of claim 9, wherein said third layer comprises at least one member selected from polyamide homopolymer or copolymer, acid-modified polyolefins, anhydride-modified polyolefins, ethylene/acrylic acid copol-

mer, ethylene/methacrylic acid copolymer, and ethylene copolymer or terpolymer having between 5 and 30 mole % ester mer units..

11. The multilayer film of claim 9, further comprising a fourth layer adhered to a surface of said third layer.
12. The multilayer film of claim 11, wherein said fourth layer comprises at least one member selected from ethylene/vinyl alcohol copolymer, polyamide MXD6, polyamide MXD6/MXDI, polyvinylidene chloride, and polyacrylonitrile.
13. The multilayer film of claim 11, wherein said film has an oxygen transmission rate of less than or equal to 30 cc of oxygen per square meter of film per 24 hour period at 101325Pa (1 atmosphere) and at a temperature of 23°C (73°F) (at 0% relative humidity).
14. The multilayer film of claim 11, further comprising a fifth layer, said fifth layer forming an exterior layer of said multilayer film opposite said second layer and comprising a material having a surface energy of at least 3.6 Pa (36 dynes/cm²).
15. The multilayer film of claim 14, wherein said fifth layer comprises at least one material selected from polyamides, polyesters, polycarbonates, polyurethanes, and polyacrylates.
16. The multilayer film of claim 14, further comprising a sixth layer adhered to a surface of said fourth layer, said sixth layer comprising at least one member selected from polyamide homopolymer or copolymer, acid-modified polyolefins, anhydride-modified polyolefins, ethylene/acrylic acid copolymer, ethylene/methacrylic acid copolymer, and ethylene copolymer or terpolymer having between 5 and 30 mole % ester mer units.
17. The multilayer film of claim 16, further comprising a seventh layer positioned between said second and sixth layers, said seventh layer comprising at least one material selected from high density polyethylene, low density polyethylene, linear low density polyethylene, cyclic olefin copolymer, polypropylene, polyamide, and polyesters.
18. The multilayer film of claim 1, wherein said film has a storage modulus of at least 175 N/cm (100 pounds/linear inch) of width at temperatures up to 140 °C.
19. The multilayer film of claim 1, wherein said film has a thickness ranging from 13 to 1270 µm (0.5 to 50 mils).
20. The multilayer film of claim 1, wherein said film is coextruded.
21. The multilayer film of claim 1, further including at least one printed image on an outer surface thereof.
22. The multilayer film of claim 1, wherein said film has a storage modulus of at least 138 MPa, (20,000 psi) at 150°C.
23. A package made from the film of claim 1.

Patentansprüche

1. Mehrschichtfolie, die
 - a. eine erste Schicht, die ein amorphes Polymer umfasst, das eine Glasübergangstemperatur aufweist, und
 - b. eine zweite Schicht umfasst, die eine äußere Schicht der Mehrschichtfolie bildet und ein Siegelmaterial umfasst, das eine Heißsiegelung bilden kann, wobei das Siegelmaterial ein Polymer umfasst, das einen Schmelzpunkt aufweist,wobei die Glasübergangstemperatur des amorphen Polymers um mindestens 45°C größer als der Schmelzpunkt des Siegelmaterials ist.
2. Mehrschichtfolie nach Anspruch 1, bei der das amorphe Polymer in der ersten Schicht eine Glasübergangstemperatur von mindestens 140°C hat.
3. Mehrschichtfolie nach Anspruch 1, bei der das amorphe Polymer in der ersten Schicht ein amorphes Polyamid

umfasst.

4. Mehrschichtfolie nach Anspruch 3, bei der das amorphe Polyamid mindestens ein Mitglied ausgewählt aus Polyamid 6I/6T, Polyamid 6I/MACMT, Polyamid 6I/MACMI, Polyamid 6I/MACMI/MACMT, Polyamid 6/MACMI/MXDI, Polyamid 6I/6T/MACMI, Polyamid 6I/6T/MACMI/MACMT, Polyamid 12/MACMT, Polyamid 12/MACMI, Polyamid 12/IPDI/PACMI, Polyamid 12/PACMI, Polyamid TMDT, Polyamid 6I/6T/IPD, Polyamid 6I/6T/PACMI/PACMT, Polyamid 6I/6, Polyamid MACMI/MACMX, Polyamid XT/MACMT, Polyamid 6/AMNBT, Polyamid PACM 12 und Polyamid MDI6/MDI9 umfasst.
5. Mehrschichtfolie nach Anspruch 3, bei der die erste Schicht ein Gemisch aus mindestens zwei amorphen Polyamiden umfasst.
6. Mehrschichtfolie nach Anspruch 1, bei der das amorphe Polymer in der ersten Schicht mindestens ein Mitglied ausgewählt aus Polycarbonat, Copolymer von cyclischem Olefin, Polysulfon, Polyethersulfon, Polyarylsulfon, Styrol-Maleinsäureanhydrid-Copolymer, Polyetherimid, Polyphenylenoxid, Polyphenylenoxid/Polystyrol-Legierungen, Polyphenylenether und Polyarylat umfasst.
7. Mehrschichtfolie nach Anspruch 1, bei der das Siegelmaterial in der zweiten Schicht einen Schmelzpunkt von weniger als 110°C hat.
8. Mehrschichtfolie nach Anspruch 1, bei der das Siegelmaterial in der zweiten Schicht mindestens ein Mitglied ausgewählt aus Ionomeren, heterogenem Ethylen/ α -Olefin-Copolymer, homogenem Ethylen/ α -Olefin-Copolymer, Ethylen/ungesättigtem Ester-Copolymer, Ethylen/ungesättigter Säure-Copolymer, Ethylen/Propylen-Copolymer und Polybutylenhomopolymer oder -copolymer umfasst.
9. Mehrschichtfolie nach Anspruch 1, die ferner eine dritte Schicht umfasst, die an einer Oberfläche der ersten Schicht haftet.
10. Mehrschichtfolie nach Anspruch 9, bei der die dritte Schicht mindestens ein Mitglied ausgewählt aus Polyamidhomopolymer oder -copolymer, säuremodifizierten Polyolefinen, anhydridmodifizierten Polyolefinen, Ethylen/Acrylsäure-Copolymer, Ethylen/Methacrylsäure-Copolymer und Ethylencopolymer oder -terpolymer mit zwischen 5 und 30 Mol.% Estermerereinheiten umfasst.
11. Mehrschichtfolie nach Anspruch 9, die ferner eine vierte Schicht umfasst, die an einer Oberfläche der dritten Schicht haftet.
12. Mehrschichtfolie nach Anspruch 11, bei der die vierte Schicht mindestens ein Mitglied ausgewählt aus Ethylen/Vinylalkohol-Copolymer, Polyamid MXD6, Polyamid MXD6/MXDI, Polyvinylidenchlorid und Polyacrylnitril umfasst.
13. Mehrschichtfolie nach Anspruch 11, bei der die Folie eine Sauerstoffdurchlässigkeit von weniger als oder gleich 30 cm³ Sauerstoff pro Quadratmeter Folie in einem Zeitraum von 24 Stunden bei 101325 Pa (1 atm) und einer Temperatur von 23°C (73°F) (bei 0 % relativer Feuchtigkeit) hat.
14. Mehrschichtfolie nach Anspruch 11, die ferner eine fünfte Schicht umfasst, wobei die fünfte Schicht eine äußere Schicht der Mehrschichtfolie gegenüber der zweiten Schicht bildet und ein Material mit einer Oberflächenenergie von mindestens 3,6 Pa (36 dyne/cm²) umfasst.
15. Mehrschichtfolie nach Anspruch 14, bei der die fünfte Schicht mindestens ein Material ausgewählt aus Polyamiden, Polyestern, Polycarbonaten, Polyurethanen und Polyacrylaten umfasst.
16. Mehrschichtfolie nach Anspruch 14, die ferner eine sechste Schicht umfasst, die an einer Oberfläche der vierten Schicht haftet, wobei die sechste Schicht mindestens ein Mitglied ausgewählt aus Polyamidhomopolymer oder -copolymer, säuremodifizierten Polyolefinen, anhydridmodifizierten Polyolefinen, Ethylen/Acrylsäure-Copolymer, Ethylen/Methacrylsäure-Copolymer und Ethylencopolymer oder -terpolymer mit zwischen 5 und 30 Mol.% Estermerereinheiten umfasst.
17. Mehrschichtfolie nach Anspruch 16, die ferner eine siebte Schicht umfasst, die zwischen der zweiten und der sechsten Schicht angeordnet ist, wobei die siebte Schicht mindestens ein Material ausgewählt aus Polyethylen

hoher Dichte, Polyethylen niedriger Dichte, linearem Polyethylen niedriger Dichte, Copolymer von cyclischem Olefin, Polypropylen, Polyamid und Polyestern umfasst.

18. Mehrschichtfolie nach Anspruch 1, die einen Speichermodul von mindestens 175 N/cm (100 lb/linearem Zoll Breite) bei Temperaturen bis zu 140°C hat.
19. Mehrschichtfolie nach Anspruch 1, die eine Dicke im Bereich von 13 bis 1270 µm (0,5 bis 50 mil) hat.
20. Mehrschichtfolie nach Anspruch 1, die coextrudiert ist.
21. Mehrschichtfolie nach Anspruch 1, die ferner mindestens ein gedrucktes Bild auf einer ihrer Außenseiten einschließt.
22. Mehrschichtfolie nach Anspruch 1, die einen Speichermodul von mindestens 138 MPa (20.000 psi) bei 150°C hat.
23. Verpackung, die aus der Folie gemäß Anspruch 1 hergestellt ist.

Revendications

1. Film multicouche qui comporte :

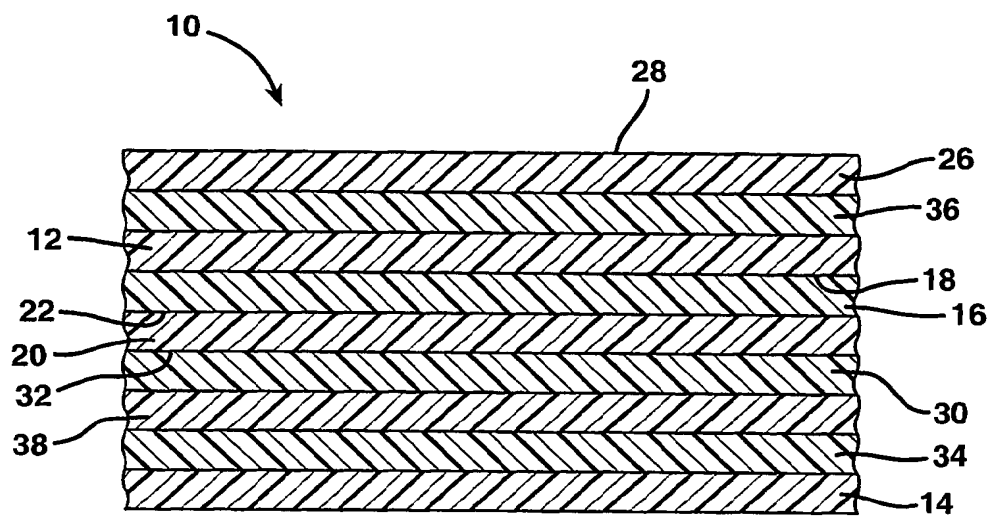
a) une première couche comprenant un polymère amorphe qui présente une température de transition vitreuse, b) et une deuxième couche constituant la couche externe dudit film multicouche et comprenant un matériau d'étanchéité capable de former un joint de thermoscellage, lequel matériau d'étanchéité comprend un polymère qui présente un point de fusion,

et dans lequel film la température de transition vitreuse dudit polymère amorphe est supérieure d'au moins 45 °C au point de fusion dudit matériau d'étanchéité.

2. Film multicouche conforme à la revendication 1, dans lequel la température de transition vitreuse dudit polymère amorphe présent dans ladite première couche vaut au moins 140 °C.
3. Film multicouche conforme à la revendication 1, dans lequel ledit polymère amorphe présent dans ladite première couche comprend un po-1 yamide amorphe.
4. Film multicouche conforme à la revendication 3, dans lequel ledit polyamide amorphe comprend au moins un polyamide choisi parmi les suivants : polyamide 6I/6T, polyamide 6I/MACMT, polyamide 6I/MACMI, polyamide 6I/MACMI/MACMT, polyamide 6I/MACMI/MXDI, polyamide 6I/6T/MACMI, polyamide 6I/6T/MACMI/MACMT, polyamide 12/MACMT, polyamide 12/MACMI, polyamide 12/IPDI/PACMI, polyamide 12/PACMI, polyamide TMDT, polyamide 6I/6T/IPD, polyamide 6I/6T/PACMI/PACMT, polyamide 6I/6, polyamide MACMI/MACMX, polyamide XT/MACMT, polyamide 6/AMNBT, polyamide PACM/12 et polyamide MDI6/MDI9.
5. Film multicouche conforme à la revendication 3, dans lequel ladite première couche comprend un mélange d'au moins deux polyamides amorphes.
6. Film multicouche conforme à la revendication 1, dans lequel ledit polymère amorphe présent dans ladite première couche comprend au moins un polymère choisi parmi les polycarbonates, copolymères d'oléfine cyclique, polysulfones, poly(éther sulfone), polyarylsulfones, copolymères de styrène et d'anhydride maléique, poly(éther imide), poly(oxyphénylène), alliages de poly(oxyphénylène) et de polystyrène, poly(phénylène éther) et polyarylates.
7. Film multicouche conforme à la revendication 1, dans lequel le point de fusion dudit matériau d'étanchéité présent dans ladite deuxième couche est inférieur à 110 °C.
8. Film multicouche conforme à la revendication 1, dans lequel ledit matériau d'étanchéité présent dans ladite deuxième couche comprend au moins un matériau choisi parmi les ionomères, copolymères hétérogènes d'éthylène et d'alpha-oléfine, copolymères homogènes d'éthylène et d'alpha-oléfine, copolymères d'éthylène et d'ester insaturé, copolymères d'éthylène et d'acide insaturé, copolymères d'éthylène et de propylène, et polybutylènes homopolymères ou copolymères.

9. Film multicouche conforme à la revendication 1, qui comporte en outre une troisième couche qui adhère à une surface de ladite première couche.
- 5 10. Film multicouche conforme à la revendication 9, dans lequel ladite troisième couche comprend au moins un matériau choisi parmi les polyamides homopolymères ou copolymères, les polyoléfines modifiées par acide, les polyoléfines modifiées par anhydride, les copolymères d'éthylène et d'acide acrylique, les copolymères d'éthylène et d'acide méthacrylique, et les copolymères ou terpolymères d'éthylène comportant de 5 à 30 % en moles de motifs de monomère ester.
- 10 11. Film multicouche conforme à la revendication 9, qui comporte en outre une quatrième couche qui adhère à une surface de ladite troisième couche.
12. Film multicouche conforme à la revendication 11, dans lequel ladite quatrième couche comprend au moins un matériau choisi parmi les copolymères d'éthylène et d'alcool vinylique, polyamide MXD6, polyamide MXD6/MXDI, 15 poly(chlorure de vinylidène) et polyacrylonitrile.
13. Film multicouche conforme à la revendication 11, lequel film laisse passer l'oxygène à une vitesse inférieure ou égale à 30 cm³ d'oxygène par mètre carré de film et par période de 24 heures, sous une pression de 101 325 Pa (1 atm) et à une température de 23 °C (73 °F), sous 0 % d'humidité relative.
- 20 14. Film multicouche conforme à la revendication 11, comportant en outre une cinquième couche, laquelle cinquième couche constitue pour ledit film multicouche une couche externe disposée à l'opposé de ladite deuxième couche et comprend un matériau dont la tension superficielle vaut au moins 3,6 Pa (36 dynes/cm²).
- 25 15. Film multicouche conforme à la revendication 14, dans lequel ladite cinquième couche comprend au moins un matériau choisi parmi les polyamides, polyesters, polycarbonates, polyuréthanes et polyacrylates.
16. Film multicouche conforme à la revendication 14, comportant en outre une sixième couche qui adhère à une surface de ladite quatrième couche, laquelle sixième couche comprend au moins un matériau choisi parmi les polyamides 30 homopolymères ou copolymères, les polyoléfines modifiées par acide, les polyoléfines modifiées par anhydride, les copolymères d'éthylène et d'acide acrylique, les copolymères d'éthylène et d'acide méthacrylique, et les copolymères ou terpolymères d'éthylène comportant de 5 à 30 % en moles de motifs de monomère ester.
- 35 17. Film multicouche conforme à la revendication 16, comportant en outre une septième couche placée entre lesdites deuxième et sixième couches, laquelle septième couche comprend au moins un matériau choisi parmi les polyéthylène haute densité, polyéthylène basse densité, polyéthylène basse densité linéaire, copolymères d'oléfine cyclique, polypropylène, polyamides et polyesters.
- 40 18. Film multicouche conforme à la revendication 1, lequel film présente un module de conservation d'au moins 175 N/cm (100 livres par pouce linéaire) de largeur, pour une température allant jusqu'à 140 °C.
19. Film multicouche conforme à la revendication 1, lequel film présente une épaisseur de 13 à 1270 µm (0,5 à 50 millièmes de pouce).
- 45 20. Film multicouche conforme à la revendication 1, lequel film est obtenu par coextrusion.
21. Film multicouche conforme à la revendication 1, qui porte en outre au moins une image imprimée sur sa surface externe.
- 50 22. Film multicouche conforme à la revendication 1, lequel film présente un module de conservation d'au moins 138 MPa (20 000 livres par pouce carré) à 150 °C.
23. Emballage fait d'un film conforme à la revendication 1.

FIG. 1



(19)



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(54) **Flexible packaging systems and process for their manufacture**

(57) The present invention concerns an easy tear flexible packaging system based on the combination of several film layers, where one or more layers is fabricated using special resin blends and/or particular extrusion/

stretching conditions in order to obtain that said special layer(s) facilitate the tearing of the whole complex and guides the tearing behaviour of the other layers, when said complex is converted into a consumer package.

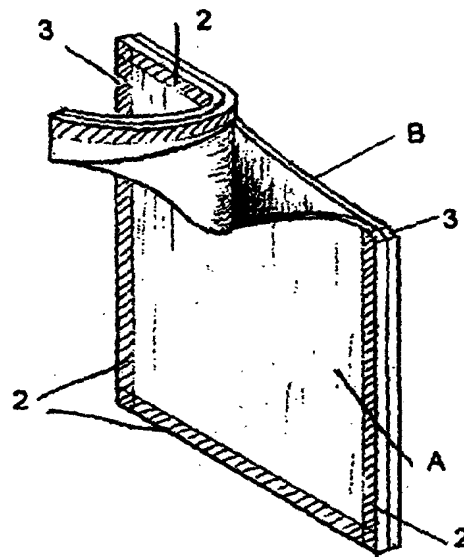


Fig. 2

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Description

[0001] The present invention relates to flexible packaging systems such as films, sheets, foils and the like, generally consisting of several layers of thermoplastic synthetic resins, and to the formed articles thereof such as packages, wrappers, containers, bags and the like, which are characterized by the fact that they can be easily opened by hand by the end user, in particular by simply tearing them, and are specifically destined to contain solid, liquid, gelatinous products that require a protection of their characteristics and, preferably, a barrier to environmental outer agents.

[0002] Basically the invention concerns systems like multilayer films comprising a master subsystem (primary layer) which generates not only its own tear opening but, in addition, guides also the opening of the other whatever associated components.

[0003] Part of this invention are also advantageous processes for the manufacture of said films, sheets, foils and the like and of the relevant packages.

Prior Art

[0004] It is of wide experience that major difficulties are faced when trying to open a package without making use of scissors, knives or other similar devices either because the package forming film is too tough and requires a quite high strain to complete the opening, even when a notch is cut on the side of the package in order to make it easy to initiate the tearing, or because, even when the operation seems apparently simple, the two films forming the opposite faces of a pouch tear nearly spontaneously along directions different from the one sought, with the actual risk that part of the content pours off in an uncontrolled manner sometimes even smearing the person who is handling the package.

[0005] The problem is particularly felt with some particular types of packages as those shown in fig. 1a (flat pouch) or those shown in fig. 1b (stand-up pouch) especially when the content is a liquid or a paste or it consists of mixtures of solid and wet products such as soups, pickles, pet food etc.

[0006] In order to eliminate such an inconvenience, several systems have been proposed, among which the most known and used consists of a controlled weakening of one of the layer components of the multilayer structure, by a rectilinear micro-incision of either spots or hatches produced by laser ray or mechanical devices (see EP's n°363540 and n°468619). This solution is rather effective; it, however, shows some drawbacks such as the need of complex equipment and production processes, difficulties to perfectly align the treated areas with the pre-cut notch and to match the treated areas of the front and the back side of the pouch, risks excessive weakening of the package.

[0007] It has also been proposed to solve this problem by using longitudinally tearable polyolefin based films, consisting of: a) - from 99 to 90% of crystalline polypropylene resin and from 1 to 10% of crystalline polyethylene (JP Patent Application H10-65193); or b) - polyolefin resins and sorbitol derivatives (JP Patent Application H01-299813); c) - resins formed of polypropylene and styrene polymers (JP Patent Application S64-56740).

[0008] Further among the Prior Art Patent documents concerning easy-open bag, the following are to be mentioned: - EP n° 112954 (laminates of L-LDPE- and bi-axially drawn Ny6); - WO2004/113193 (preferential tearing line and notch); - WO2005/113370 (stand-up pouch body formed of a laminate comprising a mono-directionally orientated film); - EP n° 0971980 (LLDPE blends with cyclic-olefin copolymers (COC) to improve toughness and processability); - EP n° 1388415 (laminate with a polyolefin core layer sandwiched between COC containing films); - WO 2004/063273 (films of a COC and PE). Notwithstanding some advantages, these conventional systems seem not to have radically solved the tear opening problem and have shown major limitations that have negatively affected their market expansion.

Summary of the Invention

[0009] First object of the present invention is to provide multilayer structure systems wherein the layer that is normally the more tear resistant one has not only been rendered easy-tearable but is also such to be able to guide the tearing behaviour of the layers that are associated to it in the multi-layer construction.

[0010] Another object of this invention is a process allowing to obtain optimal values of all the characteristics of the final packaging materials, as relates not only to tearing but also to mechanical resistance, transparency, etc. by critically coordinating resin blend compositions and mechanical treatments of the same.

[0011] The main features of the invention are reported in the claims here at the foot that have to be considered also herein incorporated.

[0012] Synthetically, the invention opens a new way for the manufacturing of tearable articles in the sense that by "modulating" now the two functions resins compositions and dimensional treatment of the same, the limits of traditional resin compositions are eliminated, and the range of resin types that can be used for this purpose is broadened by adopting, in certain cases, dimensional modification treatments preferably consisting in the use of stretching systems selected from the group of high stretching during the extrusion- or the post-extrusion-phase, and, in other cases, by adopting soft stretching systems in combination with special resin blends which allow to obtain extruded or, preferably,

co-extruded films that result to be easy-tearable, both lengthwise and crosswise.

[0013] According to the present invention, the radical solution of the package manual opening problem has been identified in the development of a complex structure, consisting of various films that are laminated one to the other by existing technologies, wherein, however, at least one of said films, preferably the inner primary sealing layer, has such characteristics to facilitate and guide the tearing of the whole package, i.e. by dragging also the other films in the desired direction and in a perfectly linear way; said inner film subsystem becomes the tearing promoter as it has been prepared by inter-coordinating said two critical factors: i) - blend composition; and ii) -dimensional modification treatment.

[0014] An advantage of this system is that the opening operation can be initiated from any point of the package lateral edges (obviously starting from the opening notch) and requires only a minimum effort of the fingers by the end user to accompany the guided tearing of the material. Said primary film must show also all the characteristics of the mechanical and chemical resistance (often required by these applications) and in several cases must also withstand the steam sterilization treatment (required for the shelf-life of certain food products) without alterations of the package behaviour.

[0015] The mostly used complex structures for these applications consist of at least two films, more often three, four and even more films. The outer layer of these films is generally a thermostable film (such as PET, OPA, Aluminium foil, EVOH, OPP etc.) suited to be printed with several colours, whereas the inner layer has thermoplastic properties that render it thermosealable and can be mono-extruded (utilizing base resins of the type LDPE, LLDPE, HDPE, PP homopolymers, PP copolymers, COC polymers etc. and their blends) or co-extruded (through combinations of polymers such as PE/PP, PE/PA/PE, PP/EVOH/PE, PPIPA/PP, PP/EVOH/PP, PE/EVOH/PP,

[0016] PP homopolymers/PP-copolymers, LLDPE/LMDPE and mixtures thereof with COC polymers etc.).

[0017] One (or more) intermediate layer(s) is often present therein acting either as a barrier to environmental outer agents (H₂O, O₂, CO₂, etc.) and to inner substances contained in the product (aromas, fragrances, flavours) or as high mechanical resistance film..

[0018] The system according to the invention based on the critical coordination of the two parameters: 1) - blend composition, and 2) - dimensional treatment, allows the obtainment of several film types. Synthetically four main classes of "tear foil"®, indicated as R, S, T, T' are provided which, once incorporated in a complex structure, can produce satisfactory and, in several cases, even surprising results to reach the main scope of the present invention.

[0019] The type R film is prepared by extruding or co-extruding polyolefin based thermoplastic resins preferably of the type HDPE, isotactic PP, block copolymer or random copolymer PP etc. with such a molecular structure to maintain an orientated state in the melt die exiting direction once some fundamental process parameters are complied with. It has indeed been found that very good results can be obtained when at least the following critical parameters are selected: - a particular value of the die gap; - a proper blow-up ratio (BUR); - a properly defined height of the so called "frozen line" (bubble zone in which the molten resin turns solid) and, above all, when those resins are selected which, either singularly or, better, in special blends, can undergo stretching processes and maintain permanent structural modifications, i.e. crystallize in a high orientation state.

[0020] It has advantageously been found that these films, once they are bound to other films by means of particular adhesives, allow the whole structure to behave in an excellent manner as to manual tear, either because the force required is very low and because the tear direction results sufficiently linear. Therefore the first combination R relates to polyolefin mixtures submitted to a notable stretching during the extrusion phase.

[0021] The type S film includes the films which are submitted to said notable stretching in a separate phase, subsequent to the extrusion phase, that imparts to the polymer macromolecules an orientation in the longitudinal direction in way that is substantially similar to type R, but through a more efficient dimensional treatment.

[0022] Also for class S the selection of the primary film resin components is important as the essential condition whereby the post-extrusion stretching action results in a crystallization of the polymeric chains in a preferential direction and thus in a condition such to make the film easy tearable along said direction.

[0023] Conceptually these resin types have to consist of polymers with a linear structure and with a configuration as isotactic as possible to reach a sufficient crystallinity. The lamination of these easy-tear films with other multifunctional films, by means of high-performance polyurethane adhesives, makes the foil complex suited to prepare easily manually openable packages. moreover, with this system it is possible to obtain a value of divergence of the tearing front and back sides of the pouch much lower than the value of the previously described system and of the order D/L=0.3 or even smaller (see Table I).

[0024] The third type of film is the most important one. This can be in either version T or version T', both not requiring a notable stretching process, but only an extremely soft pseudo-stretching and is essentially based on the specific resins used, on the ways they are blended and, in some cases, on the way they are distributed or positioned within the structure complex (layer sequence) as shown in figures 5, 6' and 6". Said films T and T' impart to said final structures easy tear characteristics not only lengthwise, but, surprisingly, also in the transversal direction.

[0025] This system is particularly advantageous for the packaging of cosmetics flat sachets where, depending on the type of packaging machine used to fabricate them, the tear preferential direction can result either longitudinal or transversal. In these applications a very high mechanical resistance (in particular to compression) is required, which normally,

is scarcely compatible with easy tearing characteristics.

[0026] The invention will now be described with reference to the attached drawings:

- Figures 1a, 1b, 2 and 3 are prospective views;
- Figure 4 is a front view of a torn bag;
- Figure 5 is a cross-section view of the T type film; and
- Figure 6' and 6" show a cross-section of a complex derived from the T' type film in the extruded and coextruded version.

[0027] Table I shows how the tearing values improve over the standard reference, in a lower or bigger measure, when process variations or, more frequently, composition variations of the sealing film base components are introduced. Indeed Table I indicates the main properties of packages rendered "tearable" through the use of R, S, T and T' films. The compositions thereof are given (as examples) in figures 5, 6 and 6'.

[0028] Figure 1a refers to a flat pouch 1 (FP) consisting of a front A and of a back B, sealed one to the other along their perimeter as per line 2 and provided with a tear notch 3. The pouch type of Figure 1b shows a stand-up pouch 4 (SU) with tear notch 8, consisting of front A and back B sealed one to the other along two sides as per line 5 and on the top as per line 7, and of a bottom sealed to the pouch faces by a shaped seal 6. Figure 2 shows how a FP type pouch (however the same behaviour can occur on the pouches SU) can lacerate when the tearing, even if relatively easy, does not follow a precise rectilinear line but propagates, without control, in a diagonal direction on a pouch face, with the consequent undesired pouring off of the content. If this divergence from an ideal rectilinear line is higher than a given value, the pouch is considered unsuitable.

[0029] On the contrary figure 3 shows how the same flat pouch FP opens perfectly when the tearing line LS remains perfectly parallel to two sides and perpendicular to the two other sides of the pouch. The same concept applies to the type SU pouch.

[0030] Figure 4 shows how to calculate the divergence value D/L of a practical tear line vs. the ideal line indicating the acceptability limits whereby an easy-open pouch can be considered safe from the view point of the content incontrollable pouring. The same figure shows an open pouch in which the two arrows F indicate the divergence distance D whose ratio to the length L indicates the acceptability value to which a maximum limit $D/L=0.1$ has been given, although obviously the lower this ratio the better the result when opening the pouch. The two faces A and B are here represented to clarify the situation after completing the tearing due to said divergence from the perfectly rectilinear ideal line vs. the real oblique line.

[0031] Figure 5 shows the cross-section of a complex sheet made up of several layers including the coextruded T type film according to the invention, wherein the dimensional modification is obtained by thinning the melt thickness as it passes through the die gap.

[0032] Figures 6' and 6" show the cross-section of a possible combination of various layers wherein the ones according to the invention are the type T' extruded or coextruded films, the easy tearing of which is obtained thanks to the specific resin mixture composition or from the disposition of the various mixtures in a coextruded film.

[0033] Table I summarizes the more representative data relevant to the R, S, T, T' films, measured after lamination of the same with other films in order to obtain structures suitable to the packaging of FP or SU pouches. Said data relate to the properties that are fundamental to judge the suitability of the various film types for the most important applications. The tearability is expressed both in grams and in joules to better estimate the behaviour to the tearing force.

Detailed description of the more important applications of films R, S, T, T'.

[0034] A first embodiment is based on the concept that when two or more films are laminated by using high performance polyurethane adhesives and when also the sealing film (here of the R type) has undergone a stretching or orientation process during the extrusion step, the final complex structure shows easy-tearing characteristics preferably in the longitudinal direction.

[0035] A typical example of use of primary film is the following three layer laminate structure (the characteristics of which are indicated in the first column of Table I) consisting of:

- a) An outer film consisting of PET 12 micron thick, reverse printed with up to 9 colours with special vinyl base inks and laminated, with adhesives (Adh) capable of developing a high adhesion strength in the presence of said printing inks, to:
- b) A gas barrier central film comprising a metal sheet (f.i. of aluminium Al 9 μ) laminated on its turn, with adhesives (Adh), for instance of polyurethane type but also of the other types used to fabricate flexible laminate packaging materials, capable to impart maximum mechanical, thermal and chemical resistance to the complex, to:
- c) A film (here of 75 μ thickness) positioned as the inner layer of the final structure having the function of sealing

layer, based on polyolefin resin which, in this specific case, include as the main component homo-or block copolymer polypropylene, fabricated on an extrusion equipment preferably of the tubular (or hot-blown) type, suitably adapted to impart to the film special characteristics as to obtain easy tearing features of the whole complex.

[0036] In details the essential conditions for a hot-blown equipment to allow that a given resin, during the solidification phase, undergoes an orientation process in a machine specific zone are:

- Die gap width from 1 to 4 mm (preferably 1,5-3 mm);
- Blow-up ratio (BUR) in the range from 1:1 to 1:2;
- Frost line height from 0.5 to 2,5 mm;
- Polyolefin resin type (preferably based on PP) which can achieve the maximum degree of crystallinity and thus of orientation in the process conditions; said resins, either alone or in specific blends) are generally composed of polymers with linear structure and high crystallinity.

[0037] The second embodiment of the invention, substantially similar to the above process as far as selection of the resins, the lamination conditions, the evaluation criteria, the results achieved etc. are concerned, shows the variant that the orientation phase of the polyolefin film (S type) is carried out in a step successive to the extrusion step (in or off line) by means of a longitudinal stretching group which provides the primary film heating and its contemporaneous orientation through a progressive orientation to achieve notable stretching ratios up to from 2 to 7 times the initial unitary value, including the stabilisation final phase.

[0038] This variant, even if involves high investment costs and a material wastage bigger than the previous process, can achieve better quality results from the standpoint both of easy tearing and of the low values of the deviation D/L (as reported in Table I), once the proper conditions of primary film stretching and extrusion (both by flat die and hot-blown) have been established.

[0039] A further very important embodiment of the invention, which is substantially independent from the specific technical solutions described for the previous versions of the extrusion process (f.i. notable stretching during-or post-extrusion) is based on the surprising discovery that the limited orientation degree that occur just as a consequence of the thinning effect by pseudo-stretching (analogically referable to the effect of a classic low stretching process) of the melt during its cooling (again both by flat die and hot-blown) is sufficient to achieve good easy tearing characteristics; here the type of resins forming the extruded or co-extruded structure, the blend type, and possibly the order in which said resins or mixtures thereof are positioned across the film thickness are of fundamental relevance (some examples of complete structures are shown in the figures 5, 6' and 6").

[0040] It has indeed been found that when the central layer of a coextruded three (preferably five) layer film is constituted of resins of the type EVOH (at various ethylene contents), PVA, PA etc. (indicated with Y in fig. 5) even at very low thickness (down to a minimum of 3 μ) obtained by pseudo stretching, and when the adhesion of said resins to the resins of the other layers (currently polyolefins) is particularly high (thanks to the use of suitable tie layers), the resulting film tears easily especially in the transversal direction but also in the longitudinal direction and behaves in the same manner even after lamination (with the use of special polyurethane adhesives) to other films and facilitates the tearing of the whole three or more layer complexes.

[0041] In figure 5 the cross-section of a type of structure useful for some of these applications is represented where the main film (indicated with "coex type T") forms the complex coextruded portion i.e. the component that is fundamental to impart to the finished package the characteristics of easy-tear and high chemical, mechanical, thermal resistance.

[0042] Even more surprisingly, it has been found that by extruding or coextruding particular blends of commonly used resins (such as LDPE, LLDPE, MDPE, HDPE, homo or copolymers PP) and of recently available resins of the type of copolymers based on of cyclic olefins (type norbornene) and ethylene, films which are easy to tear both length-and cross-wise, with respect to the extrusion direction, are obtained.

[0043] Said resins, based on cyclic-olefin copolymers (COC), are relatively recent and, in the world, are presently manufactured in rather small amounts by few companies, including Daicel (ex Hoechst-Celanese), Mitsui, Zeon Chem. Co., by a metallocene catalyst based technology.

[0044] These new grades of copolymers impart to the film made thereof very high optical, thermal and gas barrier characteristics; their nature is prevalently amorphous and are suited to be blended with the traditional polyolefin grades modifying or improving some important properties of the latter.

[0045] The films fabricated with the COC resins and their blends have been the matter of study of some prestigious Universities, with a special focus to identify their molecular structure and find the reason of some specific behaviours.

[0046] A few patents have already been filed covering some interesting characteristics of the films fabricated with blends of COC with traditional polyolefin resins.

[0047] Even our company, Safta S.p.A., since 2001 has been carrying out experimental work with these resins and the relevant films fabricated with the same, highlighting some important characteristics, such as stiffness, gas barrier

and easy tearing.

[0048] The present invention is based on certain innovative features that have been identified during the previous study, but especially on a long experimental work carried out more recently from which it has been found that, under specific conditions, a film can be developed, either mono- or multi-layer, preferably by the hot-blown extrusion technology, but also by the flat die extrusion technology, having balanced, i.e. the same in the longitudinal and in the transversal direction, characteristics in terms of easy tearing.

[0049] Said characteristic can be achieved when the blend composition is constituted by from 35% to 95% of polyethylene based resins, having densities from 0,910 g/cm³ to 0,960 g/cm³, and by from 5% to 65% of polycyclic olefin resins.

[0050] Said film will be identified as extruded type T' having composition of series X...

[0051] According to a surprising feature of the invention, films of blends of a minimum content of 40% PP (polypropylene) and a maximum content of 60% COC, have shown very low tear values lengthwise but higher values crosswise. This feature is extremely favourable when said films are used as thermosealing components in a laminated material destined to manufacture stand-up pouches considering that in these applications the tear direction is generally lengthwise.

[0052] This film will be identified as type T' with composition series Xp.

[0053] A further advantage is represented by the possibility of reducing the total thickness, by virtue of the increased stiffness and gas barrier characteristics, deriving from the presence of the COC copolymer (even in minor amounts) blended with traditional grade polyolefins.

[0054] Further formulation variations can be implemented, with referring to multilayer coextruded films, with multiple advantages for various aspects: it is possible, in fact, to increase the COC content even up to 65% when such a blend is utilized only in the central layer (either of the type XE or Xp) of a film made of three or more layers, whereas the outer layer composition (X1E and X1p in fig 6") can be "modulated" so to get blends consisting only of polyolefin resins (based on polyethylene or polypropylene) or of blends of polyolefin and resins COC, the latter up to a maximum content of 40% (preferably of 30%).

[0055] A further advantage of the coextruded film derives from the possibility to formulate the outer layer composition in function of the characteristics of sealability and adhesion strength necessary to achieve the high performances often required by several package types destined to very critical applications involving thermal (sterilization)-mechanical (compression)- and chemical (aggressiveness)- resistance.

[0056] One of the major uses of said complex films of the T and T' types concerns also the manufacturing of pouches or sachets destined to contain cosmetics (creams, perfumes, shampoo etc) or pharmaceuticals. These applications are very critical because these packages must be endowed with high resistance to compression and to chemical aggressiveness characteristics, but a low tear resistance is also appreciated by the consumer to facilitate their opening by means only of the fingers. Obviously the invention as described is susceptible of those changes additions, substitutions and the like which, being within reach of the average qualified technical person of this art, fall within the scope and spirit of the claims hereto follow.

Table I

Properties		Reference		Type R	Type S		Type T	Type T	
		Pouch FP	Pouch SU		Pouch FP	Pouch SU		Pouch FP	Pouch SU
Tear propagation resistance (9)	MD	> 900	> 1200	100 + 150	30 + 50	30 + 40	200 + 250	30 + 50	80 + 100
	TD	> 900	> 1000	250 + 500	> 1000	> 1000	150 + 200	40 + 70	150 + 200
Tear propagation resistance (J/10cm)	MD	> 0.70	> 0.80	0.25 + 0.40	0.06 + 0.08	0.05 + 0.07	0.40 + 0.50	0.08 + 0.08	0.08 + 0.12
	TD	> 0.70	> 0.40	> 0.40	> 0.60	> 0.60	0.30 + 0.40	0.07 + 0.10	0.10 + 0.20
Divergence D/L	MD	> 0.20	> 0.20	0.08 + 0.10	0.02 + 0.04	0.02 + 0.04	0.04 + 0.07	0.02 + 0.04	0.04 + 0.06
	TD	> 0.20	> 0.20	> 0.20	> 0.20	> 0.20	0.04 + 0.08	0.03 + 0.05	0.08 + 0.10
Adhesion Strength (N/15mm)		> 5.0	> 5.0	> 6.0	> 5.0	> 7.0	> 5.0	> 5.0	> 5.0
Heat Seal Strength (N/16mm)		> 50	> 50	> 50	40 + 50	30 + 40	> 60	> 50	> 80

Claims

1. Flexible, manually easy tearing packaging systems, based on one or more layer(s) of synthetic thermoplastic resins to be selected from the group of olefin, cyclic olefin, vinyl, amidic, terephthalic homopolymers and copolymers, either extruded or co-extruded by hot-blown, flat die or other suitable technologies, anyhow treated, printed, laminated, etc, including or not including a metal layer, **characterized by** one or more layers, of particular composition and processes, that have been obtained from resins that crystallize in a state of marked dimensional orientation.
2. Systems according to claim 1, including one or more primary film(s) (sheet, foil and other similar), preferably constituted by more than one layer, at least one of which has undergone a modification of the original thickness, i.e. thinning of the extruded or coextruded melt by stretching or pseudo stretching, under crystallization conditions with consequent high degree of directional orientation.
3. Systems according to claim 2, in particular multilayer primary films that have undergone a notable stretching process during the extrusion or coextrusion of resins having a molecular structure capable of maintaining permanent structural modifications, in particular of resins of the polyolefin chemical family, preferably of the high density polyethylene (HDPE) grade, isotactic homopolymers polypropylene (PP), block polypropylene copolymers, the notable stretching ratio being from 2:1 to 12:1.
4. Systems according to claim 2, in particular films with at least a primary layer, that have undergone a notable stretching process subsequent to the extrusion or coextrusion of polymers having a linear structure and an isotactic configuration, under conditions where an orientation in the longitudinal direction has been induced.
5. Systems according to claim 1, including in particular a coextruded multilayer film the thickness of which has been reduced by a pseudo stretching process of the melt passing through narrow extrusion or coextrusion dies of resins type ethylene-vinyl-alcohol (EVOH), poly-vinyl-alcohol (PVA), poly-amide (PA), cyclic olefin copolymers (COC) and blends of the same having longitudinal and transversal tearability.
6. Systems according to claim 1, including at least a thermostable, printable, high mechanically resistant outer layer, and an inner primary layer acting also as thermosealable film, **characterized by** a high macromolecular orientation, and/or some special resin blends, besides being the promoter of tearing dragging also the other layers laminated to it.
7. Systems according to claim 6, where said thermostable outer layer is a film based on PET, OPA. Aluminium foil, EVOH, OPP and other similar materials.
8. Systems according to claim 6, where the inner thermosealable layer is selected within the group consisting of: - a mono-extruded structure of LDPE, LLDPE, HDPE, homopolymers and copolymer polypropylene and blends of the same; and - a co-extruded structure of combinations type PE/PP, PE/PA/PE, PE/EVOH/PE, PP/PA/PP, PP/EVOH/PP, PE/EVOH/PP, homopolymer PP, random copolymer PP, block copolymer PP, PE/COC, PP/COC, PE/COC + polyolefin blends, PP/COC + polyolefin blends and other anyway including the resins here mentioned.
9. Systems according to at least one of the previous claims, including also an intermediate layer having function of providing a barrier to environmental outer agents and/or to emissions of substances contained in the packed product or in the atmosphere that creates inside the package from said inside package atmosphere towards the outer environment.
10. Production process for the manufacturing of flexible packaging systems destined to food, cosmetic, pharmaceutical and other similar applications, endowed with characteristics of high tearability, achieved by extrusion or co-extrusion of thermoplastic resins, in particular according to claims from 1 to 9, **characterized by** the fact that: - blends are prepared utilizing thermoplastic resins selected among the ones capable of achieving and maintaining an orientated state; - said blends are extruded or co-extruded forcing the melt to pass through selected extrusion dies and the generated extruded or co-extruded forms are submitted to dimensional modification treatments, critically co-ordinated with the composition of said blends and with the extrusion or co-extrusion conditions, said co-ordinated treatments generating the thinning of the final film by virtue of a notable stretching or pseudo stretching through the properly designed die gap width, this way by co-ordinating in a flexible manner the following two parameters i) blend composition, ii) dimensional modification treatment, the range of useful resin grades is broadened and the characteristics of tearability and mechanical, thermal, chemical resistance can be optimized.

11. Production process according to claim 10, in particular focused to the preparation of primary film according to claim 3, where blends of polyolefin resin grades are prepared and, based on the composition of the selected resin grades, the parameters of the extrusion or co-extrusion process are optimized with particular relevance to die gap width, blow-up ratio (B.U.R.), frost line height.
12. Production process according to claim 11, where the die gap width ranges from 1.0 to 4.0 mm, preferably from 1.5 mm to 3.0 mm, the blow-up ratio (B.U.R.) ranges from 1:1 to 1:2 and the frost line height ranges from 0.5 m to 2.5 m.
13. Production process according to claim 10, in particular focused to the preparation of primary film submitted to a notable stretching as a separate phase subsequent to the extrusion or co-extrusion phase, according to claim 4, where compositions are prepared consisting of blends of resin grades having linear structure and the higher isotactic configuration possible, said blends are extruded or co-extruded under optimized process conditions as a function of the specific resin grades selected, and the relevant fabricated films are submitted to an off-line notable stretching phase this way generating a macromolecular orientation in the longitudinal direction, said notable stretching ranging from 2:1 to 7:1.
14. Production process according to claim 13, where said primary films are bound to traditional commercially available multifunctional films by means of high performance polyurethane adhesives, this manner generating laminate materials particularly suited to fabricate packages the various sides of which are endowed with very high and very directional tearability, showing divergence values D/L ranging from 0.02 to 0.1.
15. Production process according to claim 10, where co-extruded structures are fabricated combining of one or more traditional commercially available resin(s) and resin grades or blends of resin grades of different chemical families, such as EVOH, PVA, PA, COC, said film having been thinned (pseudo stretching) in such a way that the functional layer can reach also low thickness values by forcing the melt to pass through extrusion or co-extrusion dies having a proper gap, and a very high layer bond strength is achieved by using proper tie layer resin grades, so that interferences are generated among the used resins in a manner so to achieve an easy tearability of the finished complex.

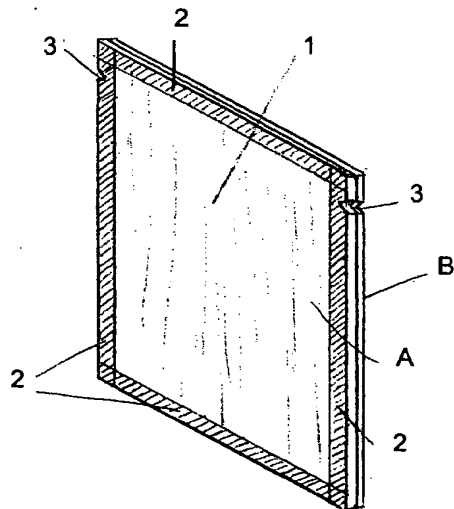
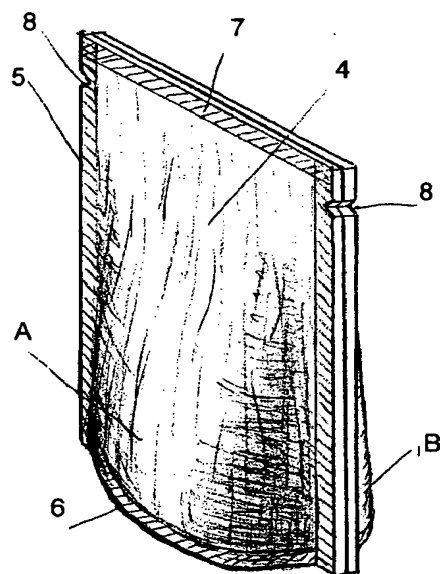


FIG. 1a

FIG. 1b



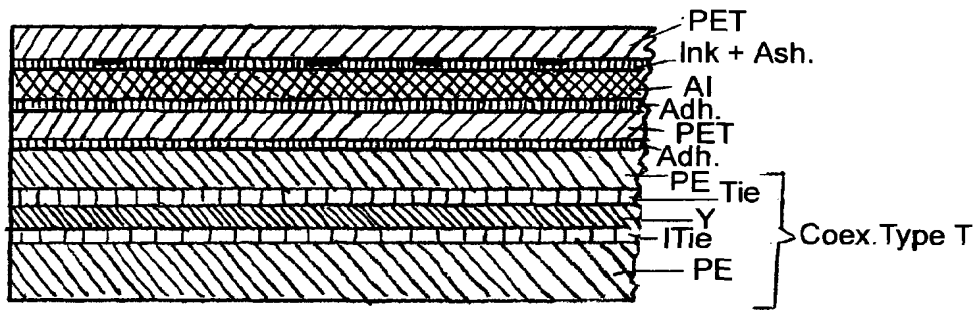


FIG. 5

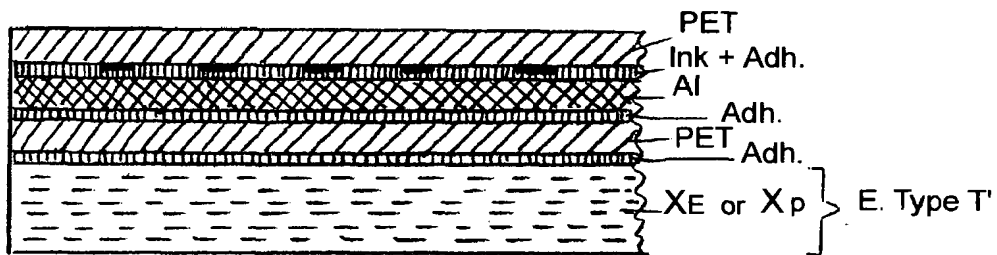


FIG. 6'

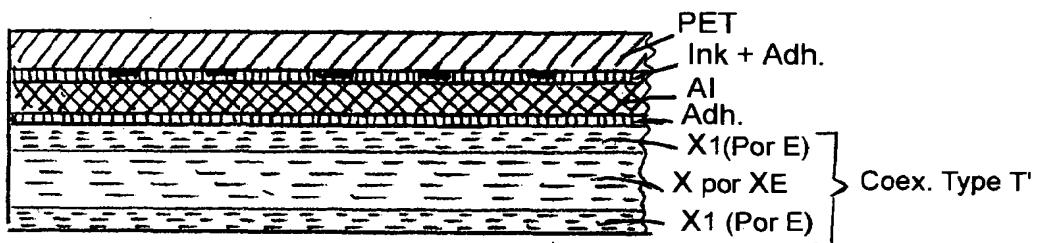


FIG. 6''



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EUROPEAN SEARCH REPORT

Application Number
EP 06 01 3028

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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 25 January 2007	Examiner Lindner, Thomas
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background C : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPC FORM 1503 03.82 (P04C01)



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EUROPEAN SEARCH REPORT

Application Number
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Place of search Munich		Date of completion of the search 25 January 2007	Examiner Lindner, Thomas
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 06 01 3028

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(54) **Easy-open reclosable films having an interior frangible interface and articles made therefrom**

Wiederverschliessbare, einfach zu öffnende Folien mit aufreissbarer, interner Zwischenschicht und daraus hergestellte Artikel

Films refermables à ouverture facile avec interface intérieure déchirable et articles fabriqués à partir de ceux-ci

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Description

[0001] The present invention generally relates to multilayer films for packaging applications, and particularly, to multilayer thermoplastic films for flexible packages which have both an easy-open and a reclosable feature.

[0002] Flexible packages which combine an easy-open feature with reclosability provide consumers with a convenient means to open a package without the use of scissors, knives or other cutting implements, and a reliable manner to reclose the package as often as needed.

[0003] Various methods have been used to provide both these features which include, for example, mechanical strips, such as interlocking fasteners or zippers, and adhesive strips positioned on an exterior film surface or within the film structure. These methods are known in the art and have been disclosed in U.S. Patent Nos. 5,063,644; 5,301,394; 5,442,837; 5,964,532; 6,409,384; 6,439,770; 6,524,002; 6,527,444; 6,609,827; 6,616,333; 6,632,021; 6,663,283; 6,666,580; 6,679,027; and U.S. Patent Application Nos. 2002/0097923; and 2002/0196987, each of which is incorporated by reference herein.

[0004] These easy-open/reclosable means all require additional steps in the manufacturing of attaching or incorporating the strips onto or into the package and the extra cost of the strips themselves.

[0005] EP 1 582 341 A1 refers to a multilayer film which may be produced by blown-film coextrusion and has a carrier layer and a surface layer connected by a layer of a pressure-sensitive hot-melt adhesive. The surface layer and the carrier layer are made from polyethylene. The surface layer comprises an effective amount of low density copolymer from ethylene and a polyolefine with at least three carbon atoms. The copolymer has an increased linearity compared to low density polyethylene and a density of 0.910 g/cm³ in order to increase the adhesion between the hot-melt adhesive and the surface layer, which hot-melt adhesive sticks to the surface layer when diving the film.

[0006] It would be thus desirable to provide a thermoplastic film having an easy-open feature and reclosability without the additional processing steps and associated cost as mentioned in the prior art.

[0007] Thus, the present invention provides a peelable resealable multilayer film as defined in independent claim 1; further, advantageous embodiments are subject-matter of the respective independent claims. According to the present invention, there is also provided a packaging article as defined in independent claim 20, said packaging article having at least one member comprising a peelable resealable multilayer film of the present invention.

[0008] The present invention thus provides - according to a first aspect of the present invention - a peelable resealable multilayer film comprising at least a first thermoplastic layer, a second thermoplastic layer and a third thermoplastic layer;

[0009] wherein said first layer comprises a homopolymer or copolymer selected from the group consisting of polyolefin, ionomer and blends thereof;

wherein said second layer is in direct contact with and bonded to both said first and third layers;

wherein said second layer comprises a tacky pressure-sensitive adhesive;

wherein said third layer comprises a polymer having a glass transition temperature of at least 5 °C as measured in accordance with ASTM D-3418 test method; and

wherein said bond between said second and third layers comprises a peelable resealable interface having a first interfacial peel strength "A" and a second interfacial peel strength "B" such that the value of A is less than 3500 gram-force/inch (1350 newton/meter) as measured in accordance with ASTM F-904 test method when peeled from a second thermoplastic film to which said film has been heat-sealed, and the value of B is at least 330 gram-force/inch (127 newton/meter) as measured in accordance with ASTM F-904 when peeled from and resealed to said second film; wherein the relative values of A and B satisfy the relationship $A \geq B$.

[0010] Especially, the present invention provides peelable resealable multilayer films comprising at least a first polymer layer, a second polymer layer, a third polymer layer such that the second layer is in direct contact with and bonded to the first and third layers. The films according to the present invention may be considered "peelable" when the bond between two interior film layers comprises a peelable resealable interface adapted to separate by application of pulling or peeling force exerted away from the film which has been heat-sealed to a second thermoplastic film. The force required to separate the interface may be dependent upon the chemical composition of each of the two interior film layers, i.e., the chemical similarities or dissimilarities of each film layer, or both the chemical composition and thickness of each interior film layer. By separating at least a portion of the interface, the face-to-face surfaces of each interior film layer are exposed. The films according to the present invention may also be considered "resealable" when the bond between the two interior layers forms an interface adapted to reseal after separation. Generally, the force required to "reseal" the interface is proportional to the manual pressure exerted on the film. Accordingly, the peelable resealable interface of the films, according to the present invention, may include a first interfacial peel strength and a second interfacial peel strength.

[0011] The present disclosure is directed to peelable resealable multilayer films which include at least a first polymer layer and a second polymer layer of pressure-sensitive adhesive in direct contact with and bonded to both the first and third layers. The bond formed between the second and third layers includes a peelable resealable interface having a first interfacial peel strength "A" and a second interfacial peel strength "B". The peelable resealable interface is adapted

to remain secure and unbroken during package fabrication, distribution and storage, and yet may be easily and repeatedly separated and rejoined. Accordingly, the peelable resealable interface includes a first interfacial peel strength, A, having a value of less than 3500 gram-force/inch (1350 newton/meter) as measured in accordance with ASTM F-904-98 test method when the films of the present invention are peeled from a second thermoplastic film to which the film has been heat-sealed. The second interfacial peel strength, B, has a value of at least 330 gram-force/inch (127 newton/meter) and, preferably, at least 400 gram-force/inch (154 newton/meter) as measured in accordance with ASTM F-904-988 test method when the films are peeled from and re-adhered to a second film. Moreover, the first interfacial peel strength, A, and the second interfacial peel strength, B, are such that the relative values of A and B satisfy the relationship $A \geq B$.

[0012] The present invention provides peelable resealable multilayer films comprising at least a first polymer layer of a material selected from the group consisting of polyolefin, ionomer or blends thereof, a second polymer layer of tacky pressure-sensitive adhesive, and a third polymer layer having a glass transition temperature of at least 5 °C. such that the bond formed between the second and third layers includes a peelable resealable interface.

[0013] The films of the present invention comprise a first polymer layer of a homopolymer or copolymer selected from the group consisting of polyolefin, ionomer or blends thereof, and more preferably, ionomer, polyethylene, polypropylene, polybutylene or blends thereof.

[0014] Preferably, the films of the present invention may comprise a second polymer layer of a pressure-sensitive adhesive comprising a tackifier first component any an elastomer second component of Styrene/rubber copolymer.

[0015] Preferably, the films of the present invention may comprise a third polymer layer which includes a material selected from the group consisting of ethylene/vinyl alcohol copolymer, polyester, polyketone, polystyrene, acrylic ester-based polymer, cyclic olefin copolymers, methylpentene homopolymer or copolymer, polyamide, and blends thereof,

[0016] Preferably, the films of the present invention may include a first polymer layer, a second polymer layer and a third polymer layer as described hereinabove and further comprise a fourth polymer layer comprising an anhydride-modified polyolefin, and a fifth polymer layer comprising a material selected from the group consisting of polyolefin, polyester, polyamide and blends thereof.

[0017] Furthermore - according to a second aspect of the present invention - the present invention provides peelable resealable packages formed of a multilayer thermoplastic film structure as set forth above in connection with the first aspect of the invention. Preferably, the films may be thermoformable or non-thermoformable such that they may be suitable for use as a lidding portion, a semi-rigid or rigid preformed tray portion, or both the lidding and tray portions of a container. Films according to the present invention may form peelable reclosable packages or a portion thereof by heat sealing together two exterior film surfaces of a single film, the exterior surface of the one film to an exterior surface of a second compositionally identical film, or the exterior surface of one film to the exterior surface of a compositionally different thermoplastic film.

Fig. 1 shows a diagrammatic cross-sectional view of a multilayer film having three polymer layers according to the present disclosure.

Fig. 2 shows a diagrammatic a cross-sectional view of a multilayer film having three polymer layers according to the present disclosure which is heat-sealed to a second thermoplastic and having a peelable resealable interface in a partially opened state.

Fig. 3 shows a diagrammatic cross-sectional view of a multilayer film having five layers according to the present disclosure.

Fig. 4 shows a diagrammatic cross-sectional view of a multilayer film having seven layers according to the present disclosure.

Fig. 5 shows a diagrammatic a cross-sectional view of a multilayer structure having three layers according to the present disclosure, in the form of a lidding sheet on a preformed container, in an opened state.

[0018] As used herein, the term "film" is use in the generic to include plastic web, regardless of whether it is a film or sheet.

[0019] As used herein, the term "thermoplastic" refers to a polymer or polymer mixture that softens when exposed to heat and then returns to its original condition when cooled to room temperature. In general, thermoplastic materials include, but are not limited to, synthetic polymers such as polyolefins, polyesters, polyamides, polystyrenes, and the like. Thermoplastic materials may also include any synthetic polymer that is cross-linked by either radiation or chemical reaction during the manufacturing or post manufacturing process operation.

[0020] As used herein, the term "polymer" refers to a material which is the product of a polymerization or copolymerization reaction of natural, synthetic, or natural and synthetic monomers and/or comonomers, and is inclusive of homopolymers, copolymers, terpolymers, etc. In general, the layers of a film of the present invention may comprise a single polymer, a mixture of a single polymer and non-polymeric material, a combination of two or more polymer materials blended together, or a mixture of a blend of two or more polymer materials and non-polymeric material. It will be noted that many polymers may be synthesized by the mutual reaction of complementary monomers. It will also be noted that some polymers are obtained by the chemical modification of other polymers such that the structure of the macromolecules

that constitute the resulting polymer can be thought of as having been formed by the homopolymerization of a hypothetical monomer.

[0021] As used herein, the term "copolymer" refers to a polymer product obtained by the polymerization reaction or copolymerization of at least two monomer species. Copolymer may also be referred to as bipolymers. The term "copolymer" is also inclusive of the polymerization reaction of three, four or more monomer species having reaction products referred to terpolymers, quaterpolymers, etc. As used herein, a copolymer identified in terms of a plurality of monomers, e.g., ethylene/propylene copolymer, refers to a copolymer in which either monomer may copolymerize in a higher weight or molar percent than the other monomer or monomers. It is appreciated by a person of ordinary skill in the art that the term "copolymer," as used herein, refers to those copolymers where the first listed comonomer is polymerized in a higher weight percent than the second listed comonomer.

[0022] As used herein, terminology employing a "/" with respect to the chemical identity of any copolymer, e.g., an ethylene/unsaturated ester copolymer, identifies the comonomers which are copolymerized to produce the copolymer.

[0023] As used herein, the phrase "polyolefin" refers to homopolymers and copolymers having a methylene linkage between monomer units which may be formed by any method known to a person of ordinary skill in the art. An example of a polyolefin includes polyethylene (PE) which includes, but is not limited to, low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), very low-density polyethylene (VLDPE), ultra low-density polyethylene (ULDPE), medium-density polyethylene (MDPE), high-density polyethylene (HDPE), ultra high-density polyethylene (UHDPE), and polyethylenes comprising ethylene/ α -olefin copolymers (E/AO). These ethylene/ α -olefin copolymers are copolymers of ethylene with one or more α -olefins (alpha-olefins) such as butene-1, hexene-1, octene-1, or the like as a comonomer. Other examples of polyolefin include cyclic olefin copolymers (COC), ethylene/propylene copolymers (PEP), polypropylene (PP), propylene/ethylene copolymer (PPE), polyisoprene, polybutylene (PB), polybutene-1, poly-3-methylbutene-1, poly-4-methylpentene-1, and propylene/ α -olefins (P/AO) which are copolymers of propylene with one or more α -olefins (alpha-olefins) such as butene-1, hexene-1, octene-1, or the like as a comonomer. Exemplary of commercially available polyethylenes suitable for use in the present invention include, but are not limited to, the linear low-density polyethylene family of resins supplied by ExxonMobil Chemical Company, Houston, Texas, U.S.A. A particularly suitable grade includes, but is not limited to, for example, ExxonMobil ESCORENE[®] LLDPE LL1001.32 having a melt index of 1.0 dg/min., a density of 0.918 g/cm³, and a melting point of 121 °C. An example of a commercially available polypropylene suitable for use in the present invention is sold under the trademark BP Amoco ACCLEAR[®] 6219 from Innovene, Chicago, Illinois, U.S.A. Exemplary of commercially available cyclic olefin copolymers suitable for use in the present invention include, but are not limited to, the TOPAS[®] family of resins, e.g., TOPAS[®] 8007 grade having a glass transition temperature of 80 °C., a tensile strength of 9600 psi, and a tensile modulus of 377,000 psi, which is supplied by Celanese-Ticona, Summit, New Jersey, U.S.A.

[0024] As used herein, the phrase "modified polyolefin", refers to a chemical derivative of a polyolefin, e.g., a polyolefin having any form of anhydride functionality, such as anhydride of maleic acid, crotonic acid, citraconic acid, itaconic acid, fumaric acid, etc., whether grafted onto a polymer, copolymerized with a polymer, or blended with one or more polymers. Exemplary of commercially available anhydride-modified polyolefins suitable for use in the present invention include, but are not limited to, the BYNEL[®] family of resins, e.g., BYNEL[®] 41E687 grade having melt index of 1.7 dg/min. (at 190 °C.), a density of 0.91 g/cm³, a melting point of 119 °C., which is supplied by du Pont de Nemours and Company, Wilmington, Delaware, U.S.A.

[0025] As used herein, the term "ionomer" refers to an ionic copolymer formed from an olefin and an ethylenically unsaturated monocarboxylic acid having the carboxylic acid moieties partially neutralized by a metal ion. Suitable metal ions may include, but are not limited to, potassium, lithium, caesium, nickel, zinc and preferably sodium. Suitable carboxylic acid comonomers may include, but are not limited to, ethylene/methacrylic acid, methylene succinic acid, maleic anhydride, vinyl acetate/methacrylic acid, methyl/methacrylate/methacrylic acid, styrene/methacrylic acid and combinations thereof. Useful ionomer resins may include an olefinic content of at least 50 % (mol.) based upon the copolymer and a carboxylic acid content of between 5-25 % (mol.) based upon the copolymer. Useful ionomers are also described in U.S. Patent No. 3,355,319 to Rees, which is incorporated herein by reference in its entirety. Exemplary of commercially available ionomers suitable for use in the present invention include, but are not limited to, the SURLYN[®] family of resins, e.g., SURLYN[®] 1601 grade having a density of 0.940 g/cm³, a melt flow index of 1.30 dg/min. (at 190 °C.), a Vicat softening point of 73.9 °C., which is supplied by du Pont de Nemours and Company, Wilmington, Delaware, U.S.A.

[0026] The phrase "glass transition temperature" as used herein means the temperature at which a polymer changes from an amorphous glassy state to a rubbery state, and in the transition region, various properties such as an elastic modulus, an expansion coefficient, a heat content, a refractive index, a dielectric constant, and so forth, are changed. The glass transition temperature can be measured from the change of these properties, but more definitely, this can be evaluated by a known method by using differential scanning calorimetry (DSC) or dynamic mechanical analysis (DMA). When measuring the glass transition temperature by the differential scanning calorimetry, the glass transition temperature can be determined by ASTM D-3417 test method, which is incorporated herein by reference. Alternatively, ASTM E-1640-04 test method may be used to determine the glass transition temperature by dynamic mechanical analysis, the

disclosure of which is incorporated herein by reference.

[0027] As used herein, the terms "coextruded" or "coextrusion" refer to the process of extruding two or more polymer materials through a single die with two or more orifices arranged so that the extrudates merge and weld together into a laminar structure before chilling, i.e., quenching. The films according to the present invention may be fabricated by any coextrusion method known to a person of ordinary skill in the art which may include, but is not limited to, for example, blown film coextrusion, slot cast coextrusion, and extrusion coating, preferably, slot cast and single-bubble blown film, and more preferably, single-bubble blown film.

[0028] As used herein, the phrase "interior film layer," as applied to film of the present invention, refers to any film layer having both its principal surfaces directly adhered to another layer of the film. In contrast, the phrase "exterior film layer" refers to any film layer having less than two of its principal surfaces directly adhered to another layer of the film.

[0029] As used herein, the phrase "direct contact and bonded" as applied to film layers of the present invention, defines a subject film layer having face-to-face contact to another film layer (presumably, over their entire planar surfaces).

[0030] As used herein, the term "heat-seal" refers to both a film layer which is heat sealable to itself or other thermoplastic film layer, and the formation of a fusion bond between two polymer surfaces by conventional indirect heating means. It will be appreciated that conventional indirect heating generates sufficient heat on at least one film contact surface for conduction to the contiguous film contact surface such that the formation of a bond interface therebetween is achieved without loss of the film integrity.

[0031] As used herein, the phrase "ethylene/vinyl alcohol copolymer" refers to hydrolyzed copolymers of ethylene and vinyl acetate monomers. Ethylene/vinyl alcohol copolymers can be represented by the general formula: $[(CH_2-CH_2)_m-(CH_2-CH(OH))_n]$. Exemplary of commercially available ethylene/vinyl alcohol copolymers suitable for use in the present invention include, but are not limited to, the SOARNOL[®] family of resins, e.g., SOARNOL[®] ET3803 grade having a reported bulk density of 0.64-0.74 g/cm³, a relative density of 1.13-1.22 g/cm³, a melting point of 164-188° C., which may be obtained from The Nippon Synthetic Chemical Industry Company, Ltd. (Nippon Gohsei), Osaka, Japan.

[0032] As used herein, the term "polyester" refers to homopolymers or copolymers having an ester linkage between monomer units which may be formed, for example, by condensation polymerization reactions between a dicarboxylic acid and a diol. The ester linkage can be represented by the general formula: $[R-C(O)O-R']_n$ where R and R' = the same or different alkyl group and may be generally formed from the polymerization of dicarboxylic acid and diol monomers or monomers containing both carboxylic acid and hydroxyl moieties. The dicarboxylic acid may be linear or aliphatic, i.e., lactic acid, oxalic acid, maleic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, and the like; or may be aromatic or alkyl substituted aromatic, i.e., various isomers of phthalic acid, such as paraphthalic acid (or terephthalic acid), isophthalic acid and naphthalic acid. Specific examples of alkyl substituted aromatic acids include the various isomers of dimethylphthalic acid, such as dimethylisophthalic acid, dimethylorthophthalic acid, dimethylterephthalic acid, the various isomers of diethylphthalic acid, such as diethylisophthalic acid, diethylorthophthalic acid, the various isomers of dimethylnaphthalic acid, such as 2,6-dimethylnaphthalic acid and 2,5-dimethylnaphthalic acid, and the various isomers of diethylnaphthalic acid. The glycols may be straight-chained or branched. Specific examples include ethylene glycol, propylene glycol, trimethylene glycol, 1,4-butane diol, neopentyl glycol and the like. The polyalkyl terephthalates are aromatic esters having a benzene ring with ester linkages at the 1,4-carbons of the benzene ring as compared to polyalkyl isophthalate, where two ester linkages are present at the 1,3-carbons of the benzene ring. In contrast, polyalkyl naphthalate are aromatic esters having two fused benzene rings where the two ester linkages may be present at the 2,3-carbons or the 1,6-carbons. Exemplary of commercially available polyethylene terephthalates suitable for use in the present invention include, but are not limited to, the EASTAPAK[®], EASTPAK[®] and EASTAR[®] families of resins which are all supplied from Eastman Chemical Company, Kingsport, Tennessee, U.S.A. A particularly suitable grade of the EASTAR[®] polyethylene terephthalate is EASTAR[®] 6763 polyethylene terephthalate copolymer, which is a copolymer formed from terephthalic acid, ethylene glycol and cyclohexane dimethanol, and has glass transition temperature of 80 °C., a tensile modulus of 300,000 psi, a flexural modulus of 300,000 psi, and a reported density of about 1.27 g/cm³.

[0033] As used herein, the term "polyamide" refers to homopolymers or copolymers having an amide linkage between monomer units which may be formed by any method known to those skilled in the art. The amide linkage can be represented by the general formula: $[R-C(O)N-R']_n$ where R and R' = the same or different alkyl group. Useful polyamide homopolymers include nylon 6 (polycaprolactam), nylon 11 (polyundecanolactam), nylon 12 (polyaurylactam), and the like. Other useful polyamide homopolymers also include nylon 4,2 (polytetramethylene ethylenediamide), nylon 4,6 (polytetramethylene adipamide), nylon 6,6 (polyhexamethylene adipamide), nylon 6,9 (polyhexamethylene azelamide), nylon 6,10 (polyhexamethylene sebacamide), nylon 6,12 (polyhexamethylene dodecanediamide), nylon 7,7 (polyheptamethylene pimelamide), nylon 8,8 (polyoctamethylene suberamide), nylon 9,9 (polynonylamine azelamide), nylon 10,9 (polydecamethylene azelamide), nylon 12,12 (polydodecamethylene dodecanediamide), and the like. Useful polyamide copolymers include nylon 6,6/6 copolymer (polyhexamethylene adipamide/caprolactam copolymer), nylon 6,6/9 copolymer (polyhexamethylene adipamide/azelamide copolymer), nylon 6/6,6 copolymer (polycaprolactam/hexamethylene adipamide copolymer), nylon 6,2/6,2 copolymer (polyhexamethylene ethylenediamide/hexamethylene ethylen-

ediamide copolymer), nylon 6,6/6,9/6 copolymer (polyhexamethylene adipamide/hexamethylene azelaamide/caprolactam copolymer), as well as other nylons which are not particularly delineated here. Exemplary of even more suitable polyamides include nylon 4,I, nylon 6,1, nylon 6,6/6I copolymer, nylon 6,6/6T copolymer, MXD6 (poly-m-xylylene adipamide), nylon 6T/6I copolymer, nylon 6/MXDT/I copolymer, nylon MXDI, poly-p-xylylene adipamide, polyhexamethylene terephthalamide, polydodecamethylene terephthalamide and the like. The generic source-based nomenclature convention is used to name the hereinabove nylon polymers and copolymers. See "Generic Source-Based Nomenclature for Polymers," Pure Applied Chemistry, Vol. 73, No. 9, pp. 1511-1519 (International Union of Pure and Applied Chemistry 2001). Exemplary of commercially available polyamides suitable for use in the present invention include, but are not limited to, the ULTRAMID® family of resins supplied by BASF, Mount Olive, New Jersey, U.S.A. and ZYTEL® family of resins provided by du Pont de Nemours and Company, Wilmington, Delaware, U.S.A. A particularly suitable grade of the ULTRAMID® polyamide includes ULTRAMID® B36 nylon 6 having a glass transition temperature of 127 °C., a density of 1.13 g/cm³, and tensile strength (at yield) of 131,000 psi.

[0034] As used herein, the term "acrylic ester" refers to acrylate-functional homopolymers and copolymers which can be represented by the general formula: $[C(R)(C(O)OCH_3)CH_2]_n$ where R is an alkyl group, such as, but not limited to, for example, methyl, ethyl, butyl and 2-ethylhexyl. Exemplary of commercially available acrylic ester-based polymer suitable for use in the present invention include, but are not limited to, the PERSPEX® family of resins having tensile strength of at least 7800 psi, a flexural modulus of at least 400,000 psi which are supplied by Lucite International, Ltd., Southampton, U.K.

[0035] As used herein, the term "polyketone" refers to homopolymers and copolymers having at least one ketone linkage between monomer units which may be formed by any method known to those skilled in the art. The ketone linkage can be represented by the general formula: $[R-C(O)-R']_n$ where R and R' = the same or different alkyl group. Exemplary of formerly commercially available polyketones suitable for use in the present invention include, but are not limited to, the CAR-ILON® family of resins having a flexural modulus of about 240,000 psi which are supplied by Shell Chemical Company, Houston, Texas, U.S.A.

[0036] As used herein, the term "methylpentene" refers to polyolefin homopolymers and copolymers derived from 4-methylpentene-1. These polymers can be represented by the general formula: $[CH(CH_2(CH_3)_2-CH_2)]_n$. Exemplary of commercially available methylpentene suitable for use in the present invention include, but are not limited to, the TPX® family of resins which are supplied by Mitsui Petrochemical Industries, Ltd., Tokyo, Japan.

[0037] As used herein, the term "polystyrene" refers to homopolymers and copolymers having at least one styrene monomer (benzene, i.e., C₆H₅, having an ethylene substituent) linkage within the repeating backbone of the polymer. The styrene linkage can be represented by the general formula: $[(C_6R_5)CH_2CH_2]_n$ where R = H or an alkyl group. Polystyrene may be formed by any method known to those skilled in the art. Suitable polystyrene include, for example, but are not limited to, oriented polystyrene (OPS) film and resins, i.e., polystyrene (PS), syndiotactic polystyrene (SPS), acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN), ethylene/styrene copolymers, styrene/acrylic copolymers, styrene block copolymers (SBC), and the like. Exemplary of commercially available polystyrenes suitable for use in the present invention include, but are not limited to, POLYSTYRENE® 535 having a tensile modulus of 430,000, a flexural modulus of 450,000 which is supplied by Total Petrochemicals USA, Inc., Houston, Texas, U.S.A.

[0038] As used herein, the phrase "tacky pressure-sensitive adhesive" refers to adhesives which may be used to affix the surface of one film layer to the surface of another film layer with application of manual pressure. Preferably, the tacky pressure-sensitive adhesive may also allow one surface to be removed and/or repositioned from the other surface. Pressure-sensitive adhesives may include a combination of a tackifier first component and an elastomer second component of rubber, acrylic, silicone, or blends thereof. These pressure-sensitive adhesives are known in the art and are described in U.S. Patent Nos. 4,673,601 and 5,089,320, which are incorporated herein by reference in their entireties. Preferably, the pressure-sensitive adhesive may comprises both a tackifier and an elastomer of styrene/rubber copolymer. A particular suitable tacky pressure-sensitive adhesive for use in the present invention includes, but is not limited to, for example, a material having a density of 0.96 g/cm³ which is sold under the product name FINDLEY® M3156 from Bostik Findley, Inc., Wauwatosa, Wisconsin, U.S.A.

[0039] As used herein, the phrase "styrene/rubber copolymer" refers to block copolymers including di-block, tri-block, radial block, multi-block and mixtures thereof of styrene and rubber. Suitable rubber segment of styrene/rubber copolymers may include, but are not limited to, butadiene, isoprene, butylene, ethylenebutylene, propylene, ethylene-propylene, ethylene and blends thereof. Exemplary styrene/rubber copolymers which are commercially available include styrene/rubber copolymers sold under the trademark KRATON® by Kraton Polymers, Houston, Texas, U.S.A. Styrene/rubber copolymers are fully disclosed in U.S. Patent No. 5,221,534, the disclosure of which is incorporated herein by reference. As used herein, the term "tackifier" is generally an adhesive additive which serves to modify the rheological properties of the final adhesive. Specifically, a tackifier resin is used to improve the tack of the adhesive composition. As used herein, the term "tack" refers to the "stickiness" of the adhesive or its resistance to removal or deformation from a substrate. The tackifier may comprise any suitable material, preferably, a hydrocarbon resin material or mixtures thereof. Exemplary tackifiers are ESCOREZ® 1102, ESCOREZ® 1304, ES-COREZ® 1315, available from ExxonMobil

Chemical Company, Houston, Texas, U.S.A.; WINGTAK® resins available from Sartomer Company, Inc., Exton, Pennsylvania, U.S.A.; PICCOTAC® 1100 and POLYPAL® 100 available from Eastman Chemicals, Kingsport, Tennessee, U.S.A.

[0040] As used herein, the phrase "peel strength" refers to the force required to separate at least a portion of the interface between two adjoining interior film layers of the present invention when the film has been sealed to a second thermoplastic film. The peel strength may depend on the chemical similarity or dissimilarity of the two film layers and their individual thickness. Peel strength may also be affected by the composition and thickness of adjacent film layers which are ruptured during the separation of the interface. Peel strength may still further be affected by environmental conditions during film fabrication, the packaging process and whether there has been an initial separation of the interface and the number of times the interface has been separated and resealed. One method for determining bond strength is ASTM F-904 test method entitled, "Standard Test Method for Comparison of Bond Strength or Ply Adhesion of Similar Laminates Made from Flexible Materials" and published by ASTM International, West Conshohocken, Pennsylvania, U.S.A., which is herein incorporated by reference in its entirety. As referred to film structures of the present invention, peel strengths were determined in accordance with ASTM F-904 test method and included a modification to the test procedure. The modification entailed preparing test specimens by heat-sealing the surface of the subject film along its entire length to a second thermoplastic film with an end-portion of the subject film unsealed to the second film. With the test specimens prepared in this manner, the unsealed end-portion of the subject film was then peeled from the second film at an angle of at least 180° relative to the second film.

[0041] With reference to the drawings, there is seen in FIG. 1 a peelable resealable multilayer film 10 having a first polymer layer 11, a second polymer layer 12 of pressure-sensitive adhesive, and a third polymer layer 13. As depicted, second polymer layer 12 is in direct contact and bonded to both first polymer layer 11 and third layer 13. The bond formed between polymer layers 12 and 13 creates a peelable resealable interface 100 therebetween. The force required to separate peelable resealable interface 100 may vary depending upon the individual chemical composition and thickness of both second and third polymer layers 12 and 13. It has been discovered that peelable resealable interface 100 may be formed by bonding second polymer layer 12 of pressure-sensitive adhesive to a third polymer layer 13, preferably, when a third polymer layer 13 comprises a material having a glass transition temperature of at least 5 °C., and more preferably, when a third polymer layer 13 comprises a material having a glass transition temperature of at least 5 °C. which is selected from the group consisting of ethylene/vinyl alcohol copolymer, polyester, polyketone, polystyrene, acrylic ester polymer, cyclic olefin copolymers, methylpentene copolymers, polyamide, and blends thereof. It will be noted that the force required to separate the interface formed by the bond between first polymer layer 11 and second polymer layer 12 is greater than the force needed to separate peelable resealable interface 100. It will be appreciated that first polymer layer 11 may comprise any material which bonds to second polymer layer 12 and provides an interface therebetween exhibiting a peel strength which is greater than peelable resealable interface 100. It has been also discovered that when first polymer layer 11 comprises a homopolymer or copolymer selected from the group consisting of polyolefin, ionomer or blends thereof, and preferably, ionomer, polyethylene, polypropylene, polybutylene or blends thereof, and is bonded to second polymer layer 12 of a pressure-sensitive adhesive, the interface formed therebetween may have a peel strength which is greater than peelable resealable interface 100. It will be also appreciated by those skilled in the art that film 10 may be formed as a unitary three-layer film structure or a three-layer substructure of a film having 4-7 or more film layers. It will be still further appreciated that film 10 may be formed by coextrusion of three separate polymer layers using either cast slot or blown film coextrusion methods.

[0042] In FIG. 2, peelable resealable multilayer film 10 is shown heat-sealed to a second thermoplastic film 400 and partially separated from film 400. FIG. 2 also illustrates peelable resealable interface 100 (see FIG. 1) in the partially open state. It will be appreciated that the film 10 may seal to itself or a second thermoplastic film structure by any chemical, thermal, or surface modification technique known to those skilled in the art. It will be also noted that the force required for separating the interface between film 10 and second thermoplastic film 400 is greater than the force required for separating peelable resealable interface 100. It will be further appreciated that the force required for separating peelable resealable interface 100 may be weaker after the interface 100 is initially separated and resealed to itself.

[0043] Turning now to FIG. 3, there is shown a five-layer peelable resealable multilayer film 20 having first polymer layer 21, second polymer layer 22, third polymer layer 23, fourth polymer layer 24, and fifth polymer layer 25. First, second and third polymer layers 21, 22 and 23 correspond to and may be selected according to the disclosure of the first through third polymer layers 11-13 of multilayer film 10 above. Fourth polymer layer 24 may comprise any suitable resin which will adhere third polymer layer 23 to fifth polymer layer 25. Preferably fourth polymer layer 24 includes an adhesive and more preferably, an anhydride-modified polyolefin. Fifth polymer layer 25 may comprise any polymer resin which can function as an exterior film layer, and preferably, is a material selected from the group consisting of polyolefin, polyester, polyamide and blends thereof. FIG. 3 also illustrates peelable resealable interface 200 in the closed state, with interface 200 being formed by the bond between polymer layers 22 and 23. Peelable resealable interface 200 may have the same interfacial peel strengths as peelable resealable interface 100 of film 10 in FIG. 2. It will be also appreciated that film 20 may be formed by coextrusion of five separate polymer layers using either slot cast or blown film coextrusion

methods, preferably single-bubble blown film coextrusion methods. It will be also appreciated by those skilled in the art that film 20 may be alternatively formed by coextrusion of seven polymer layers as described in film 30, hereinbelow.

[0044] In FIG. 4, there is shown a seven-layer peelable resealable multilayer film 30 having first polymer layer 31, second polymer layer 32, third polymer layer 33, fourth polymer layer 34, and fifth polymer layer 35, a sixth polymer layer 36, and a seventh polymer layer 37. First, third, fourth, fifth and seventh polymer layers 31, 33, 34, and 37 of film 30 may correspond to and be selected according to the disclosure of the first, second, third, fourth and fifth polymer layers 21, 22, 23, 24 and 25 of multilayer film 20 (see FIG. 3), respectively. In film 30, second polymer layer 32 may have an identical chemical composition as that of third polymer layer 33, and be disposed between first and third polymer layers 31 and 33. Sixth polymer layer 36 may have an identical chemical composition as that of seventh polymer layer 37 and be disposed between fifth and seventh polymer layers 35 and 37. As depicted, polymer layer 32 is in direct contact with and bonded to polymer layer 33, and polymer layer 36 is in direct contact with and bonded to polymer layer 37. Also illustrated in FIG. 4 is peelable resealable interface 300 which forms by the bond between second polymer layer 32 and third polymer layer 33. It will be appreciated that peelable resealable interface 300 may have interfacial peel strengths as that described for peelable resealable interfaces 100 of films 10 (see FIG. 2) and 200 of film 20 (see FIG. 3). It will be also appreciated by those skilled in the art that film 30 may be formed by coextrusion of seven separate polymer layers using either slot cast or blown film coextrusion methods, preferably single-bubble blown film coextrusion methods.

[0045] Turning now to FIG. 5, there is shown film 10 (see FIG. 1) in the form of a packaging lid 500 removed from a container 510. Container 510 may be formed from a second thermoplastic film 600 and may include a top opening 520 and a substantially flat peripheral rim 530 around the opening 520. It will be appreciated that film 10 may be heat-sealed and bonded to film 600 around the circumference of rim 530 and conform to the shape of opening 520. As depicted in FIG. 5, first and second polymer layers 11 and 12 remain sealed to container 510 in the area of the rim 530, and fractures such that the peel failure propagates internally from the interface between first polymer layer 11 and second film 600 to interface 100 (see FIGS. 1 and 2).

[0046] Preferably, multilayer films 10, 20 and 30 are non-oriented films such that each film has a heat shrinkage value of less than about 5 % at 90 °C., more preferably less than about 2 % at 90 °C. as measured in accordance with ASTM D-2732-96 test method. Heat shrinkage test is defined to be values obtained by measuring unrestrained shrink at 90 °C. for five seconds. Four test specimens are cut to 10 cm. in the machine direction by 10 cm. in the transverse direction. Each specimen is completely immersed for 5 seconds in a 90 °C. water bath (or other specified non-reactive liquid). The distance between the ends of the shrunken specimen is measured. The difference in the measured distance for the shrunken specimen and the original 10 cm. is multiplied by ten to obtain the percent of shrinkage for the specimen for each direction. The machine direction shrinkage for the four specimens is averaged for the machine direction shrinkage value of the given film sample, and the transverse direction shrinkage for the four specimens is averaged for the transverse direction shrinkage value.

[0047] Small amounts of additives, such as slip or anti-block agents, pigments and other processing aids, can be included in any of the layers in the peelable resealable multilayer films 10, 20 and 30 or in any layers further added to the structure which may be formed into a flexible film. Similarly, such additives may also be included in any of the layers discussed above in connection with peelable resealable multilayer film structures 10, 20 and 30 illustrated in FIGS. 1-5.

[0048] The disclosure will now be further described in the following non-limiting examples.

[0049] In the following examples, all film structures are produced using a single-bubble coextrusion apparatus and method. The single-bubble blown film apparatus includes a multi-manifold annular die head for blown bubble film through which the film composition is forced and formed into a cylindrical tube or bubble. The bubble is immediately quenched, e.g., via cooled water bath, solid surface and/or air, and then ultimately collapsed and formed into a film.

Example 1

[0050] The following resins were coextruded in the following structural relationship in accordance with film 30 of FIG. 4:

Layer 31: first polymer layer comprised 60.00 % (wt.) of low-density polyethylene having a density of 0.921 g/cm³, a melt index of 1.8 dg/min., a melting point of 109 °C., available under the trademark PETROTHENE® NA 345-013 from Lyondell (Equistar) Chemical Company, Houston, Texas, U.S.A., 10.00 % (wt.) cyclic olefin copolymer having a glass transition temperature of 136 °C., which is sold under the trademark TOPAS® 5013S-04 by Celanese-Ticona, Summit, New Jersey, U.S.A., 20.00 % (wt.) of linear low-density polyethylene having a density of 0.920 g/cm³, a melt index of 1.0 dg/min., a melting point of 122 °C., available under the trademark DOWLEX® 2045G from The Dow Chemical Company, Midland, Michigan, U.S.A., 10.00 % (wt.) of processing, antiblock and slip additives, and provided 10.0 % of the total weight of multilayer film 30;

Layer 32: second polymer layer comprised 100 % (wt.) pressure-sensitive adhesive available under the product

name FINDLEY® M3156 from Bostik Findley, Inc., Wauwatosa, Wisconsin, U.S.A., and provided 20.0 % of the total weight of multilayer film 30;

Layer 33: third polymer layer comprised 100 % (wt.) pressure-sensitive adhesive available under the product name FINDLEY® M3156 from Bostik Findley, Inc., Wauwatosa, Wisconsin, U.S.A., and provided 10.0 % of the total weight of multilayer film 30;

Layer 34: fourth layer comprised 100 % (wt.) of ethylene/vinyl alcohol copolymer having density of 1.17 g/cm³, a melt index of 1.7 dg/min. (at 190 °C.), a melting point of 172 °C., a glass transition temperature of 53 °C., which is available under the trademark EVAL® H171 from Kuraray Company, LTD, Tokyo, Japan, and provided 10.1 % of the total weight of multilayer film 30;

Layer 35: fifth layer comprised 100 % (wt.) anhydride-modified polyolefin polyethylene having a density of 0.916 g/cm³, a melt index of 1.1 dg/min., a Vicat softening point of 103 °C., available under the trademark PLEXAR® PX3084 from Lyondell (Equistar) Chemical Company, Houston, Texas, U.S.A. and provided 4.9 % of the total weight of multilayer film 30;

Layer 36: sixth polymer layer comprised of 47.35 % (wt.) butene linear low-density polyethylene having a density of 0.918 g/cm³, a melt index 1.0 dg/min and sold under the trademark NOVAPOL® PF-0118-F from Nova Chemicals, Inc. Moon Township, Pennsylvania, U.S.A., 47.35 % (wt.) ethylene/vinyl acetate copolymer having a density of 0.93 g/cm³, a melt index of 0.35 dg/min and sold under the trademark DUPONT™ ELVAX® 3135XZ from by du Pont de Nemours and Company, Wilmington, Delaware, U.S.A., 5.3 % (wt.) processing, antiblock and slip additives, and provided 24.8 % of the total weight of multilayer film 30;

Layer 37: seventh polymer layer comprised 47.35 % (wt.) butene linear low-density polyethylene having a density of 0.918 g/cm³, a melt index 1.0 dg/min and sold under the trademark NOVAPOL® PF-0118-F from Nova Chemicals, Inc., Moon Township, Pennsylvania, U.S.A., 47.35 % (wt.) ethylene/vinyl acetate copolymer having a density of 0.93 g/cm³, a melt index of 0.35 dg/min and sold under the trademark DUPONT™ ELVAX® 3135XZ from by du Pont de Nemours and Company, Wilmington, Delaware, U.S.A., 5.3 % (wt.) processing, antiblock and slip additives, and provided 20.2 % of the total weight of multilayer film 30. The film described in Example 1 had a thickness of approximately 2.75 mils.

Example 2

[0051] In Example 2, the resins were coextruded in the following structural relationship in accordance with FIG. 4. The film layers were identical in chemical composition and weight as described in Example 1, but with the following exceptions:

Layer 31: first polymer layer comprised 67.00 % (wt.) of low-density polyethylene having a density of 0.923 g/cm³, a melt index of 2.6 dg/min., a melting point of 113 °C., available under the trademark DOW POLYETHYLENE® 608A from The Dow Chemical Company, Midland, Michigan, U.S.A., 18.00 % (wt.) of linear low-density polyethylene having a density of 0.926, a melt index of 0.6 dg/min. which is sold under the product name VORIDIAN® SC74580 from Eastman Chemical Company, Kingsport, Tennessee, U.S.A., 10.00 % (wt.) cyclic olefin copolymer having a glass transition temperature of 80 °C., sold under the trademark TOPAS® 8007 by Celanese-Ticona, Summit, New Jersey, U.S.A., 5.00 % (wt.) of processing, antiblock and slip additives, and provided 10.0 % of the total weight of multilayer film 30;

Layers 32, 33 and 37 provided 17.0 %, 8.00 % and 31.20 %, respectively, of the total weight of the multilayer film 30. The film described in Example 2 had a thickness of approximately 2.31 mils.

Example 3

[0052] In Example 3, the resins were coextruded in the following structural relationship in accordance with FIG. 4. The film layers were identical in chemical composition and weight as described in Example 2, but with the following exceptions:

Layer 31: first polymer layer comprised 60.00 % (wt.) of low-density polyethylene having a density of 0.923 g/cm³, a melt index of 2.6 dg/min., a melting point of 113 °C., available under the trademark DOW POLYETHYLENE® 608A from The Dow Chemical Company, Midland, Michigan, U.S.A., 30.00 % (wt.) of linear low-density polyethylene having a density of 0.926, a melt index of 0.6 dg/min. which is sold under the product name VORIDIAN® SC74580

from Eastman Chemical Company, Kingsport, Tennessee, U.S.A., 5.00 % (wt.) cyclic olefin copolymer having a glass transition temperature of 80 °C., sold under the trademark TOPAS® 8007 by Celanese-Ticona, Summit, New Jersey, U.S.A., 5.00 % (wt.) of processing, antiblock and slip additives, and provided 10.0 % of the total weight of multilayer film 30;

Layers 32, 33 and 37 provided 15.00 %, 5.00 %, and 36.2 %, respectively, of the total weight of the multilayer film 30. The film described in Example 3 had a thickness of approximately 2.75 mils.

Example 4

[0053] In Example 4, the resins were coextruded in the following structural relationship in accordance with FIG. 4. The film layers were identical in chemical composition and weight as described in Example 2, but with the following exceptions:

Layers 32, 33 and 37 provided 17 %, 8.00 % and 31.20 %, respectively, of the total weight of the multilayer film 30. The film described in Example 4 had a thickness of approximately 2.75 mils.

Example 5

[0054] In Example 5, the resins were coextruded in the following structural relationship in accordance with FIG. 4. The film layers were identical in chemical composition and weight as described in Example 2, but with the following exceptions:

Layer 31: first polymer layer comprised 72.00 % (wt.) of low-density polyethylene having a density of 0.923 g/cm³, a melt index of 2.6 dg/min., a melting point of 113 °C., available under the trademark DOW POLYETHYLENE® 608A from The Dow Chemical Company, Midland, Michigan, U.S.A., 20.00 % (wt.) of linear low-density polyethylene having a density of 0.926, a melt index of 0.6 dg/min. which is sold under the product name VORIDIAN® SC74580 from Eastman Chemical Company, Kingsport, Tennessee, U.S.A., 5.00 % (wt.) cyclic olefin copolymer having a glass transition temperature of 80 °C., sold under the trademark TOPAS® 8007 by Celanese-Ticona, Summit, New Jersey, U.S.A., 3.00 % (wt.) of processing, antiblock and slip additives, and provided 9.0 % of the total weight of multilayer film 30. The film described in Example 5 had a thickness of approximately 2.75 mils.

Example 6

[0055] In Example 6, the resins were coextruded in the following structural relationship in accordance with FIG. 4. The film layers were identical in chemical composition and weight as described in Example 2, but with the following exceptions:

Layer 31: first polymer layer comprised 75.00 % (wt.) of low-density polyethylene having a density of 0.923 g/cm³, a melt index of 2.6 dg/min., a melting point of 113 °C., available under the trademark DOW POLYETHYLENE® 608A from The Dow Chemical Company, Midland, Michigan, U.S.A., 10.00 % (wt.) of linear low-density polyethylene having a density of 0.926, a melt index of 0.6 dg/min. which is sold under the product name VORIDIAN® SC74580 from Eastman Chemical Company, Kingsport Tennessee, U.S.A., 10.00 % (wt.) cyclic olefin copolymer having a glass transition temperature of 80 °C., sold under the trademark TOPAS® 8007 by Celanese-Ticona, Summit, New Jersey, U.S.A., 5.00 % (wt.) of processing, antiblock and slip additives, and provided 10.0 % of the total weight of the multilayer film 30;

Layers 32, 33 and 37 provided 20.0 %, 7.0 % and 29.2 %, respectively, of the total weight of the multilayer film 30. The film described in Example 6 had a thickness of approximately 2.75 mils.

[0056] Multilayer film 30 described above in Examples 1-6 was formed via a coextrusion process. The film was formed by combining different streams of melt-plastified polymers into a single structure by slot or flat cast or blown bubble coextrusion. The flat die or slot cast process includes extruding polymer streams through a flat or slot die onto a chilled roll and subsequently winding the film onto a core to form a roll of film for further processing. In the blown bubble coextrusion process, streams of melt-plastified polymers are forced through an annular die having a central mandrel to form a tubular extrudate. The tubular extrudate is preferably expanded to a desired wall thickness by a volume of air or other gas entering the hollow interior of the extrudate via the mandrel, and then rapidly cooled or quenched by any of various methods known to those of skill in the art. The peelable resealable multilayer film of the present invention may vary in thickness of between 0.5-10 mil.

[0057] Table 1 illustrates peel strengths of the peelable resealable interfacial formed between Layer 33 and Layer 34 for films described in Examples 1-6. The peel strengths were measured by heat-sealing Layer 31 of the films in Examples 1-6 to a second thermoplastic film of polyethylene at a temperature of about 149 °C, under a pressure of 30 psi and

dwel time of one second, All peel strengths were determined in accordance to ASTM F-904 test method as described herein. The initial peel strength is identified as the "1st" peel strength and indicates the peak and average values. Peel strengths measured after the first film was separated from and re-adhered to the second film are identified as "2nd", "3rd" and "4th" peel strength, respectively, and indicate the peak and average values.

TABLE 1

Film Structure	1st Peel Strength Peak/Average (gram-force/inch)	2 nd Peel Strength Peak/Average (gram-force/inch)	3 rd Peel Strength Peak/Average (gram-force/inch)	4 th Peel Strength Peak/Average (gram-force/inch)
Example 1	2101/1471	856/743	711/604	620/529
Example 2	2548/1598	771/668	651/525	571/481
Example 3	2191/1500	561/472	458/360	399/333
Example 4	2344/1848	754/626	663/530	586/470
Example 5	1789/1433	734/630	581/498	516/430
Example 6	2265/1574	765/572	715/548	574/471

[0058] Unless otherwise noted, the physical properties and performance characteristics reported herein were measured by test procedures similar to the following methods. The following ASTM test procedures are incorporated herein by reference in their entireties:

Density	ASTM D-1505
Flexural Modulus	ASTM D-790
Glass Transition Temperature	ASTM D-3417
Heat Shrinkage	ASTM D-2732-96
Melt Index	ASTM D-1238
Melting Point	ASTM D-3417
Peal Strength	ASTM F-904
Tensile Modulus	ASTM D-638
Tensile Strength	ASTM D-638
Vicat Softening Point	ASTM D-1525

[0059] While various embodiments of the disclosure are herein described, it is envisioned that those skilled in the art may devise various modifications and equivalents without departing from the spirit and scope of the disclosure. The disclosure is not intended to be limited by the foregoing detailed description.

Claims

1. A peelable resealable multilayer film comprising:

at least a first thermoplastic layer, a second thermoplastic layer and a third thermoplastic layer;
 wherein said first layer comprises a homopolymer or copolymer selected from the group consisting of polyolefin, ionomer and blends thereof;
 wherein said second layer is in direct contact with and bonded to both said first and third layers; wherein said second layer comprises a tacky pressure-sensitive adhesive;

wherein said third layer comprises a polymer having a glass transition temperature of at least 5 °C as measured in accordance with ASTM D-3418 test method; and

wherein said bond between said second and third layers comprises a peelable resealable interface having a first interfacial peel strength "A" and a second interfacial peel strength "B" such that the value of A is less than 3500 gram-force/inch (1350 newton/meter) as measured in accordance with ASTM F-904 test method when peeled from a second thermoplastic film to which said film has been heat-sealed, and the value of B is at least 330 gram-force/inch (127 newton/meter) as measured in accordance with ASTM F-904 when peeled from and resealed to said second film; wherein the relative values of A and B satisfy the relationship $A \geq B$.

2. The film according to claim 1, wherein said film is coextruded by either slot cast or blown film coextrusion.
3. The film according to claim 1 or 2, wherein said polyolefin comprises a homopolymer or copolymer selected from the group consisting of polyethylene, polypropylene, polybutylene and blends thereof.
4. The film according to claim 1 or 2, wherein said first layer comprises an ionomer or blend thereof.
5. The film according to any of claims 1 to 4, wherein said bond between said first and second layers has an interfacial peel strength of at least 1350 newton/meter (3500 gram-force/inch) as measured in accordance with ASTM F-904 test method when peeled from a second thermoplastic film to which said film has been heat-sealed.
6. The film according to any of claims 1 to 5, wherein said value of B is at least 154 newton/meter (400 gram-force/inch) as measured in accordance with ASTM F-904.
7. The film according to any of claims 1 to 6, wherein said first layer is an exterior film layer.
8. The film according to any of claims 1 to 7, wherein said tacky pressure sensitive adhesive comprises a tackifier first component and an elastomer second component of styrene/rubber copolymer.
9. The film according to any of claims 1 to 8, wherein said third layer comprises an ethylene/vinyl alcohol copolymer or blends thereof.
10. The film according to any of claims 1 to 9, wherein said third layer comprises polyester.
11. The film according to any of claims 1 to 9, wherein said third layer comprises polyamide.
12. The film according to any of claims 1 to 9, wherein said third layer comprises polystyrene.
13. The film according to any of claims 1 to 9, wherein said third layer comprises polyketone.
14. The film according to any of claims 1 to 9, wherein said third layer comprises acrylic ester-based polymer.
15. The film according to any of claims 1 to 9, wherein said third layer comprises methylpentene homopolymer or copolymer.
16. The film according to any of claims 1 to 9, wherein said third layer comprises cyclic olefin copolymer.
17. The film according to any of claims 1 to 16, wherein said film further comprises a fourth polymer layer comprising an anhydride-modified polyolefin.
18. The film according to claim 17, wherein said film further comprises a fifth polymer layer comprising a material selected from the group consisting of polyolefin, polyester, polyamide and blends thereof.
19. The film according to any of claims 1 to 18, wherein said film has a heat shrinkage value less than about 5 % in the machine direction at 90 °C and less than about 5 % in the transverse direction at 90 °C, as measured in accordance with ASTM D-2732-96 test method.
20. A packaging article having at least one member comprising a peelable resealable multi-layer film as defined in any of claims 1 to 19.

Patentansprüche

1. Abziehbare wiederverschließbare Mehrschichtfolie, aufweisend:

5 mindestens eine erste thermoplastische Schicht, eine zweite thermoplastische Schicht und eine dritte thermoplastische Schicht;
 wobei die erste Schicht ein Homopolymer oder Copolymer aufweist, ausgewählt aus der Gruppe von Polyolefinen, Ionomen und deren Mischungen;
 wobei die zweite Schicht sowohl mit der ersten als auch mit der dritten Schicht in direktem Kontakt steht und
10 verbunden ist; wobei die zweite Schicht einen klebrigen Haftkleber aufweist;
 wobei die dritte Schicht ein Polymer mit einer Glasübergangstemperatur von mindestens 5 °C, bestimmt gemäß der Testmethode nach ASTM D-3418, aufweist; und
 wobei die Verbindung bzw. Verklebung zwischen der zweiten und dritten Schicht eine abziehbare wiederversiegelbare Grenzschi-
15 cht umfasst, aufweisend eine erste Schälfestigkeit (Abziehfestigkeit) "A" und eine zweite Schälfestigkeit (Abziehfestigkeit) "B" derart, dass der Wert von A weniger als 3.500 Gramm-Pond/Inch (1.350 Newton/Meter), bestimmt gemäß der Testmethode nach ASTM F-904 beim Abziehen von einer zweiten thermoplastischen Folie, an welcher die Folie heißversiegelt ist, beträgt und der Wert von B wenigstens 330 Gramm-Pond/Inch (127 Newton/Meter), bestimmt gemäß der Testmethode nach ASTM F-904, beim Abziehen und erneutem Versiegeln mit dem zweiten Film beträgt; wobei die relativen Werte von A und B das Verhältnis bzw.
20 die Bedingung $A \geq B$ erfüllen.

2. Folie gemäß Anspruch 1, wobei die Folie entweder durch Schlitzdüsengieß- oder Blascoextrusion coextrudiert ist.

25 3. Folie gemäß Anspruch 1 oder 2, wobei das Polyolefin ein Homopolymer oder Copolymer, ausgewählt aus der Gruppe von Polyethylen, Polypropylen, Polybutylen und deren Mischungen, aufweist.

4. Folie gemäß Anspruch 1 oder 2, wobei die erste Schicht ein Ionomer oder dessen Mischung aufweist.

30 5. Folie gemäß einem der Ansprüche 1 bis 4, wobei die Verbindung bzw. Verklebung zwischen der ersten und zweiten Schicht eine Schälfestigkeit (Abziehfestigkeit) von mindestens 1.350 Newton/Meter (3.500 Gramm-Pond/Inch), bestimmt gemäß der Testmethode nach ASTM F-904, beim Abziehen von einer zweiten thermoplastischen Folie, an welcher die Folie heißversiegelt ist, aufweist.

35 6. Folie gemäß einem der Ansprüche 1 bis 5, wobei der Wert von B mindestens 154 Newton/Meter (400 Gramm-Pond/Inch), bestimmt gemäß ASTM F-904, beträgt.

7. Folie gemäß einem der Ansprüche 1 bis 6, wobei die erste Schicht eine äußere Folienschicht ist.

40 8. Folie gemäß einem der Ansprüche 1 bis 7, wobei der klebrige Haftklebstoff eine klebende erste Komponente und eine elastische zweite Komponente von Styrol/Kautschuk-Copolymer aufweist.

9. Folie gemäß einem der Ansprüche 1 bis 8, wobei die dritte Schicht ein Ethylen/Vinyl-Alkohol-Copolymer oder dessen Mischungen aufweist.

45 10. Folie gemäß einem der Ansprüche 1 bis 9, wobei die dritte Schicht Polyester aufweist.

11. Folie gemäß einem der Ansprüche 1 bis 9, wobei die dritte Schicht Polyamid aufweist.

50 12. Folie gemäß einem der Ansprüche 1 bis 9, wobei die dritte Schicht Polystyrol aufweist.

13. Folie gemäß einem der Ansprüche 1 bis 9, wobei die dritte Schicht Polyketon aufweist.

14. Folie gemäß einem der Ansprüche 1 bis 9, wobei die dritte Schicht ein Acrylesterbasiertes Polymer aufweist.

55 15. Folie gemäß einem der Ansprüche 1 bis 9, wobei die dritte Schicht ein Methylpenten-Homopolymer oder -Copolymer aufweist.

16. Folie gemäß einem der Ansprüche 1 bis 9, wobei die dritte Schicht ein Cyclo-Olefin-Copolymer aufweist.

17. Folie gemäß einem der Ansprüche 1 bis 16, wobei die Folie weiterhin eine vierte Polymerschicht, aufweisend ein Anhydrid-modifiziertes Polyolefin, aufweist.
18. Folie gemäß Anspruch 17, wobei die Folie weiterhin eine fünfte Polymerschicht, aufweisend ein Material, ausgewählt aus der Gruppe von Polyolefin, Polyester, Polyamid und deren Mischungen, aufweist.
19. Folie gemäß einem der Ansprüche 1 bis 18, wobei die Folie einen Wärmeschumpfwert von weniger als ungefähr 5 % in Maschinenrichtung bei 90 °C und von weniger als ungefähr 5 % in Querrichtung bei 90 °C aufweist, bestimmt gemäß der Testmethode nach ASTM D-2732-96.
20. Verpackungsartikel, welcher mindestens ein Element umfasst, aufweisend eine abziehbare wiederversiegelbare Mehrschichtfolie, wie in einem der Ansprüche 1 bis 19 definiert.

Revendications

1. Film multicouche décollable rescellable comprenant:

au moins une première couche thermoplastique, une deuxième couche thermoplastique et une troisième couche thermoplastique ;
dans lequel ladite première couche comprend un homopolymère ou copolymère choisi dans le groupe constitué de polyoléfine, ionomère et des mélanges de ceux-ci ;
dans lequel ladite deuxième couche est en contact direct avec et fixé à la fois auxdites première et troisième couches ; dans lequel ladite deuxième couche comprend un adhésif autocollant ;
dans lequel ladite troisième couche comprend un polymère ayant une température de transition vitreuse d'au moins 5 °C mesurée selon la méthode d'essai ASTM D-3418 ; et
dans lequel ladite liaison entre lesdites deuxième et troisième couches comprend une interface rescellable décollable ayant une première résistance au décollement interfacial "A" et une deuxième résistance au décollement interfacial "B" de sorte que la valeur de A soit inférieure à 3500 gramme-force/pouce (1350 newton/mètre) telle que mesurée selon la méthode d'essai ASTM F-904 lorsqu'il est décollé d'un deuxième film thermoplastique auquel ledit film a été thermoscellé, et la valeur de B est d'au moins 330 gramme-force/pouce (127 newton/mètre) telle que mesurée selon l'ASTM F-904 lorsqu'il est décollé et détaché dudit deuxième film ; les valeurs relatives de A et B satisfaisant à la relation $A \geq B$.

2. Film selon la revendication 1, ledit film étant coextrudé par coextrusion à filière à fente ou à film soufflé.
3. Film selon la revendication 1 ou 2, dans lequel ladite polyoléfine comprend un homopolymère ou copolymère choisi dans le groupe constitué des polyéthylène, polypropylène, polybutylène et mélanges de ceux-ci.
4. Film selon la revendication 1 ou 2, dans lequel ladite première couche comprend un ionomère ou un mélange de celui-ci.
5. Film selon l'une quelconque des revendications 1 à 4, dans lequel ladite liaison entre lesdites première et deuxième couches a une résistance au décollement interfacial d'au moins 1350 newton/mètre (3500 gramme-force/pouce) telle que mesurée selon la méthode d'essai ASTM F-904 lorsqu'il est décollé d'un deuxième film thermoplastique auquel ledit film a été thermoscellé.
6. Film selon l'une quelconque des revendications 1 à 5, dans lequel ladite valeur de B est d'au moins 154 newton/mètre (400 gramme-force/pouce) telle que mesurée selon l'ASTM F-904.
7. Film selon l'une quelconque des revendications 1 à 6, dans lequel ladite première couche est une couche de film extérieure.
8. Film selon l'une quelconque des revendications 1 à 7, dans lequel ledit adhésif autocollant comprend un premier composant collant et un deuxième composant élastomère de copolymère de styrène/caoutchouc.
9. Film selon l'une quelconque des revendications 1 à 8, dans lequel ladite troisième couche comprend un copolymère d'éthylène/alcool vinylique ou des mélanges de ceux-ci.

10. Film selon l'une quelconque des revendications 1 à 9, dans lequel ladite troisième couche comprend du polyester.
11. Film selon l'une quelconque des revendications 1 à 9, dans lequel ladite troisième couche comprend du polyamide.
- 5 12. Film selon l'une quelconque des revendications 1 à 9, dans lequel ladite troisième couche comprend du polystyrène.
13. Film selon l'une quelconque des revendications 1 à 9, dans lequel ladite troisième couche comprend de la polycétone.
- 10 14. Film selon l'une quelconque des revendications 1 à 9, dans lequel ladite troisième couche comprend un polymère à base d'ester acrylique.
- 15 15. Film selon l'une quelconque des revendications 1 à 9, dans lequel ladite troisième couche comprend un homopolymère ou copolymère de méthylpentène.
- 16 16. Film selon l'une quelconque des revendications 1 à 9, dans lequel ladite troisième couche comprend un copolymère d'oléfine cyclique.
- 20 17. Film selon l'une quelconque des revendications 1 à 16, ledit film comprenant en outre une quatrième couche de polymère comprenant une polyoléfine modifiée par anhydride.
- 25 18. Film selon la revendication 17, ledit film comprenant en outre une cinquième couche de polymère comprenant un matériau choisi dans le groupe constitué d'une polyoléfine, un polyester, un polyamide et des mélanges de ceux-ci.
- 30 19. Film selon l'une quelconque des revendications 1 à 18, ledit film ayant une valeur de retrait thermique inférieure à environ 5 % dans le sens machine à 90 °C et moins d'environ 5 % dans la direction transversale à 90 °C, mesurée selon la méthode d'essai ASTM D-2732-96.
- 35 20. Article d'emballage ayant au moins un composant comprenant un film multicouche décollable rescellable tel que défini dans l'une quelconque des revendications 1 à 19.

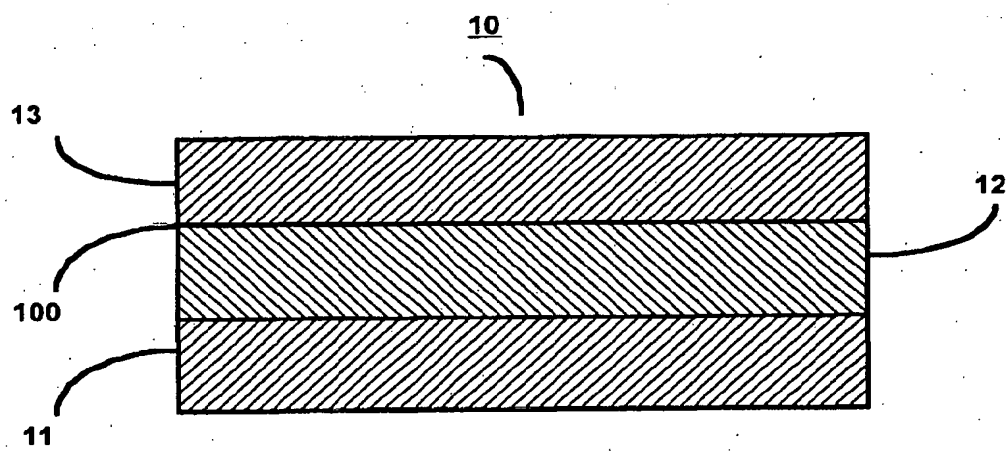


FIG. 1

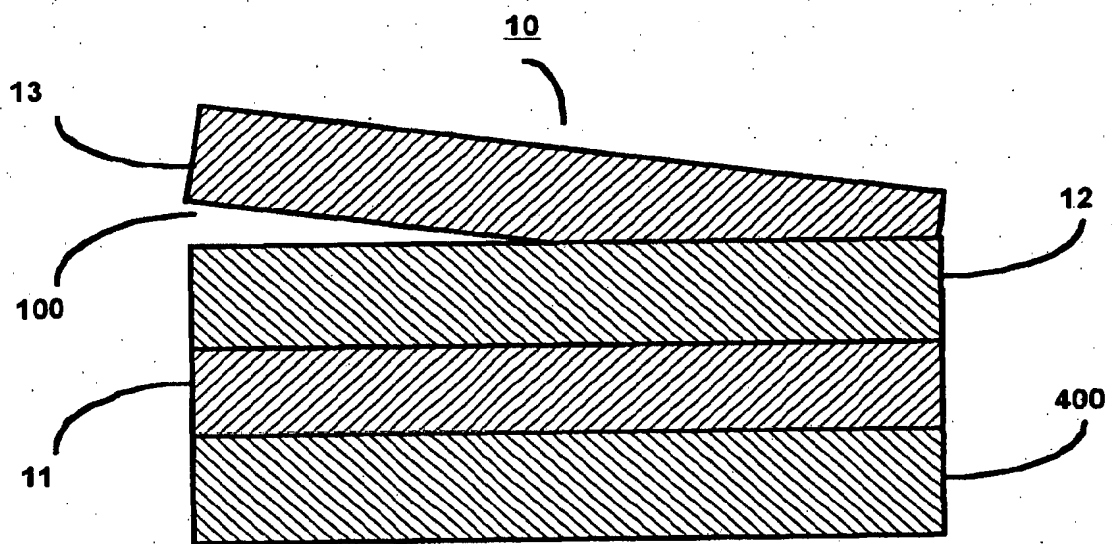


FIG. 2

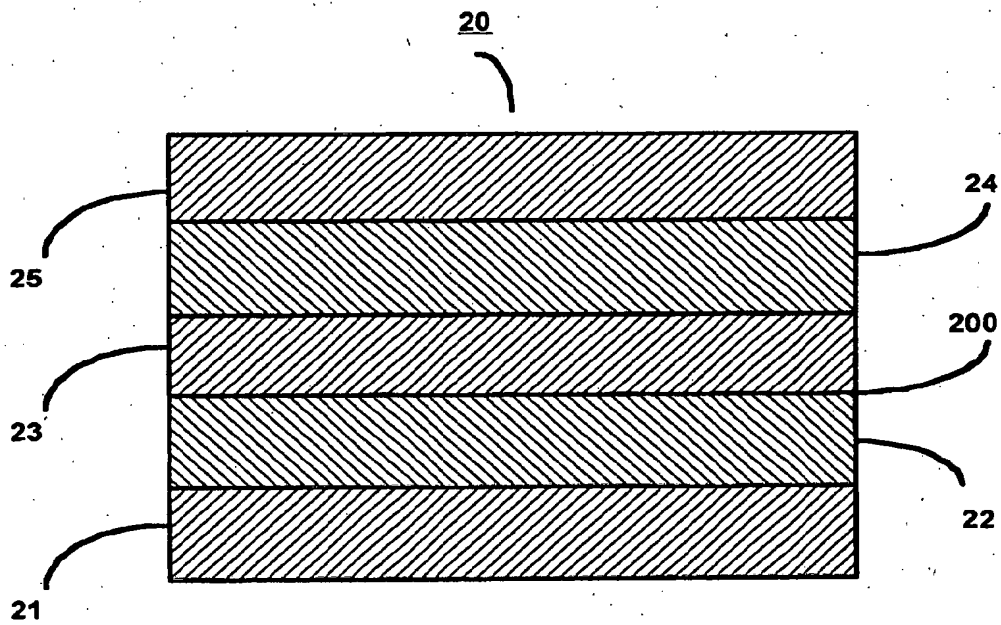


FIG. 3

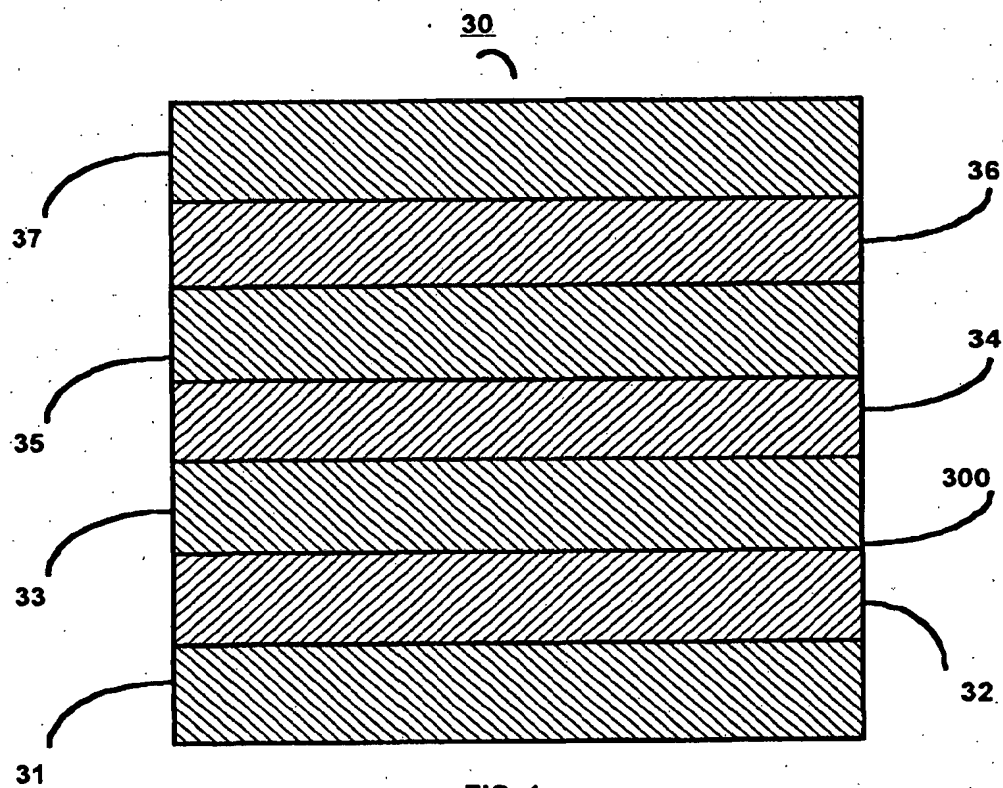


FIG. 4

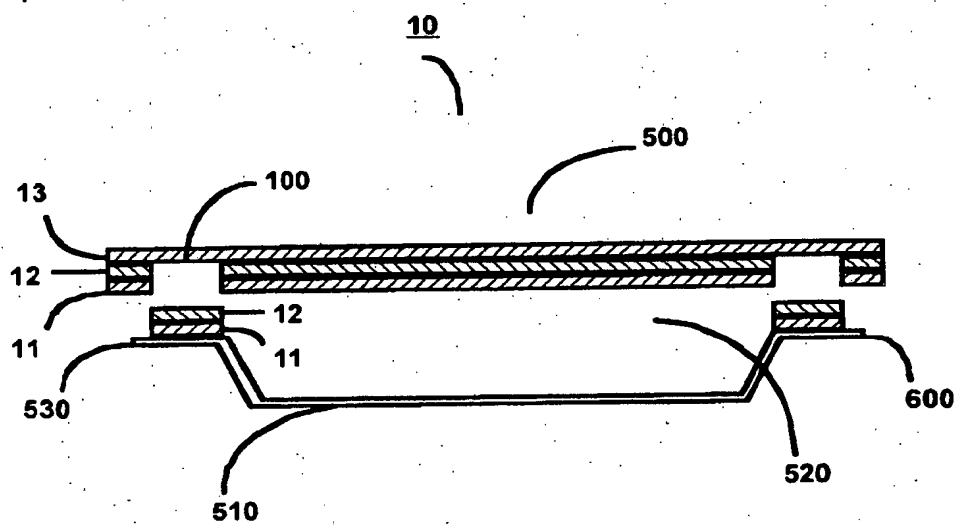


FIG. 5

REFERENCES CITED IN THE DESCRIPTION

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(54) **EASY OPENING PACKAGING ARTICLE MADE FROM HEAT-SHRINKABLE FILM EXHIBITING DIRECTIONAL TEAR**

LEICHT ZU ÖFFNENDER VERPACKUNGSARTIKEL HERGESTELLT AUS EINER
WÄRMESCHRUMPFENDEN, EINE REISSRICHTUNG AUFWEISENDER FOLIE

ARTICLE D'EMBALLAGE À OUVERTURE FACILE RÉALISÉ À PARTIR D'UN FILM
THERMORÉTRACTABLE PRÉSENTANT UNE DÉCHIRURE DIRECTIONNELLE

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DescriptionField

5 **[0001]** The present invention pertains to heat-shrinkable packaging articles that are easy to open, particularly packaging articles for food packaging end use.

Background

10 **[0002]** For several decades, heat-shrinkable packaging articles have been used for the packaging of a variety of products. Food, particularly meat, has been vacuum packaged in such packaging articles. Through the years, these heat-shrinkable packaging articles have developed higher impact strength and higher seal strength, while simultaneously becoming easier to seal, having improved oxygen and moisture barrier properties, and having higher total free shrink at lower temperatures. High seal strength, high impact strength, and high puncture-resistance are particularly important
15 for the packaging of fresh meat products, as leaking packages are less desirable to consumers and retailers alike. Moreover, leaking packages reduce shelf life by allowing atmospheric oxygen and microbes to enter the package.

[0003] As a result, the packaging articles used for food packaging, particularly meat packaging, have evolved into being quite tough, and therefore difficult to open. Typically, knives and scissors are used for opening the packaging articles that have been evacuated, sealed around, and shrunken against the food product in the package. The use of
20 knives and scissors to open these tough packaging articles increases the risk of injury for consumers and retailers. Moreover, the opening of such tough packaging requires more time and effort due to the toughness of the shrunken packaging article. For many years, the marketplace has desired a tough, heat-shrinkable, packaging article that can be opened quickly and easily, without the need for knives and scissors, so that the product can be easily removed from the packaging article.

Summary

[0004] The present invention provides a heat-shrinkable packaging article comprising a heat-shrinkable multilayer film having an inside seal layer heat sealed to itself at a heat seal, the article having a first side and a second side, the article
30 having a skirt or header outward of the heat seal, the skirt or header comprising an article edge and a pair of tear initiators, each pair of tear initiators having a first tear initiator and a second tear initiator, the first tear initiator of the pair being in the first side of the article, and the second tear initiator of the pair being in the second side of the article, the article being capable of having a manually-initiated, manually-propagated first tear in the first side of the article, and a manually-initiated and manually-propagated second tear in the second side of the article, the first tear and the second tear each
35 being capable of being propagated in a machine direction from the pair of first and second tear initiators, with each tear being propagated in the machine direction through the heat seal and down the length of the article, or across the article, with each tear being capable of being manually propagated in the machine direction through and to an opposite article edge, so that upon using the multilayer film to make a packaged product by placing a product inside the article with the article being sealed closed around the product so that a package is formed, and thereafter shrinking the film around the product, the resulting package can be manually opened, and the product readily removed from the package, by manually
40 initiating machine-direction tears from the first and second tear initiators, with the tears being manually propagated through the seal and toward the opposite edge of the article, with the multilayer film exhibiting a Peak Load Impact Strength of at least 50 Newtons per mil measured using ASTM D 3763-95A, with at least one layer of the multilayer film containing at least one incompatible polymer blend selected from the group consisting of: (A) a blend of from 80 to 40
45 weight percent ethylene homopolymer and/or ethylene/alpha-olefin copolymer with from 20 to 60 weight percent ethylene/unsaturated ester copolymer having an unsaturated ester content of at least 10 weight percent; (B) a blend of ionomer resin with ethylene/unsaturated ester copolymer, and/or polybutylene, and/or propylene homopolymer and/or propylene copolymer; (C) a blend of homogeneous ethylene/alpha-olefin copolymer with recycled polymer blend comprising ethylene homopolymer, propylene homopolymer, ethylene copolymer, propylene copolymer, polyamide, ethylene/vinyl alcohol copolymer, ionomer resin, anhydride-modified ethylene/alpha-olefin copolymer, and/or antiblock; (D)
50 a blend of from 10 to 75 weight percent ethylene/unsaturated ester copolymer with from 90 to 15 weight percent polypropylene and/or propylene/ethylene copolymer, and/or polybutylene, and/or modified ethylene/alpha-olefin copolymer, and/or styrene homopolymer, and/or styrene/butadiene copolymer; (E) a blend of ethylene/norbornene copolymer with ethylene/unsaturated ester copolymer and/or polypropylene and/or polybutylene; (F) a blend of from 90 to 15 weight
55 percent ethylene/alpha-olefin copolymer with from 10 to 75 weight percent polypropylene and/or polybutylene and/or ethylene/norbornene; (G) a blend of from 90 to 25 weight percent homogeneous propylene homopolymer and/or homogeneous propylene copolymer with from 10 to 75 weight percent homogeneous ethylene/alpha-olefin copolymer and/or ethylene/unsaturated ester copolymer; (H) a blend of propylene homopolymer and/or propylene/ethylene copolymer

and/or polybutylene with ethylene/methyl acrylate copolymer and/or ethylene/acrylic acid copolymer and/or ethylene/butyl acrylate copolymer; (I) a blend of polyamide with polystyrene and/or ethylene/alpha-olefin copolymer and/or ethylene/vinyl acetate copolymer and/or styrene/butadiene copolymer; and (J) a blend of polyamide 6 and polyamide 6I6T; and wherein at least a portion of the skirt or header is heatset with a remainder of the film remaining heat-shrinkable, so that upon forming the package and shrinking the film around the product, the shrinkage and curl of the skirt or header is reduced, and wherein the heat-shrinkable packaging article does not comprise a patch thereon.

[0005] The heat-shrinkable packaging article described has tear initiators for manually initiating a manual tear that opens the packaging article and allows the product to be readily removed from the torn packaging article, without the use of a knife or scissors or any other implement. A first aspect is directed to a heat-shrinkable packaging article comprising a heat-shrinkable multilayer film having an inside seal layer heat sealed to itself at a heat seal. The packaging article further comprises a first side, a second side, and a skirt or header outward of the heat seal. The skirt or header comprises an article edge and a first tear initiator. The first tear initiator is in the first side of the article. The article skirt or header further comprises a second tear initiator in the second side of the article. The article is capable of having a manually-initiated, manually-propagated first tear in the first side, and a manually-initiated and manually-propagated second tear in the second side, with the first tear and the second tear each being capable of being propagated in a machine direction from the respective first and second tear initiators, with each tear being propagated in the machine direction through the heat seal and down the length of the article, or across the article, with each tear being capable of being manually propagated through to an opposite article edge, so that upon using the multilayer film to make a packaged product by providing a product inside the article with the article being sealed closed around the product so that a package is formed, and thereafter shrinking the film around the product, the resulting package can be manually opened, and the product readily removed from the article, by manually initiating machine-direction tears from the first and second tear initiators, with the tears being manually propagated through the seal and toward the opposite edge of the article. The multilayer film exhibits a Peak Load Impact Strength of at least 50 Newtons per mil measured using ASTM D 3763-95A. The multilayer film has at least one layer containing at least one incompatible polymer blend selected from the group consisting of:

(A) a blend of from 90 to 30 weight percent ethylene homopolymer and/or ethylene/alpha-olefin copolymer with from 10 to 70 weight percent ethylene/unsaturated ester copolymer having an unsaturated ester content of at least 10 weight percent; (B) a blend of ionomer resin with ethylene/unsaturated ester copolymer, and/or polybutylene, and/or propylene homopolymer and/or propylene copolymer

(C) a blend of homogeneous ethylene/alpha-olefin copolymer with recycled polymer blend comprising ethylene homopolymer, propylene homopolymer, ethylene copolymer, propylene copolymer, polyamide, ethylene/vinyl alcohol copolymer, ionomer resin, anhydride-modified ethylene/alpha-olefin copolymer, and antiblocking agent; (D) a blend of ethylene/unsaturated ester copolymer with polypropylene and/or propylene/ethylene copolymer, and/or polybutylene, and/or modified ethylene/alpha-olefin copolymer, and/or styrene homopolymer, and/or styrene/butadiene copolymer;

(E) a blend of ethylene/norbornene copolymer with ethylene/unsaturated ester copolymer and/or polypropylene and/or polybutylene; (F) a blend of ethylene/alpha-olefin copolymer with polypropylene and/or polybutylene and/or ethylene/norbornene;

(G) a blend of homogeneous propylene homopolymer and/or homogeneous propylene copolymer with homogeneous ethylene/alpha-olefin copolymer and/or ethylene/unsaturated ester copolymer;

(H) a blend of propylene homopolymer and/or propylene/ethylene copolymer and/or polybutylene with ethylene/methyl acrylate copolymer and/or ethylene/acrylic acid copolymer and/or ethylene/butyl acrylate copolymer;

(I) a blend of polyamide with polystyrene and/or ethylene/alpha-olefin copolymer and/or ethylene/vinyl acetate copolymer and/or styrene/butadiene copolymer; and

(J) a blend of polyamide 6 and polyamide 6I6T.

[0006] In one embodiment, the packaging article can be torn in the machine direction after the product is placed into the article and the atmosphere evacuated from the packaging article before the article is sealed closed around the product and the film thereafter shrunk around the product.

[0007] A second aspect is directed to a heat-shrinkable packaging article as in the first aspect, except that instead of the multilayer, heat-shrinkable film having at least one layer containing an incompatible polymer blend, at least one layer of the multilayer film contains: (A) at least one member selected from the group consisting of ethylene/alpha-olefin copolymer, polypropylene, propylene/ethylene copolymer, polybutylene, polystyrene/butadiene copolymer, ionomer resin, ethylene/vinyl acetate copolymer, ethylene/butyl acrylate copolymer, ethylene/methyl acrylate copolymer, ethylene/acrylic acid copolymer, polyester, and polyamide, and (B) an inorganic filler selected from the group consisting of silicates, silica, siloxane, silicone resin, zinc sulfide, wollastonite, microspheres, glass fiber, metal oxide, calcium carbonate, sulfate, aluminum trihydrate, feldspar, perlite, gypsum, iron, fluoropolymer, crosslinked polymethylmethacrylate,

talc, diatomaceous earth, zeolites, mica, kaolin, carbon black, and graphite. The inorganic filler is present in the at least one layer in an amount of at least 5 weight percent, based on layer weight.

[0008] A third aspect is directed to a heat-shrinkable packaging article as in the first aspect, except that instead of at least one of the film layers comprising an incompatible polymer blend, at least one of one layer of the multilayer film comprises a polymer having a Young's modulus of at least 552 Mpa (80,000 psi), the polymer comprising at least one polymer selected from the group consisting of high density polyethylene, ultra high molecular weight polyethylene, polypropylene, styrene copolymer, ethylene/norbornene copolymer, polycarbonate, and polyester.

[0009] A fourth aspect is directed to a plurality of heat-shrinkable bags in a continuous strand. Each of the bags is connected to an adjacent bag along a weakened tear line. Each bag is a packaging article in accordance with the first, second, and/or third aspects set forth above.

[0010] A fifth aspect is directed to a process for making an easy-open packaged product. The process comprises (A) inserting a product into a lay-flat packaging article having at least one layer comprising an incompatible polymer blend in accordance with the first aspect or an inorganic filler in accordance with the second aspect or a high modulus polymer in accordance with the third aspect; (B) sealing the packaging article closed with at least one heat seal, thereby forming a packaged product in which the packaging article surrounds or substantially surrounds the product, with the packaging article having at least one header portion between the at least one heat seal and at least one edge of the package; (C) making a first tear initiator at a first location of the packaging article that is, or later becomes, the header portion of a first side of the packaging article, and a second tear initiator at a second location of the packaging article that is, or later becomes, the header portion of a second side of the packaging article, wherein the first side of the packaging article corresponds with the first lay-flat side of the packaging article, and the second side of the packaging article corresponds with the second lay-flat side of the packaging article; and (D) heating the heat-shrinkable film to shrink the package around the product. The heat-shrinkable multilayer film exhibits a Peak Load Impact Strength, determined using ASTM D 3763-95A, of at least 2000 N/mm (50 Newtons per mil). While this process can be carried out using a packaging article that is a bag or pouch, it can also be carried out using a seamless or backseamed lay-flat tubing, wherein after the product is inserted into the tubing, a first heat seal is made across the tubing on a first end of the product and a second heat seal is made across the tubing on a second end of the product.

[0011] A sixth aspect is directed to a process for making a package and manually opening the package, comprising: (A) placing a product inside a heat-shrinkable packaging article in accordance with the first, second, or third aspects above; (B) sealing the bag closed so that a package is formed; (C) shrinking the film around the product; and (D) manually initiating and manually propagating a first tear in the first side of the package, and a second tear in the second side of the package, the first tear and the second tear each being manually propagated from the respective first and second tear initiators, with each tear being manually propagated through the heat seal and across the package, or down the length of the bag, with the first and second tears being manually propagated towards an opposite edge of the packaging article, so that the product can be readily removed from the package.

[0012] In one embodiment, the atmosphere is evacuated from the packaging article before the packaging article is sealed closed with the product therein. The packaging article used in the process is a packaging article in accordance with the first aspect and/or the second aspect and/or the third aspect set forth above.

[0013] A seventh aspect is directed to a heat-shrinkable packaging article comprising a heat-shrinkable multilayer film having an inside seal layer heat sealed to itself at a heat seal, with the article having a first side and a second side, a skirt or header outward of the heat seal. The skirt or header comprises an article edge and a plurality of pairs of tear initiators. Each pair of tear initiators having a first tear initiator and a second tear initiator, with the first tear initiator being in the first side of the article, and the second tear initiator being in the second side of the article. Each pair of tear initiators is at a location for generating a manually-initiated, manually-propagated first tear in the first side of the article, and a manually-initiated and manually-propagated second tear in the second side of the article. The first tear and the second tear are each capable of being propagated in a machine direction from the respective first and second tear initiators. Each tear is capable of being propagated in the machine direction through the heat seal and down the length of the article, or across the article. Each tear is capable of being manually propagated in the machine direction through and to an opposite article edge, so that upon using the multilayer film to make a packaged product by providing a product inside the article with the article being sealed closed around the product so that a package is formed, and thereafter shrinking the film around the product, the resulting package can be manually opened. Tearing from one or more of the pairs of tear initiators allows a portion of the package to be removed from the packaged product so that an uncovered portion of the product can be separated from a remainder of the product, leaving a remainder of the package around at least a portion of the remainder of the product, by initiating first and second machine-direction tears from at least one pair of tear initiators, with the tears being propagated through the seal and toward the opposite edge of the article. The multilayer film exhibits a Peak Load Impact Strength of at least 2000 N/mm (50 Newtons per mil) measured using ASTM D 3763-95A. At least layer of the multilayer film containing at least one incompatible polymer blend selected from the group set forth in the first aspect described above, which is further discussed below.

[0014] The heat-shrinkable packaging article can be a lay-flat, side-seal bag made from a seamless tubing, the side-

seal bag having an open top, a folded bottom edge, and first and second side seals with respective first and second bag skirts outward of respective first and second side seals, with the plurality of pairs of tear initiators being spaced apart along the first bag skirt, with each tear being capable of being manually propagated across the full width of the side-seal bag through both side seals and through second skirt.

[0015] In the heat-shrinkable packaging article, at least a portion of the skirt or header comprising the plurality of tear initiators can be heatset, in order to reduce the shrinkage of the skirt or header upon shrinking the film around the product.

[0016] In the heat-shrinkable packaging article, at least a portion of a first side of the skirt or header can be heat sealed to the second side of the skirt or header in at least one heat seal.

[0017] In the heat-shrinkable packaging article, the first side of the skirt or header can be heat sealed to the second side of the skirt or header in a plurality of spot seals.

[0018] In the heat-shrinkable packaging article, the first side of the skirt or header can be heat sealed to the second side of the skirt or header in a heat seal along an outer edge of the skirt or header.

[0019] In the heat-shrinkable packaging article, the plurality of pairs of tear initiators can be located at intervals of from 25.4 to 76.2 mm (1 to 3 inches), or at intervals of from 25.4 to 50.8 mm (1 to 2 inches). In the heat-shrinkable packaging article, each of the first tear initiators can be coincident or substantially coincident with the second tear initiator with which it is paired, and each of the first tear initiators can be a slit through the first side of the article, and each of the second tear initiators can be a slit through the second side of the article, and each of the slits can be oriented in the machine direction.

[0020] In the heat-shrinkable packaging article, each of the slits can be oriented within 20 degrees of the machine direction, or within 10 degrees of the machine direction.

[0021] In the heat-shrinkable packaging article, the multilayer film can have been biaxially oriented in the solid state and can have a total free shrink, as measured by ASTM D 2732, of from 20 percent to 105 percent at 85°C (185°F), or a total free shrink of from 40 percent to 100 percent at 85° (185°F).

[0022] In the heat-shrinkable packaging article, the heat-shrinkable multilayer film can exhibit a Peak Load Impact Strength, determined using ASTM D 3763-95A, of from 2000-10000 N/mm (50 to 250 Newtons per mil), and the multilayer film can have a total thickness, before shrinking, of from 0.038 mm (1.5 mils) to 0.13 mm (5 mils).

[0023] In the heat-shrinkable packaging article, the multilayer film can comprise an O₂-barrier layer, and can exhibit an oxygen transmission rate of from 1 to 20 cc/m² day atm at 23°C and 100% relative humidity.

[0024] In the heat-shrinkable packaging article, the multilayer film can comprise: (A) a first layer that is an outer food-contact layer and that also serves as a seal layer, the first layer comprising a blend of homogeneous ethylene/alpha-olefin copolymer and linear low density polyethylene; (B) a second layer comprising a blend of heterogeneous ethylene/alpha-olefin copolymer and ethylene/vinyl acetate copolymer; (C) a third layer comprising ethylene/vinyl acetate copolymer; (D) a fourth layer comprising polyvinylidene chloride; (E) a fifth layer comprising ethylene/vinyl acetate copolymer; (F) a sixth layer comprising a blend of heterogeneous ethylene/alpha-olefin copolymer and ethylene/vinyl acetate copolymer; (G) a seventh layer comprising a blend of homogeneous ethylene/alpha-olefin copolymer and linear low density polyethylene. The layers can be present in the order of first / second / third / fourth / fifth / sixth / seventh.

[0025] An eighth aspect is directed to a heat-shrinkable packaging article comprising a heat-shrinkable multilayer film having an inside seal layer heat sealed to itself at a heat seal, with the article having a first side and a second side. The article has a skirt or header outward of the heat seal. The skirt or header comprises an article edge and a pair of tear initiators, each pair of tear initiators having a first tear initiator and a second tear initiator. The first tear initiator of the pair is in the first side of the article, and the second tear initiator of the pair is in the second side of the article. The article is capable of having a manually-initiated, manually-propagated first tear in the first side of the article, and a manually-initiated and manually-propagated second tear in the second side of the article. The first tear and the second tear are each being capable of being propagated in a machine direction from the pair of first and second tear initiators, with each tear being propagated in the machine direction through the heat seal and down the length of the article, or across the article. Each tear is capable of being manually propagated in the machine direction through and to an opposite article edge, so that upon using the multilayer film to make a packaged product by placing a product inside the article with the article being sealed closed around the product so that a package is formed, and thereafter shrinking the film around the product, the resulting package can be manually opened, and the product readily removed from the package, by manually initiating machine-direction tears from the first and second tear initiators, with the tears being manually propagated through the seal and toward the opposite edge of the article. The multilayer film exhibits a Peak Load Impact Strength of at least 2000 N/mm (50 Newtons per mil) measured using ASTM D 3763-95A. At least one layer of the multilayer film containing at least one incompatible polymer blend selected from the group set forth in the first aspect described above, and as further discussed below. At least a portion of the skirt or header is heatset, so that upon forming the package and shrinking the film around the product, the shrinkage and curl of the skirt or header is reduced. The header or skirt further comprises at least one grip assister for assisting grip of the multilayer film during manual tearing.

[0026] In the heat-shrinkable article a portion of the skirt or header on the first side of the article can be heatset, and a corresponding portion of the skirt or header on the second side of the article can also be heat-set.

[0027] The heat-shrinkable packaging article can be an end-seal bag and the first and second tear initiators can be present in the bag skirt, and a heat seal can be present within the heatset portion of the first and second sides of the article.

[0028] In the heat-shrinkable article, the first tear initiator can be aligned over the second tear initiator, and the heat seal present within the heatset portion can be a perimeter seal, and the skirt can further comprise a first grip assister between the pair of tear initiators and a first end of the skirt, and a second grip assister between the pair of tear initiators and a second end of the skirt.

[0029] In the heat-shrinkable article, a first portion of a first side of the skirt or header can be spot sealed to the second side of the skirt or header at a first spot seal, and a second portion of the first side of the skirt or header can be spot sealed to the second side of the skirt or header at a second spot seal.

[0030] In the heat-shrinkable article, the heat-set portions of the first and second sides of the skirt or header can comprise a perimeter seal in the skirt or header.

[0031] In the heat-shrinkable article, the first tear initiator can align directly over the second tear initiator, and the skirt or header can further comprise a first spot seal within 1 inch of the first and second tear initiators and a first end of the skirt, and a second spot seal within 1 inch of the first and second tear initiators and a second end of the skirt or header.

[0032] In the heat-shrinkable article, the header or skirt can further comprise a first grip assister between the first spot seal and the first end of the header or skirt, and a second grip assister between the first and second tear initiator and a second end of the header or skirt.

[0033] The heat-shrinkable article can be a side seal bag or pouch having a skirt comprising a plurality of pairs of first and second tear initiators, with each first tear initiator being aligned directly over the second tear initiator with which is it paired.

[0034] The heat-shrinkable article can be a side-seal bag having a skirt that comprises, for each pair of first and second tear initiators, a first spot seal within 25.4 mm (1 inch) of the pair of tear initiators, the first spot seal being between the pair of tear initiators and a first end of the skirt, and a second spot seal within 1 inch of the pair of tear initiators, with the second spot seal being between the pair of tear initiators and the a second end of the skirt.

[0035] The heat-shrinkable article can comprise a multilayer film having an oxygen transmission rate of at least 50 cc/m² day at stp and 100% relative humidity, or at least 100 cc/m² day at stp and 100% relative humidity, or at least 150 cc/m² day at stp and 100% relative humidity.

[0036] The heat-shrinkable packaging article can comprise a multilayer film having a non-symmetrical polymeric layer arrangement.

Brief Description of the Drawings

[0037]

FIG. 1A is a schematic of a first heat-shrinkable, end-seal bag in lay-flat configuration.

FIG. 1B is a schematic of a second heat-shrinkable, end-seal bag in lay-flat configuration.

FIG. 1C is an enlarged, detailed view of a portion of the bag of FIG. 1B.

FIG. 1D is an enlarged, detailed view of a first less desirable embodiment of a bag otherwise corresponding with the bag of FIG. 1B.

FIG. 1D is an enlarged, detailed view of a second less desirable embodiment of a bag otherwise corresponding with the bag of FIG. 1B.

FIG. 1E is an enlarged, detailed view of a third less desirable embodiment of a bag otherwise corresponding with the bag of FIG. 1B.

FIG. 2 is a transverse cross-sectional view of the heat-shrinkable, end-seal bag of FIG. 1.

FIG. 3 is a schematic of a first heat-shrinkable, side-seal bag in lay-flat configuration.

FIG. 4 is a transverse cross-sectional view of the heat-shrinkable, side-seal bag of FIG. 3.

FIG. 5 is a schematic of a second heat-shrinkable, side-seal bag in lay-flat configuration.

FIG. 6A is an enlarged detailed view of the tear initiation feature of the heat-shrinkable, end-seal bag of FIG. 1.

FIG. 6B is an enlarged detailed view of an alternative tear initiation feature to be used on an alternative heat-shrinkable, end-seal bag.

FIG. 6C is an enlarged detailed view of an alternative tear initiation feature to be used on another alternative heat-shrinkable, end-seal bag.

FIG. 6D is an enlarged detailed view of an alternative tear initiation feature to be used on another alternative heat-shrinkable, end-seal bag.

FIG. 6E is an enlarged detailed view of an alternative tear initiation feature to be used on another alternative heat-shrinkable, end-seal bag.

FIG. 6F is an enlarged detailed view of an alternative tear initiation feature to be used on another alternative heat-shrinkable, end-seal bag.

FIG. 6G is an enlarged detailed view of an alternative tear initiation feature to be used on another alternative heat-shrinkable, end-seal bag.

FIG. 6H is an enlarged detailed view of an alternative tear initiation feature to be used on another alternative heat-shrinkable, end-seal bag.

5 FIG. 6I is an enlarged detailed view of the tear initiation feature of the bag of FIG. 1, with the further addition of a manual grip-enhancer.

FIG. 6J is an enlarged detailed view of the tear initiation feature of the bag of FIG. 1, with the further addition of another manual grip enhancer.

10 FIG. 6K is an enlarged detailed view of the tear initiation feature of the bag of FIG. 1, with the further addition of another manual grip enhancer.

FIG. 6L is an enlarged detailed view of the tear initiation feature of the bag of FIG. 1, with the further addition of another manual grip enhancer.

FIGs. 6M, 6N, 6O, 6P, 6Q, 6R, 6S, 6T, 6U, 6V, 6W, 6X, 6Y, 6Z, 6AA, 6BB, 6CC, 6DD, 6EE, and 6FF are enlarged detailed views of various alternative tear initiation features, some of which include manual grip enhancer.

15 FIG. 7A is a schematic view of a first embodiment of a continuous strand of bags connected by a serration line.

FIG. 7B is a schematic view of a second embodiment of a continuous strand of bags connected by a serration line.

FIG. 7C is a schematic view of a third embodiment of a continuous strand of bags connected by a serration line.

20 FIG. 8 is a schematic view of the process used to make various heat-shrinkable, seamless film tubings set forth in several of the examples below, this tubing thereafter being converted into end-seal and side-seal bags by heat sealing and cutting operations (not illustrated).

FIG. 9 is a schematic of a packaged product made up of a meat product vacuum packaged in a shrunken end-seal bag having the tear initiation feature in the bag skirt.

FIG. 10 is a schematic of the packaged product of FIG. 9 after the tearing has been initiated, but as the tearing remains in an intermediate state, the tearing proceeding down the bag film in the machine direction.

25 FIG. 11 is a schematic of the packaged product of FIG. 8 and 9, after the tearing is completed.

FIG. 12 is a schematic of a comparative packaged product exhibiting a tear character that does not allow tearing for the full length of the bag.

FIG. 13 is a schematic of an alternative heat-shrinkable end-seal bag in lay-flat configuration.

FIG. 14 is a schematic of an alternative heat-shrinkable side-seal bag in lay-flat configuration.

30 FIG. 15 is a schematic of another alternative side-seal bag in lay-flat configuration. FIG. 16 is a schematic of yet another side-seal bag in lay-flat configuration.

FIG. 17 is a schematic of an apparatus for carrying out the process of placing tear initiators in the header region of a packaging article.

35 FIG. 18 illustrates a schematic of an easy open package in which the easy open feature is similar to the feature in FIG. 6J, but which is designed for automated package opening.

FIG. 19 illustrates a schematic of a heat-shrinkable, easy-open, side-seal bag having a plurality of pairs of tear initiators at intervals along one of the bag skirts.

FIG. 20 illustrates a schematic of a portion of a heat-shrinkable, easy-open, end-seal bag 370 having a pair of tear initiators along at intervals along the bag skirt.

40 FIG. 21 is an enlarged detailed view of a portion of a header or skirt having a pair of tear initiators with heatset, bonded regions on each side of the pair of tear initiators.

FIG. 22 is an enlarged, detailed view of a portion of a header or skirt having a pair of tear initiators with heatset, bonded regions and grip assisters.

45 FIG. 23 is an enlarged, detailed view of a portion of a header or skirt having a plurality of pairs of tear initiators, with a pair of heatset, bonded regions associated with each pair of tear initiators and a pair of grip assisters associated with each pair of tear initiators.

FIG. 24 is a perspective partial view of a packaged product made from an end-seal bag shrunk around a product, with curling of the shrunken skirt obscuring tear initiators and grip assisters.

50 FIG. 25 is a perspective view of a packaged product as in FIG. 24, but with two spot seals of the skirt to itself.

FIG. 26 is a perspective view of a packaged product as in FIG. 24, but with four spot seals of the skirt to itself.

FIG. 27 is a perspective view of a packaged product as in FIG. 24, but with a perimeter seal of the skirt to itself.

FIG. 28 illustrates a schematic of a heat-shrinkable, easy-open, side-seal bag having a plurality of pairs of tear initiators at intervals along one of the bag skirts, as well as an elongated heat set area on either side of each pair of tear initiators.

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Detailed Description

[0038] As used herein, the term "film" is inclusive of plastic web, regardless of whether it is film or sheet. The film can

have a total thickness of 0.25 mm or less, or a thickness of from 0.038 mm (1.5 mils) to 0.25 mm (10 mils), or from 0.038 mm to 0.13 mm (1.5 to 5 mils), or from 0.046 mm (1.8 mils) to 0.10 mm (4 mils), or from 0.051 mm (2 mils) to 0.076 mm (3 mils).

[0039] The multilayer, heat-shrinkable film from which the packaging article is made exhibits a Peak Load Impact Strength, determined using ASTM D 3763-95A, of at least 2000 N/mm (50 Newtons per mil). ASTM D 3763-95A is hereby incorporated, in its entirety, by reference thereto. The heat-shrinkable film can have a Peak Load Impact Strength, determined using ASTM 3763-95A, of from 2000 to 10000 N/mm (50 to 250 Newtons per mil), or from 2400 to 8000 N/mm (60 to 200 Newtons per mil), or from 2800 to 7000 N/mm (70 to 170 Newtons per mil); or from 3200 to 5900 N/mm (80 to 150 Newtons per mil); or from 3300 TO 5500 N/mm (85 to 140 Newtons per mil); or from 3700 to 5300 N/mm (95 to 135 Newtons per mil). In one embodiment, the heat-shrinkable multilayer film exhibits a Peak Load Impact Strength, determined using ASTM D 3763-95A, of from 2000 to 10000 N/mm (50 to 250 Newtons per mil), and the multilayer film has a total thickness, before shrinking, of from 0.038 mm (1.5 mils) to 0.25 mm (5 mils).

[0040] The multilayer film has a seal layer and at least one additional layer. At least one layer of the multilayer film contains a blend of incompatible polymers.

[0041] As used herein, the phrase "machine direction" refers to the direction in which the film emerges from the die. Of course, this direction corresponds with the direction the extrudate is forwarded during the film production process. The phrase "machine direction" corresponds with "longitudinal direction". Machine direction and longitudinal direction are abbreviated as "MD" and "LD", respectfully. However, as used herein, the phrase "machine direction" includes not only the direction along a film that corresponds with the direction the film traveled as it passed over idler rollers in the film production process, it also includes directions that deviate up to 44 degrees from the direction the film traveled as it passed over idler rollers in the production process.

[0042] As used herein, the phrase "transverse direction" refers to a direction perpendicular to the machine direction. Transverse direction is abbreviated as "TD". The transverse direction also includes directions that deviate up to 44 degrees from the direction the film traveled as it passed over idler rollers in the production process.

[0043] As used herein, the phrase "packaging article" is inclusive end-seal bags, side-seal bags, L-seal bags, U-seal bags (also referred to as "pouches"), gusseted bags, backseamed tubings, and seamless casings, as well as packages made from such articles by placing a product in the article and sealing the article so that the product is substantially surrounded by the heat-shrinkable multilayer film from which the packaging article is made.

[0044] As used herein, packaging articles have two "sides". Generally, a "side" of a packaging article corresponds with half of the article. For example, an end-seal bag is a lay-flat bag and has two sides (in this case two lay-flat sides), with each side corresponding with a lay-flat side of the seamless tubing from which the end-seal bag is made. Each lay-flat side of a seamless tubing is bounded by the creases formed as the tubing is collapsed into its lay-flat configuration between nip rollers. Each side of an end-seal bag is bounded by the bag top edge, the bag bottom edge, and the two tubing creases running the length of the bag. Likewise, a side-seal bag also has two sides, with each side also being a lay-flat side, with each side of the side-seal bag being bounded by bag side edges, a bag top edge, and a bag bottom corresponding with a tubing crease. A casing, whether seamless or backseamed, also has two sides, with each side being bounded by the ends of the casing and by creases formed as the casing is configured into its lay-flat configuration. While gusseted bags and other packaging articles may not be fully lay-flat in their structure because they have more than two flat sides, they nevertheless have "sides" bounded by creases and edges.

[0045] As used herein, the term "package" refers to packaging materials configured around a product being packaged. As such, the term "package" includes all of the packaging around the product, but not the product itself.

[0046] As used herein, the phrase "packaged product" refers to the combination of a product and the package that surrounds or substantially surrounds the product. The packaged product can be made by placing the product into a packaging article made from the heat-shrinkable multilayer film, with the article then being sealed closed so that the multilayer film surrounds or substantially surrounds the product. The film can then be shrunk around the product.

[0047] As used herein, the term "bag" refers to a packaging article having an open top, side edges, and a bottom edge. The term "bag" encompasses lay-flat bags, pouches, casings (seamless casings and backseamed casings, including lap-sealed casings, fin-sealed casings, and butt-sealed backseamed casings having backseaming tape thereon). Various casing configurations are disclosed in USPN 6,764,729 B2, to Ramesh et al, entitled "Backseamed Casing and Packaged Product Incorporating. Various bag configurations, including L-seal bags, backseamed bags, and U-seal bags (also referred to as pouches), are disclosed in USPN 6,970,468, to Mize et al, entitled "Patch Bag and Process of Making Same". While the bag configurations illustrated in the '468 patent have a patch thereon, in the present invention, the heat-shrinkable packaging article does not comprise a patch thereon.

[0048] In one embodiment, the packaging article is a lay-flat, end-seal bag made from a seamless tubing, the end-seal bag having an open top, first and second folded side edges, and an end seal across a bottom of the bag, with the first and second tear initiators being in the bag skirt that is outward of the end seal, with the first tear being a machine-direction tear of the film, and the second tear being a machine-direction tear of the film, with each tear being capable of being manually propagated down the length of the end-seal bag to the opposite edge of the end-seal bag.

[0049] In one embodiment, the packaging article is a lay-flat, side-seal bag made from a seamless tubing, the side-seal bag having an open top, a folded bottom edge, and first and second side seals with respective first and second bag skirts outward of respective first and second side seals, with the first and second tear initiators being in the first bag skirt and outward of the first side seal, with the first tear being a machine-direction tear and the second tear being a machine-direction tear, with each tear being capable of being manually propagated across the full width of the side-seal bag to the opposite edge of the side-seal bag.

[0050] In one embodiment, the packaging article is a lay-flat, side-seal bag made from a seamless tubing, the side-seal bag having an open top, a folded bottom edge, a first side seal with a first bag skirt outward thereof, a second side seal with a second bag skirt outward thereof, and a third seal that extends from the first side seal to the second side seal, the third seal being at an opposite end of the bag from the open top, the third seal having a third bag skirt outward thereof, the folded bottom edge being in the third bag skirt, the third bag skirt comprising the first and second tear initiators, with the first tear being a transverse-direction tear and the second tear being a transverse-direction tear, with the first and second tears each being capable of being manually propagated down the length of the side-seal bag and to the opposite edge of the side-seal bag.

[0051] In one embodiment, the packaging article is a lay-flat pouch made by heat sealing two flat films to one another, the pouch having an open top, a first side seal with a first bag skirt outward thereof, a second side seal with a second bag skirt outward thereof, a bottom seal with a third bag skirt outward thereof, the bottom seal extending from the first side seal to the second side seal, the bottom seal being at an opposite end of the bag from the open top, with at least one of the bag skirts having first and second tear initiators for tearing each of the two flat films in the machine direction.

[0052] End-seal bags, side-seal bags, L-seal bags, T-seal bags (also referred to as backseamed bags), and U-seal bags all have an open top, closed sides, a closed bottom, and at least one heat seal. Each of these heat seals is referred to as a "factory seal" because these seals are made in a bag-making factory, rather than in a packaging factory where the bag is used to package a product. Each of the heat seals illustrated in FIGs. 1A-1F, 3, 4, 5, 6A-6FF, 7A-C, and 13-16 is a factory seal. Each of the factory seals is generally made a short distance inward of the edge of the article, so that a relatively small amount of film remains outward of the heat seal, i.e., on the other side of the seal from the film that envelopes the product. A gusseted bag can also be made with a bottom seal that has a skirt, and a casing (backseamed or seamless) can have a transverse heat seal with a skirt. As used herein, the term "skirt" refers to that portion of the film that is outward of any one or more of the factory seals. The "length" of a skirt is the distance corresponding to the length of the seal inward of the skirt, and the "width" of the skirt is the distance taken perpendicular to from this seal, across the skirt, to the edge of the article. Length and width of a header (described below) are determined in the same manner. The length of a skirt or header terminates in the "ends" of the skirt or header.

[0053] In contrast, only one of the heat seals on the packaged product of FIGs. 9-12 is a factory seal. The other seal is made after the product is placed in the packaging article, and is herein referred to as a "packers seal" or as an "applied seal" or as a "customer seal". While the film outward of a factory heat seal is referred to as a "skirt", the film outward of a customer seal is referred to as a "tail" or "header" of the packaging article. In the packaged product illustrated in FIGs. 9-12 and 18, one of the heat seals is a factory seal and the other heat seal is a customer seal. If tear initiator 53 in FIG. 9 is in the skirt, then heat seal 51 is the factory seal and heat seal 55 is the customer seal. While a tear initiator may be in a skirt, it may also be in a header region of the bag. If tear initiator 53 is in the header, then heat seal 51 is the customer seal and heat seal 55 is the factory seal. Usually, the header is larger (i.e., longer) than the skirt.

[0054] The term "bag" also includes that portion of a package that is derived from a bag. That is, once a product is placed inside a bag, the bag is sealed closed so that it surrounds the product. Excess bag length (i.e., the bag tail or bag header) can optionally be cut off along a line close to the seal made across the bag to enclose the product within the bag, and thereafter optionally the film can be shrunk around the product. The portion of the bag that remains and is configured around the product is herein also within the term "bag". The phrase "an opposite edge of the packaging article" refers to the edge of the bag that is directly across from the edge of the packaging article having the tear initiator. For example, a bag top edge is opposite the bag bottom edge; a first bag side edge is opposite the second bag side edge. As used herein, the phrase "a side of the bag" is used with reference to each of the first and second sides of a lay-flat bag, as well as each of the two principal, flat sides of a gusseted bag.

[0055] As used herein, the phrase "skirt" refers to that portion of the packaging article that is outward of a heat seal, e.g., the excess length or width on the non-product side of any factory heat seal on the packaging article. In an end-seal bag, the bag skirt is short in the machine direction and long in the transverse direction. In a side-seal bag, the bag skirt is long in the machine direction and short in the transverse direction. In either case, the "width" of the bag skirt is the shorter dimension of the skirt, and the "length" of the bag skirt is the longer dimension of the skirt. A bag skirt (or any skirt of any packaging article) can have a width, before the film is shrunk, of at least 5 millimeters, or at least 10 millimeters, or at least 15 millimeters, or at least 20 millimeters, or at least 25 millimeters, or at least 30 millimeters. Alternatively, the skirt can have a width of from 5 to 100 millimeters, or from 10 to 50 millimeters, or from 15 to 40 millimeters, or from 20 to 35 millimeters.

[0056] As used herein, the phrase "lay-flat bag" refers generically to non-gusseted bags used for the packaging of a

variety of products, particularly food products. More specifically, the phrase "lay-flat bag" includes side seal bag, end-seal bag, L-seal bag, U-seal bag (also referred to as a pouch), and backseamed bag (also referred to as T-seal bag). The backseam can be a fin seal, a lap seal, or a butt-seal with a backseaming tape.

Before the bag is shrunk, it can have a length-to-width ratio of from 1:1 to 20:1; or from 1.5:1 to 8:1; or from 1.8:1 to 6:1; or from 2:1 to 4:1.

[0057] The tear initiator can be a cut in the skirt or header of the packaging article. As used herein, the term "cut" refers to the penetration through the film, or shearing through the film, with a shearing means or edged instrument. Preferably the cut is made through both sides of the packaging article. The term "cut" is inclusive of both slits and notches. As used herein, the term "slit" refers to a cut through the film without the separation and removal of a piece of film from the packaging article. A slit can be from the edge of the packaging article (i.e., an "edge slit") or internal, i.e., not extending to an edge (i.e., "internal slit" also referred to as a "slit hole"). The slit can be straight or curved or wavy.

[0058] The term "hole", as used herein, includes both an internal puncture (i.e., internal hole) or internal cut (i.e., an internal slit) through the packaging article, as well as an internal cut that removes a piece of film from the article. The hole can utilize a straight cut or a curved cut. The hole can be round or square or rectangular or irregular in shape.

[0059] A "notch" is formed by a cut that removes a piece of film along an otherwise straight or smooth curved edge of an article skirt or tail, producing a point for stress concentration during the subsequent manual application of tearing force. A notch can be V-shaped or round or square or rectangular or oval or of any regular or irregular profile.

[0060] The slit or notch or hole in the skirt or tail can extend across at least 10 percent of the width of the skirt before the bag is shrunk; or at least 20 percent, or at least 30 percent or at least 40 percent, or at least 50 percent, or at least 60 percent, or at least 70 percent, or at least 80 percent, or at least 90 percent, of the width of the skirt or tail. The slit or notch or hole can angle inward, toward the center of the packaging article.

[0061] In end-seal and side-seal bags, as well as other packaging articles, a portion of the skirt is in a first lay-flat side of the article (e.g., bag), and a portion of the same skirt is in a second lay-flat side of the article (e.g., bag). The first lay-flat side of the skirt can have a first tear initiator, and the second lay-flat side of the skirt can have a second tear initiator.

[0062] The first tear initiator can overlap the second tear initiator when the end-seal or side-seal bag (or any other packaging article) is in its lay-flat configuration, as well as in the shrunken package. Overlapping enhances the ease of simultaneously initiating and propagating the tears in the first and second sides of the packaging article. Moreover, the first tear initiator can coincide (i.e., be positioned directly over and correspond with in length and shape) with the second tear initiator when the packaging article is in its lay-flat configuration.

[0063] The packaging article can be provided with both a first tear initiator that is overlapping or coincident with the second tear initiator, and a third tear that is overlapping or coincident with a fourth tear initiator. The first and second tear initiators can be positioned in a skirt or header portion of the article for making a manual tear in a machine direction, with the third and fourth tear initiators being positioned for making a manual tear in a transverse direction. The third and fourth tear initiators can be positioned in a skirt or a header.

[0064] As used herein, the verb "to tear" refers to pulling an object apart by force. The noun "tear" refers to the resulting break in the object being torn. The tearing of the film results from placing the film under enough tension that it is pulled apart by the force. The pulling force is concentrated by the tear initiator, which allows a smaller pulling force to pull the film apart, i.e., tear the film. High impact strength heat-shrinkable films are not susceptible to being manually torn without the presence of the tear initiator. In the heat-shrinkable packaging article, the high impact strength multilayer film undergoes tearing from the tear initiator toward the opposite edge of the packaging article.

[0065] The phrase "tear initiator", as used herein, refers to any one or more of a variety of means that can be located in the skirt or header of a packaging article. The tear initiator allows manual tearing force to be concentrated on a point or small region of the film(s), so that tear initiation and tear propagation can be produced manually. A slit in the bag skirt, as illustrated in FIG. 6A, can serve as the tear initiator. Alternatively, the tear initiator can be a V-shaped notch in a bag skirt (see FIG. 6B) or a rounded notch in the bag skirt (see FIG. 6C), or a rectangular notch in the bag skirt (see FIG. 6D), or a slit hole in the bag skirt (see FIG. 6E) or a round hole in the bag skirt (see FIG. 6F), or a pointed oval hole in the bag skirt (see FIG. 6G), or a rectangular hole in the bag skirt (see FIG. 6H).

[0066] As used herein, the terms "overlapping" and "coincident" are used with respect to the relative positioning of paired tear initiators both when the article is in its lay-flat configuration and/or after a product is placed in the article and the article sealed closed around the product. The term "coincident" refers to two paired tear initiators that are directly on top of one another. The term "overlapping" refers to two paired tear initiators that are close enough to one another than an effort to manually tear one side of the packaging article at one of the tear notches results in tearing both sides of the article, i.e., from each of the paired tear initiators. The phrase "substantially coincident" is used interchangeably with the term "overlapping". Typically, tear initiators within one half inch of being coincident with one another are deemed to be "overlapping".

[0067] As used herein, the phrase "manual" and the term "manually" are both used with reference to tearing with the hands alone i.e., without the need for a knife, scissors, or any other implement to assist with initiating or propagating tearing of the film. The term "manual" is used with respect to tear initiation, i.e., the manual starting of the tearing action,

as well as with respect to tear propagation, i.e., the manual continuation (i.e., extension) of a tear that has been manually initiated.

[0068] In addition to the tear initiator, the packaging article can be provided with "grip assister", also referred to herein as a "grip enhancer". The grip assister can enhance the ease with which the film can be torn. The grip assister can be in one lay-flat side of the packaging article or in both lay-flat sides of the packaging article. The grip assister can be a hole in the skirt (and/or in the header), an integral extension of the skirt or header, or a separate film tab fastened to the skirt or header. The separate film tab can be made from a thermoplastic polymer, paper, or other material, and can be heat-shrinkable or non-heat-shrinkable. The packaging article can be provided with the combination of a tear-initiator and a grip-assister. For example, the skirt can have a slit as the tear-initiator and a hole as the grip-assister. See FIG. 6I. The skirt can have a slit as the tear initiator and two holes providing serving as the grip assister. See FIG. 6J. Alternatively, the grip assister can be a tab, as illustrated in FIG. 6K, this figure further illustrating the tab being used in combination with a slit.

[0069] With respect to the tearing of the film from which the packaging article is made, as used herein the phrase "the tear is capable of being propagated..." refers to the manner in which the film tends to propagate the tear when the bag is subjected to an ordinary manual opening thereof, i.e., the packaging article can be "gripped and ripped" or "gripped and torn" in the ordinary course of opening. The packaging article exhibits substantially linear tear. Usually, the linear tear is substantially in line with the machine direction, or substantially in line with the transverse direction. The tearing is carried out after shrinking the heat-shrinkable film.

[0070] If the tear is being made in the machine direction of the film, the tear may be within from 0 to 44 degrees of the actual machine direction of the film, i.e., so long as the tear can be propagated toward and to the opposite side edge of the bag; or the tear may be within from 0 to 20 degrees, or within from 0 to 15 degrees, or within from 1 to 20 degrees, or within from 0 to 10 degrees; or within from 0 to 5 degrees, or within from 0 to 2 degrees of the machine direction of the film. The same holds true of transverse direction tearing, i.e., the tear may be within from 0 to 44 degrees of the actual transverse direction of the film; or the tear may be within 0 to 20 degrees, or within 1 to 20 degrees, or within from 0 to 10 degrees; or within from 0 to 5 degrees, or within from 0 to 2 degrees of the transverse direction of the film.

[0071] As used herein, the phrase "readily removed" is applied to the removal of a product from a packaging article surrounding or substantially surrounding the product. As used herein, the phrase "readily removed" refers to the manual removal of the product from within the confines of the packaging article without any further substantial amount of tearing, and without any substantial further permanent deformation of the film. As used herein, the phrase "substantial tearing of the film" refers to tearing greater than or equal to 2 millimeters in length. As used herein, the phrase "substantial permanent deformation of the film" refers to a permanent stretching of the film greater than or equal to 2 millimeters at any location on the film.

[0072] As used herein, the phrases "seal layer," "sealing layer," "heat seal layer," and "sealant layer," refer to an outer film layer, or layers, involved in heat sealing the film to itself, another film layer of the same or another film, and/or another article which is not a film. Heat sealing can be performed in any one or more of a wide variety of manners, such as melt-bead sealing, thermal sealing, impulse sealing, ultrasonic sealing, hot air sealing, hot wire sealing, infrared radiation sealing, ultraviolet radiation sealing, electron beam sealing, etc.). A heat seal is usually a relatively narrow seal (e.g., 0.51 mm to 25 mm (0.02 inch to 1 inch wide)) across a film. One particular heat sealing means is a heat seal made using an impulse sealer, which uses a combination of heat and pressure to form the seal, with the heating means providing a brief pulse of heat while pressure is being applied to the film by a seal bar or seal wire, followed by rapid cooling.

[0073] In some embodiments, the seal layer can comprise a polyolefin, particularly an ethylene/alpha-olefin copolymer and/or an ionomer resin. For example, the seal layer can contain a polyolefin having a density of from 0.88 g/cc to 0.917 g/cc, or from 0.90 g/cc to 0.917 g/cc. More particularly, the seal layer can comprise at least one member selected from the group consisting of very low density polyethylene and homogeneous ethylene/alpha-olefin copolymer. Very low density polyethylene is a species of heterogeneous ethylene/alpha-olefin copolymer. The heterogeneous ethylene/alpha-olefin (e.g., very low density polyethylene) can have a density of from 0.900 to 0.917 g/cm³. The homogeneous ethylene/alpha-olefin copolymer in the seal layer can have a density of from 0.880 g/cm³ to 0.910 g/cm³, or from 0.880 g/cm³ to 0.917 g/cm³. Homogeneous ethylene/alpha-olefin copolymers useful in the seal layer include metallocene-catalyzed ethylene/alpha-olefin copolymers having a density of from 0.917 g/cm³ or less, as well as a very low density polyethylene having a density of 0.912 g/cm³, these polymers providing excellent optics. Plastomer-type metallocene sealants with densities less than 0.910 g/cm³ also provided excellent optics.

[0074] As used herein, the term "barrier", and the phrase "barrier layer", as applied to films and/or film layers, are used with reference to the ability of a film or film layer to serve as a barrier to one or more gases. The multilayer heat-shrinkable film used to make the article can optionally comprise a barrier layer. In the packaging art, oxygen (i.e., gaseous O₂) barrier layers can comprise, for example, at least one member selected from the group consisting of hydrolyzed ethylene/vinyl acetate copolymer (designated by the abbreviations "EVOH" and "HEVA", and also referred to as "saponified ethylene/vinyl acetate copolymer" and "ethylene/vinyl alcohol copolymer"), polyvinylidene chloride, amorphous polyamide, polyamide MXD6 (particularly MXD6/MXD1 copolymer), polyester, polyacrylonitrile, etc., as known to those of skill

in the art. In addition to the first and second layers, the heat-shrinkable film may further comprise at least one barrier layer.

[0075] The heat-shrinkable film can exhibit O_2 -transmission rate of from 1 to 20 cc/m² day atm at 23°C and 100% relative humidity, or from 2 to 15 cc/m² day atm at 23°C and 100% relative humidity, or from 3 to 12 cc/m² day atm at 23°C and 100% relative humidity, or from 4 to 10 cc/m² day atm at 23°C and 100% relative humidity. Alternatively, the heat-shrinkable film can exhibit an O_2 -transmission rate of from 21 cc/m² day atm to 15,000 cc/m² day atm, or from 500 cc/m² day atm to 10,000 cc/m² day atm, or from 2000 cc/m² day atm to 6,000 cc/m² day atm. O_2 -transmission rate can be measured in accordance with ASTM-D-3985.

[0076] As used herein, the phrase "tie layer" refers to any internal layer having the primary purpose of adhering two layers to one another. Tie layers can comprise any polymer having a polar group grafted thereon. Such polymers adhere to both nonpolar polymers such as polyolefin, as well as polar polymers such as polyamide and ethylene/vinyl alcohol copolymer. Tie layers can comprise at least one member selected from the group consisting of polyolefin (particularly homogeneous ethylene/alpha-olefin copolymer), anhydride-modified polyolefin, ethylene/vinyl acetate copolymer, and anhydride-modified ethylene/vinyl acetate copolymer, ethylene/acrylic acid copolymer, and ethylene/methyl acrylate copolymer. Typical tie layer polymers comprise at least one member selected from the group consisting of anhydride modified linear low density polyethylene, anhydride modified low density polyethylene, anhydride modified polypropylene, anhydride modified methyl acrylate copolymer, anhydride modified butyl acrylate copolymer, homogeneous ethylene/alpha-olefin copolymer, and anhydride modified ethylene/vinyl acetate copolymer.

[0077] As used herein, the phrases "inner layer" and "internal layer" refer to any layer, of a multilayer film, having both of its principal surfaces directly adhered to another layer of the film.

[0078] As used herein, the phrase "outer layer" refers to any film layer having less than two of its principal surfaces directly adhered to another layer of the film. A multilayer film has two outer layers, each of which has a principal surface adhered to only one other layer of the multilayer film.

[0079] As used herein, the term "adhered" is inclusive of films which are directly adhered to one another using a heat seal or other means, as well as films which are adhered to one another using an adhesive which is between the two films. This term is also inclusive of layers of a multilayer film, which layers are of course adhered to one another without an adhesive therebetween. The various layers of a multilayer film can be "directly adhered" to one another (i.e., no layers therebetween) or "indirectly adhered" to one another (i.e., one or more layers therebetween).

[0080] Once a multilayer film is heat sealed to itself or another member of the package being produced (i.e., is converted into a packaging article, e.g., a bag, pouch, or casing), one outer layer of the film is an inside layer of the packaging article and the other outer layer becomes the outside layer of the packaging article. The inside layer can be referred to as an "inside heat seal/product contact layer", because this is the film layer that is sealed to itself or another article, and it is the film layer closest to the product, relative to the other layers of the film. The other outer layer can be referred to as the "outside layer" and/or as the "outer abuse layer" or "outer skin layer", as it is the film layer furthest from the product, relative to the other layers of the multilayer film. Likewise, the "outside surface" of a packaging article (i.e., bag) is the surface away from the product being packaged within the article.

[0081] While the multilayer heat-shrinkable film can be sealed to itself to form a packaging article, optionally a heat-shrinkable patch film can be adhered to article (particularly to a bag). The patch film can be heat-shrinkable, and can have a total free shrink at 185°F of at least 35 percent, measured in accordance with ASTM D-2732. The bag film and the patch film can have a total free shrink at 185°F that are within 50 percent of one another, or within 20 percent of one another, or with 10 percent of one another, or within 5 percent of one another, or within 2 percent of one another. The patch may or may not cover the heat seal. If the patch covers a heat seal, optionally the heat seal may be made through the patch. If the tear is to be made through the bag and through the patch, the patch should cover a heat seal, and the tear initiator should be through both the bag film and the patch film. The bag can have a curved seal and the patch can extend into and through the region of the curved seal and over and past the curved seal. If the bottom edge of the bag is curved, a bottom edge of the patch can also be curved. The patch bag can have any desired configuration of patch on bag as disclosed in any one or more of U.S. Patent Nos.: 4,755,403, 5,540,646, 5,545,419, 6,296,886, 6,383,537, 6,663,905, and 6,790,468.

[0082] End-seal bags with curved heat seals, and end-seal patch bags with curved heat seals, can be designed for have manual tear initiation and manual directional tear propagation. While the end-seal may be curved, the bottom edge of the bag may be straight across the tubing, or may also be curved. A curved bottom heat seal and a straight across bag bottom edge leaves more space in the bottom corners of the bag skirt for providing tear initiators, as well as for grip assisters. Patch bags with curved end seals are disclosed in U.S. Patent No. 6,270,819, to Wiese.

[0083] The term "polymer", as used herein, is inclusive of homopolymer, copolymer, terpolymer, etc. "Copolymer" includes copolymer, terpolymer, etc.

[0084] Blends of incompatible polymers in one or more film layers can enhance the tear initiation, tear propagation, and linear tear properties of the film, including the ability to manually tear down the full length or across the full width of a package made from a packaging article comprising a multilayer packaging film, i.e., tearing through a seal and through and to an opposite edge of the package. For a package made from an end-seal bag, a machine-direction tear can be

manually initiated in the bag skirt, and the machine-direction tear can be manually propagated through the seal and down the length of the bag, for a distance up to the full length of the package, i.e., to that portion of the package that corresponds with the opposite edge of the package after the packaging article is used to make the package. For a package made from a side-seal bag, the machine direction tear can be manually initiated in a bag skirt, and the machine direction tear can be manually propagated through the skirt and through the associated heat seal, with the tear thereafter being propagated in the machine direction, across the full width of the package, i.e., to that portion of the package that corresponds with the opposite edge of the side-seal bag after the bag is used to make the package.

[0085] As used herein, the phrase "incompatible polymers" refers to two polymers (i.e., a blend of at least two polymers) that are incapable of forming a solution or even a stable two-phase blend, and that tend to separate after being mixed. When blended, incompatible polymers are not miscible with one another, and phase separate into a continuous domain and a discontinuous domain that may be finely dispersed. The presence of one or more film layers comprising a blend of incompatible polymers may assist, enhance, or even cause the linear tear property of the multilayer heat-shrinkable film used to make the heat-shrinkable bag.

[0086] The blend of incompatible polymers comprises at least one blend selected from the group of (A) through (I) set forth above under the first aspect of the invention. In the (A) blend above, the ethylene homopolymer and/or ethylene/alpha-olefin copolymer is present in an amount of from 80 to 40 weight percent, or from 70 to 50 weight percent, based on total blend weight. The ethylene/unsaturated ester is present in an amount of from 20 to 60 weight percent, or from 30 to 50 weight percent, based on total blend weight. The ethylene/unsaturated ester copolymer can have an unsaturated ester content of from 10 to 85 weight percent, or 10 to 50 weight percent, or 10 to 30 weight percent, or 12 to 30 weight percent, based on weight of ethylene/unsaturated ester copolymer.

[0087] In the (D) blend above, the ethylene/unsaturated ester copolymer can be present in an amount of from 10 to 75 weight percent, 20 to 50 weight percent, or 25 to 40 weight percent, or 25 to 35 weight percent, based on total blend weight. The polypropylene and/or propylene/ethylene copolymer and/or polybutylene and/or modified ethylene/alpha-olefin copolymer, and/or styrene homopolymer, and/or styrene/butadiene copolymer can be present in the blend in an amount of from 90 to 15 weight percent, or from 80 to 50 weight percent, or from 75 to 60 weight percent, or from 75 to 65 weight percent, based on total blend weight.

[0088] In the (F) blend above, the ethylene/alpha-olefin copolymer can be present in the blend in an amount of from 90 to 15 weight percent, based on total blend weight, or from 80 to 50 weight percent, or from 75 to 60 weight percent, or from 25 to 65 weight percent, based on total blend weight, with polypropylene (particularly propylene/ethylene copolymer) and/or polybutylene and/or ethylene/norbornene in an amount of from 10 to 85 weight percent, or from 20 to 50 weight percent, or from 25 to 40 weight percent, or from 25 to 35 weight percent, based on total blend weight.

[0089] In the (G) blend above, the homogeneous propylene homopolymer and/or homogeneous propylene copolymer can be present in the blend in an amount of from 90 to 25 weight percent, or 85 to 50 weight percent, or 80 to 60 weight percent, or 75 to 65 weight percent, based on total blend weight, with homogeneous ethylene/alpha-olefin copolymer and/or ethylene/unsaturated ester copolymer in an amount of from 10 to 75 weight percent, or 15 to 50 weight percent, or 20 to 40 weight percent, or 25 to 35 weight percent, based on total blend weight.

[0090] In one embodiment, the film comprises an incompatible blend of ethylene/alpha-olefin copolymer and ethylene/vinyl acetate copolymer having a vinyl acetate content of from 10 to 50 weight percent based on copolymer weight, the blend containing the ethylene/alpha-olefin copolymer in an amount of from 80 to 35 weight percent based on blend weight and ethylene/unsaturated ester copolymer in an amount of from 20 to 65 weight percent based on blend weight, with the multilayer film containing the blend in an amount of from 20 to 95 weight percent, based on the weight of the multilayer film, wherein the multilayer film has been biaxially oriented in the solid state and has a total free shrink, as measured by ASTM D 2732, of from 15 percent to 120 percent at 85°C (185°F).

[0091] In another embodiment the film can comprises an incompatible blend of ethylene/alpha-olefin copolymer and ethylene/vinyl acetate copolymer having a vinyl acetate content of from 10 to 30 weight percent based on copolymer weight, the blend containing the ethylene/alpha-olefin copolymer in an amount of from 75 to 45 weight percent based on blend weight and ethylene/unsaturated ester copolymer in an amount of from 25 to 55 weight percent based on blend weight, with the multilayer film containing the blend in an amount of from 30 to 70 weight percent, based on the weight of the multilayer film, wherein the multilayer film has been biaxially oriented in the solid state and has a total free shrink, as measured by ASTM D 2732, of from 20 percent to 105 percent at 85°C (185°F).

[0092] In another embodiment, the film can comprise an incompatible blend of ethylene/alpha-olefin copolymer and ethylene/vinyl acetate copolymer having a vinyl acetate content of from 12 to 30 weight percent, the blend containing the ethylene/alpha-olefin copolymer in an amount of from 70 to 50 percent based on blend weight and ethylene/unsaturated ester copolymer in an amount of from 30 to 50 weight percent based on blend weight, the multilayer film containing the blend in an amount of from 30 to 70 weight percent, based on the weight of the multilayer film, and wherein the multilayer film has been biaxially oriented in the solid state and has a total free shrink, as measured by ASTM D 2732, of from 40 percent to 100 percent at 85°C (185°F). The shrinking is typically carried out by immersion in hot water, such as water at 85°C (185°F), for a period of from 2 to 60 seconds.

[0093] If any one or more of the incompatible blends comprises an ethylene/alpha-olefin copolymer, the ethylene/alpha-olefin copolymer can comprise at least one member selected from the group consisting of: (i) ethylene/hexene copolymer having a density of from about 0.90 g/cc to about 0.925 g/cc, and (ii) ethylene/octene copolymer having a density of from about 0.90 g/cc to about 0.925 g/cc.

[0094] Other blends of incompatible polymers that may be used include the following: (i) a blend of 50 weight percent cyclic olefin copolymer with 50 weight percent propylene homopolymer; (ii) a blend of 70 wt. percent polystyrene with 30 wt. percent ethylene/vinyl acetate copolymer having a vinyl acetate content of 9 percent or 15 percent; (iii) a blend of 70 wt. percent very low density polyethylene and 30 wt. percent cyclic olefin copolymer; (iv) a blend of 70 weight percent ethylene/propylene copolymer and 30 weight percent homogeneous ethylene/alpha-olefin copolymer; (v) a blend of 70 weight percent ethylene/propylene copolymer and 30 wt. percent ethylene/vinyl acetate copolymer having a vinyl acetate content of 9 percent or 15 percent; (vi) a blend of 70 weight percent ethylene/propylene copolymer and 30 weight percent ethylene/methyl acrylate copolymer; (vii) a blend of 70 weight percent polystyrene with 30 weight percent amorphous nylon; (viii) a blend of 70 weight percent ionomer resin with 30 weight percent ethylene/vinyl acetate copolymer having a vinyl acetate content of 4 percent; (ix) a blend of 70 weight percent polyamide with 30 weight percent low density polyethylene; (x) a blend of 65 weight percent amorphous polyamide with 35% styrene/butadiene/styrene block copolymer.

[0095] The tear initiation, tear propagation, and linear tear property of a multilayer heat-shrinkable film may also be enhanced by providing one or more layers of the film with a filler material, such as an inorganic filler. Polymeric systems that incorporate high filler concentrations may also enhance linear tear behavior. Depending on the particle size and dispersion, a filler concentration as low as 5 weight percent filler (i.e., based on total layer weight) in ethylene/alpha-olefin copolymer, polypropylene, propylene/ethylene copolymer, polybutylene, polystyrene/butadiene copolymer, ionomer resin, ethylene/vinyl acetate copolymer, ethylene/butyl acrylate copolymer, ethylene/methyl acrylate copolymer, ethylene/acrylic acid copolymer, polyester, polyamide, etc., may contribute to the linear tear behavior. More particularly, the presence of filler in an amount of from 5 to 95 weight percent, or in an amount of from 5 to 50 weight percent, or in an amount of from 10 to 40 weight percent, or from 20 to 35 weight percent, may be used.

[0096] Suitable fillers include silicates (particularly sodium silicate, potassium silicate, and aluminum silicate, alkali alumino silicate), silica (particularly amorphous silica), siloxane, silicone resin, zinc sulfide, wollastonite, microspheres, glass fiber, metal oxide (particularly oxides of titanium, zinc, antimony, magnesium, iron, and aluminum), calcium carbonate, sulfate (particularly barium sulfate and calcium sulfate), aluminum trihydrate, feldspar, perlite, gypsum, iron, fluoropolymer, crosslinked polymethylmethacrylate, talc, diatomaceous earth, zeolites, mica, kaolin, carbon black, and graphite.

[0097] The filler concentration required to achieve low tear initiation force is dependent on particle geometry, particle size, particle aspect ratio, and compatibility of the filler and the polymer matrix. Some fillers are chemically treated to improve the compatibility of the particle and the polymer into which it is dispersed.

[0098] The tear initiation, tear propagation, and linear tear property of a multilayer heat-shrinkable film may also be enhanced by providing one or more layers of the film with a polymer that provides the film with a relatively high Young's modulus, e.g., a polymer having a Young's modulus of at least 80,000 psi. Such polymers can comprise at least one member selected from the group consisting of high density polyethylene, ultra high molecular weight polyethylene, polypropylene (particularly propylene homopolymer), styrene copolymer (particularly styrene/butadiene block copolymer), ethylene/norbornene copolymer, polycarbonate, and polyester. The multilayer heat-shrinkable film may have a Young's Modulus of at least 80,000 psi. Young's modulus may be measured in accordance with one or more of the following ASTM procedures: D638, D882; D5026-95a; D4065-89, each of which is incorporated herein in its entirety by reference. The film may have a Young's modulus of at least about, and/or at most about, any of the following: 689; 897; 1034; 1379; 1724; 2068; 2413 and 2758 MPa (100,000; 130,000; 150,000; 200,000; 250,000; 300,000; 350,00 and 400,000 pounds/square inch), measured at a temperature of 23°C (73°F). The film may have any of the foregoing ranges of Young's modulus in at least one direction (e.g., in the machine direction or in the transverse direction) or in both directions (i.e., the machine (i.e., longitudinal) and the transverse directions).

[0099] As used herein, terms such as "polyamide", "polyolefin", "polyester", etc are inclusive of homopolymers of the genus, copolymers of the genus, terpolymers of the genus, etc, as well as graft polymers of the genus and substituted polymers of the genus (e.g., polymers of the genus having substituent groups thereon).

[0100] As used herein, the phrase "propylene/ethylene copolymer" refers to a copolymer of propylene and ethylene wherein the propylene mer content is greater than the ethylene mer content. Propylene/ethylene copolymer is not a species of "ethylene/alpha-olefin copolymer".

[0101] The phrase "ethylene/alpha-olefin copolymer" is particularly directed to heterogeneous copolymers such as linear low density polyethylene (LLDPE), very low and ultra low density polyethylene (VLDPE and ULDPE), as well as homogeneous polymers such as metallocene catalyzed polymers such as EXACT® resins obtainable from the Exxon Chemical Company, and TAFMER® resins obtainable from the Mitsui Petrochemical Corporation. All these latter copolymers include copolymers of ethylene with one or more comonomers selected from C₄ to C₁₀ alpha-olefin such as

butene-1 (i.e., 1-butene), hexene-1, octene-1, etc. in which the molecules of the copolymers comprise long chains with relatively few side chain branches or cross-linked structures. This molecular structure is to be contrasted with conventional low or medium density polyethylenes which are more highly branched than their respective counterparts. The heterogeneous ethylene/alpha-olefins commonly known as LLDPE have a density usually in the range of from about 0.91 grams per cubic centimeter to about 0.94 grams per cubic centimeter. Other ethylene/alpha-olefin copolymers, such as the long chain branched homogeneous ethylene/alpha-olefin copolymers available from the Dow Chemical Company, known as AFFINITY® resins, are also included as another type of homogeneous ethylene/alpha-olefin copolymer useful in the film and process described herein.

[0102] As used herein, the phrase "heterogeneous polymer" refers to polymerization reaction products of relatively wide variation in molecular weight and relatively wide variation in composition distribution, i.e., typical polymers prepared, for example, using conventional Ziegler-Natta catalysts. Heterogeneous copolymers typically contain a relatively wide variety of chain lengths and comonomer percentages. Heterogeneous copolymers have a molecular weight distribution (Mw/Mn) of greater than 3.0.

[0103] As used herein, the phrase "homogeneous polymer" refers to polymerization reaction products of relatively narrow molecular weight distribution and relatively narrow composition distribution. Homogeneous polymers are useful in various layers of the multilayer heat-shrinkable film. Homogeneous polymers are structurally different from heterogeneous polymers, in that homogeneous polymers exhibit a relatively even sequencing of comonomers within a chain, a mirroring of sequence distribution in all chains, and a similarity of length of all chains, i.e., a narrower molecular weight distribution. Furthermore, homogeneous polymers are typically prepared using metallocene, or other single-site type catalysis, rather than using Ziegler Natta catalysts. Homogeneous ethylene/alpha-olefin copolymer can have a Mw/Mn of ≤ 3.0 .

[0104] As used herein, the term "polyamide" refers to a polymer having amide linkages, more specifically synthetic polyamides, either aliphatic or aromatic, either in semi-crystalline or amorphous form. It is intended to refer to both polyamides and co-polyamides. The polyamides can be selected from nylon compounds approved for use in producing articles intended for use in processing, handling, and packaging food, including homopolymers, copolymers and mixtures of the nylon materials described in 21 C.F.R. 177.1500 *et seq.*, which is incorporated herein by reference. Exemplary of such polyamides include nylon homopolymers and copolymers such as those selected from the group consisting of nylon 4,6 (poly(tetramethylene adipamide)), nylon 6 (polycaprolactam), nylon 6,6 (poly(hexamethylene adipamide)), nylon 6,9 (poly(hexamethylene nonanediamide)), nylon 6,10 (poly(hexamethylene sebacamide)), nylon 6,12 (poly(hexamethylene dodecanediamide)), nylon 6/12 (poly(caprolactam-co-laurallactam)), nylon 6,6/6 (poly(hexamethylene adipamide-co-caprolactam)), nylon 6/66 (poly(caprolactam-co-hexamethylene adipamide)), nylon 66/610 (e.g., manufactured by the condensation of mixtures of nylon 66 salts and nylon 610 salts), nylon 6/69 resins (e.g., manufactured by the condensation of epsilon-caprolactam, hexamethylenediamine and azelaic acid), nylon 11 (polyundecanolactam), nylon 12 (polyaurylactam), nylon MXD6, nylon MXDI, nylon 6I/6T, and copolymers or mixtures thereof. Unless otherwise indicated, the phrase "semi-crystalline polyamide" includes all polyamides that are not considered to be amorphous polyamides. All semi-crystalline polyamides have a determinable melting point.

[0105] The film is a heat-shrinkable film. The film can be produced by carrying out only monoaxial orientation, or by carrying out biaxial orientation. As used herein, the phrase "heat-shrinkable" is used with reference to films which exhibit a total free shrink (i.e., the sum of the free shrink in both the machine and transverse directions) of at least 10% at 85°C (185°F), as measured by ASTM D 2732, which is hereby incorporated, in its entirety, by reference thereto. All films exhibiting a total free shrink of less than 10% at 85°C (185°F) are herein designated as being non-heat-shrinkable. The heat-shrinkable film multilayer film can have a total free shrink at 85°C (185°F) of from 10 percent to 150 percent, or from 15 percent to 120 percent, or from 20 percent to 100 percent, or from 45 to 95 percent, or from 40 to 90 percent, or from 30 percent to 80 percent, or from 35 percent to 60 percent, as measured by ASTM D 2732.

[0106] Heat shrinkability can be achieved by carrying out orientation in the solid state (i.e., at a temperature below the glass transition temperature of the polymer). The total orientation factor employed (i.e., stretching in the transverse direction multiplied by drawing in the machine direction) can be any desired factor, such as at least 2X, at least 3X, at least 4X, at least 5X, at least 6X, at least 7X, at least 8X, at least 9X, at least 10X, at least 16X, or from 1.5X to 20X, from 2X to 16X, from 3X to 12X, or from 4X to 9X.

[0107] In the packaging of a product in a heat-shrinkable film that is thereafter shrunk around the product, the header and/or skirt of the packaging article tends to shrink and curl. This is because the shrinkage of the film making up the header and/or skirt is relatively unrestrained during the period it is heated to induce shrinkage. Since the tear initiators are present in the header and/or skirt, the relatively unrestrained shrinking and curling of the header and/or skirt makes it more difficult for a consumer to detect the presence and location of the tear initiators, as well as making it more difficult to manually (or automatically) grab and use the tear initiators to tear the package open or to tear off a portion of the package.

[0108] Heatsetting at least a portion of the header and/or skirt reduces the unrestrained shrink and curling of the header and/or skirt as the film shrinks around the product. As used herein, the term "heatsetting" refers to reheating the film under restraint, i.e., so that it cannot undergo substantial shrinkage during reheating. Heatsetting is carried out by

heating the film (while under restraint) to a temperature, and for a time, so that the resulting heatset portion of the film exhibits a total free shrink at 85°C (185°F) of no more than 49% of the total free shrink at 85°C (185°F) of the film before the onset of the heatsetting process. The reheating is of one or more regions of the skirt and/or header or can be of the entire skirt and/or header. Small regions can be heatset, including isolated spots or lines or even elongated regions across the skirt or header, such as heat seal lines and areas extending outward therefrom. The heatsetting of at least a portion of the header and/or skirt allows the packaging article to later be shrunk around the product while leaving the header and/or skirt more apparent and more accessible for the consumer to use.

[0109] Heatsetting can be carried out in a variety of manners. For example, the skirt and/or header (or any portion thereof) can be subjected to heat and pressure by contact with a hot platen, such as applying heat and pressure using a hot iron, a heated platen press, or even a seal bar, such as an impulse sealer. Heat sealing devices, such as a spot sealer or an impulse sealer using a hot wire or hot seal bar, inherently heatset that portion (i.e., region) of the film being heat sealed during the heat sealing process, as the amount of heat required to heatset is less than the amount of heat needed to seal the film to itself or another component of the package. Heat sealing utilizes enough heat that regions extending outward from the seal are also heatset. The size of these regions outward of the seal depends upon the manner in which the heat seal is made, and the characteristics of the film being heat sealed. The processes used for heatsetting generally cause both lay-flat sides of a packaging article to be heatset in "corresponding" areas or portions or regions, i.e., areas or portions or regions of substantially equal size that are in contact with one another but which are on opposite sides of the article.

[0110] Heatsetting reduces the total free shrink exhibited by the heatset portion of the heat-shrinkable film. While heatsetting can be carried out to any desired degree, the heatset film can exhibit a total free shrink at 85°C (185°F) of up to 50 percent; or up to 40%; or up to 30%; or up to 20%, or up to 10%; or from 0 to 5%. Heatsetting a skirt or header of a package, or regions of the skirt or header, reduces the unrestrained shrinkage of at least the heatset regions of the skirt or header during the heating of the package to shrink the film against the product inside the package. Reducing the unrestrained shrinkage of the even a portion of the skirt or header allows the skirt and/or header to remain closer to its initial size and shape after the remainder of the film is shrunk around the product. Heatsetting also reduces the curling of the skirt and/or header as the film is shrunk around the product, particularly when the heatsetting is carried out by heat sealing a first side of the skirt and/or header to the second side of the skirt and/or header. Reductions in unrestrained shrinkage and unrestrained curling of the skirt and/or header make it easier for a consumer to detect and utilize tear initiators located in the skirt and/or header.

[0111] As used herein, the term "spot" is used with reference to heat sealing and heat-setting, the term referring any discrete area of a packaging article in which (i) the film of one or both sides of the article are heat-set in the discrete area, or (ii) a first side of the article is heat sealed to a second side of the article in the discrete area. The term "spot" is used with reference to both a "spot seal" as well as a "spot heatset area". Spot seals of a first side of a skirt to the second side of the skirt have been made using a HAKO 936 soldering station set for 100°C, attached to which is a HAKO 907 soldering iron designated as being 24V/ 50W.

[0112] As used herein, the phrase "perimeter seal" refers to a seal in a skirt or header of an article, the seal extending along at least 51 percent of the length of the skirt or header, the seal being outward of any tear initiators and grip assisters present in the skirt or header.

[0113] In one embodiment, the film does not comprise a crosslinked polymer network. In another embodiment, the film comprises a crosslinked polymer network. Optionally, the film can be irradiated to induce crosslinking of polymer, particularly polyolefin in the film. The film can be subjected to irradiation using an energetic radiation treatment, such as corona discharge, plasma, flame, ultraviolet, X-ray, gamma ray, beta ray, and high energy electron treatment, which induce cross-linking between molecules of the irradiated material. The irradiation of polymeric films is disclosed in U.S. Patent No. 4,064,296, to BORNSTEIN, et. al., BORNSTEIN, et. al. discloses the use of ionizing radiation for crosslinking polymer present in the film.

[0114] Radiation dosages are referred to herein in terms of the radiation unit "RAD", with one million RADS, also known as a megarad, being designated as "MR", or, in terms of the radiation unit kiloGray (kGy), with 10 kiloGray representing 1 MR, as is known to those of skill in the art. A suitable radiation dosage of high energy electrons is in the range of up to about 16 to 166 kGy, more preferably about 30 to 90 kGy, and still more preferably, 30 to 50 kGy. Preferably, irradiation is carried out by an electron accelerator and the dosage level is determined by standard dosimetry processes. Other accelerators such as a van der Graaf or resonating transformer may be used. The radiation is not limited to electrons from an accelerator since any ionizing radiation may be used.

[0115] The heat-shrinkable, multilayer film in the packaging article can be fully coextruded, or prepared using an extrusion-coating process. Optionally, an annular extrudate (herein also referred to as a "tape") can be irradiated before the additional layers are extrusion coated onto the substrate tape. Irradiation produces a stronger polymer network by crosslinking the polymer chains. Extrusion-coating allows a portion of the final multilayer structure to be crosslinked by irradiation (and thereby strengthened), in combination with avoiding irradiation of, for example, a layer of polyvinylidene chloride applied to the substrate via extrusion coating. Irradiation of polyvinylidene chloride is undesirable because

irradiation can cause degradation of polyvinylidene chloride. Extrusion coating and irradiation are disclosed in U.S. Patent No. 4,278,738, to Brax et al. In the multilayer, heat-shrinkable film, all of the film layers can be arranged symmetrically with respect to the polymeric composition of each film layer. In addition, all of the film layers can be arranged symmetrically with respect to both composition and thickness. In one embodiment, the seal layer is thicker than the second outer layer. The seal layer can have a thickness of from 110% to 300% of the thickness of the second outer layer, or from 150% to 250% of the thickness of the second outer layer.

[0116] One heat-shrinkable multilayer film from which the packaging article can be made comprises seven layers in the order: 1/2/3/4/5/6/7. The first layer is an outer food-contact layer and seal layer, and comprises homogeneous ethylene/alpha-olefin copolymer. The second layer comprising ethylene/methyl acrylate copolymer. The third layer comprises a blend of polyamide 6 with polyamide 6I,6T. The fourth layer comprises EVOH. The fifth layer comprises a blend of polyamide 6 with polyamide 6I,6T. The sixth layer comprises ethylene/methyl acrylate copolymer. The seventh layer comprises a blend of low density polyethylene and linear low density polyethylene. See Example 16, below.

[0117] Another heat-shrinkable film from which the packaging article can be made has the structure: seal / tie / barrier / blend of polyamide 6 and/or polyamide 6/66 with polyamide 6I6T / tie / outer abuse layer. The seal layer can contain ethylene/alpha-olefin copolymer or other polymer suitable for use in a seal layer. The tie layers can contain an anhydride-modified ethylene/alpha-olefin copolymer or other suitable polymer for use in a tie layer. The barrier layer can contain EVOH or any other suitable polymer for use in a barrier layer. The outer abuse layer can contain polyester or any other suitable polymer for use in an outer abuse layer, e.g., polyolefin or polyamide, particularly high density polyethylene or linear low density polyethylene.

[0118] Another heat-shrinkable multilayer film from which the packaging article can be made comprises three layers in the order: 1/2/3. The first layer is an outer food-contact layer that also serves as a seal layer. The first layer comprises a blend of ethylene/vinyl acetate copolymer, linear low density polyethylene, and homogeneous ethylene/alpha-olefin copolymer. The second layer comprising polyvinylidene chloride. The third layer comprises a blend of ethylene/vinyl acetate copolymer, linear low density polyethylene, and homogeneous ethylene/alpha-olefin copolymer. See Example 12, below.

[0119] Another heat-shrinkable multilayer film from which the packaging article can be made comprises seven layers in the order: 1/2/3/4/5/6/7. The first layer that is an outer food-contact layer and that also serves as a seal layer. The first layer comprises a blend of homogeneous ethylene/alpha-olefin copolymer and linear low density polyethylene. The second layer comprises a blend of heterogeneous ethylene/alpha-olefin copolymer and ethylene/vinyl acetate copolymer. The third layer comprises ethylene/vinyl acetate copolymer. The fourth layer comprises polyvinylidene chloride. The fifth layer comprises ethylene/vinyl acetate copolymer. The sixth layer comprises a blend of heterogeneous ethylene/alpha-olefin copolymer and ethylene/vinyl acetate copolymer. The seventh layer comprises a blend of homogeneous ethylene/alpha-olefin copolymer and linear low density polyethylene. See Examples 1 and 2, below.

[0120] FIG.s 1A and 2 together illustrate a schematic of end-seal bag 10, in a lay-flat position. End-seal bag 10 can be made from a seamless film tubing. FIG. 2 is a transverse cross-sectional view of end-seal bag 10 of FIG. 1A, taken through section 2-2 of FIG. 1A. Viewing FIG.s 1A and 2 together, end-seal bag 10 comprises heat-shrinkable bag film 11, bag top edge 12 defining an open top, folded first side edge 13, folded second side edge 14, bottom edge 15, and end seal 16. End seal 16 is commonly referred to as a "factory seal" because it is a seal made at the bagmaking factory, rather than at the site where the bag is used to package a product. End-seal bag 10 further has first lay-flat side 17, second lay-flat side 18, and bag skirt 19. Bag skirt 19 is outward of end seal 16 (i.e., "outward" in that bag skirt 19 is further from the center of end-seal bag 10, and exterior of the product-containing cavity within end-seal bag 10). Bag skirt 19 includes a portion of first lay-flat side 17 and a portion of second lay-flat side 18. Bag skirt 19 further comprises first tear initiator 20 in first lay-flat side 17, and second tear initiator 21 (illustrated by a dashed line because it is underneath first lay-flat side 17) in second lay-flat side 18.

[0121] FIG. 1B illustrates a schematic of an alternative end-seal bag 10', in a lay-flat position. End-seal bag 10' can be made from a seamless film tubing. End-seal bag 10' comprises heat-shrinkable bag film 11', bag top edge 12' defining an open top, folded first side edge 13', folded second side edge 14', bottom edge 15', and curved end seal 16'. End-seal bag 10' further has first lay-flat side 17', second lay-flat side 18', and bag skirt 19'. Bag skirt 19' is outward of curved end seal 16'. Bag skirt 19' comprises first tear initiator 20' in first lay-flat side 17', and second tear initiator 21' (illustrated by a dashed line because it is underneath first lay-flat side 17') in second lay-flat side 18'. Both first tear-initiator 20' and second tear initiator 21' are slits through the bag that do not extend to either curved end seal 16' or bag bottom edge 15'. End seal bag 10' also has grip assist hole 35 in first lay-flat side 17' and second grip assist hole (not illustrated) in second lay-flat side 18'. These grip-assist holes facilitate gripping the bag for the manual tear initiation and manual tear propagation.

[0122] Grip assist holes can be sized to allow a user's finger(s) to be inserted therethrough to assist in gripping the film. Grip assist holes work in conjunction with the tear initiators, by providing a secure manual grip of the bag in a location designed to assist in generating tear initiation force along a tear line emanating from the tear initiators.

[0123] The grip assist hole in a first lay-flat side of the packaging article can overlap or coincide with the grip assist

hole in a second lay-flat side of the packaging article. While grip assist holes can have any desired shape (e.g., round, rectangular, square, triangular, pentagonal, hexagonal, etc.), preferably the holes are round, or any "corners" on the holes are rounded, to reduce the presence of stress concentration points that could cause a tear to initiate from the grip assist hole, as an objective is to have the tear initiated from the tear initiator, with the tear running to an opposite side edge of the bag.

[0124] In one embodiment, the grip-assist holes can be made by cutting through both lay-flat sides of the packaging article to remove a piece of film to form the holes. However, this process is more difficult to carry out, and it produces small, loose pieces of film corresponding with the size of the cut hole. These pieces of film may lodge inside the packaging article and thereafter adhere to a food product placed in the packaging article, which of course is an undesirable result. In order to prevent the production of a small, loose pieces of film, a cut can be made in the film in a shape that corresponds with a "partial hole cut", i.e., a cut through the film to make a portion of the hole, the cut not being complete so that a hole is formed. Such a cut leaves a "hanging chad" so that no separated small pieces of film are produced by the cut.

[0125] FIG. 1B and FIG. 1C each illustrate hanging chad 36 formed by the partial hole cut made in bag 10'. As illustrated in FIG. 1C, hanging chad 36 is formed by a cut having endpoints 63 and 64. It has been found that leaving hanging chad 36 connected to film 11' by a the film connecting cut endpoints 63 and 64 results in a tear emanating from tear initiation cuts 20' and 21', with the tear running through seal 16' and through the length of bag 11'. On the other hand, if a hanging chad is formed by a cut as illustrated in FIG. 1D, or FIG. 1E, or FIG. 1F, use of the partial hole cut as a grip assistors results in a tear that likely will not emanate from tear initiation cuts 20' and 21', but rather is likely to initiate a tear from the partial hole cut towards side edge 13' or towards bottom edge 15', as illustrated by the dashed lines in each of FIG. 1D, 1E, and 1F.

[0126] Hanging chad 36 can be made so that it is connected to film 11' at a region oriented towards tear initiation cuts 20' and 21', as illustrated in FIG. 1B and FIG. 1C. The cut that forms hanging chad 36 can have endpoints that, if connected by a line, provide a line that is parallel to side edge 13' and/or parallel to tear initiation cuts 20' and 21', or by a line within plus or minus 30 degrees of being parallel to side edge 13' and/or tear initiation cuts 20' and 21', or by a line within plus or minus 25 degrees of being parallel to side edge 13' and/or tear initiation cuts 20' and 21', or by a line within plus or minus 20 degrees of being parallel to side edge 13' and/or tear initiation cuts 20' and 21', or by a line within plus or minus 15 degrees of being parallel to side edge 13' and/or tear initiation cuts 20' and 21', or by a line within plus or minus 10 degrees of being parallel to side edge 13' and/or tear initiation cuts 20' and 21', or by a line within plus or minus 5 degrees of being parallel to side edge 13' and/or tear initiation cuts 20' and 21', or by a line within plus or minus 3 degrees of being parallel to side edge 13' and/or tear initiation cuts 20' and 21', or by a line within plus or minus 2 degrees of side edge 13' and/or tear initiation cuts 20' and 21'.

[0127] FIG.s 3 and 4 together illustrate a schematic of side-seal bag 22, in a lay-flat position. Side-seal bag 22 can be made from a seamless film tubing. FIG. 4 is a transverse cross-sectional view of side-seal bag 22 of FIG. 3, taken through section 4-4 of FIG. 3. Side-seal bag 22 comprises heat-shrinkable bag film 23, top edge 24 defining an open top, folded bottom edge 25, first side seal 26, and second side seal 27. Side-seal bag 22 has first lay-flat side 28, second lay-flat side 29, first bag skirt 30, and second bag skirt 31. First bag skirt 30 is outward of first side seal 26 and second bag skirt 31 is outward of second side seal 27. First bag skirt 30 includes a portion of first lay-flat side 28 and a portion of second lay-flat side 29. First bag skirt 30 further comprises first tear initiator 31 in first lay-flat side 28, and second tear-initiator 33 (illustrated by a dashed line because it is underneath first lay-flat side 28) in second lay-flat side 29.

[0128] FIG. 5 illustrates a schematic of alternate side-seal bag 70, also in lay-flat position. Alternate side-seal bag 70 can be made from a seamless film tubing. Alternate side-seal bag 70 comprises heat-shrinkable bag film 71, top edge 72 defining an open top, folded bottom edge 73, first side seal 74, second side seal 75, and bottom seal 76. Alternate side-seal bag 70 has first lay-flat side 77, second lay-flat side 78, first bag skirt 79, second bag skirt 80, and third bag skirt 81. First bag skirt 79 is outward of first side seal 74. Second bag skirt 80 is outward of second side seal 75. Third bag skirt 81 is outward of bottom seal 76. Third bag skirt 81 includes a portion of first lay-flat side 77 and a portion of second lay-flat side 78. Third bag skirt 81 further comprises first tear initiator 82 in first lay-flat side 77, and second tear initiator 83 (illustrated by a dashed line because it is underneath first lay-flat side 77) in second lay-flat side 78.

[0129] Figures 6A through 6L illustrate enlarged cutaway portions of various embodiments of for a heat-shrinkable end-seal bag such as the bag illustrated in FIG. 1 and FIG. 2.

[0130] In FIG. 6A, bag 10A has end seal 16A and bag skirt 19A in first and second lay-flat sides of bag 10A. First lay-flat side 17A of bag 10A has slit 20A, and second lay-flat side 18A of bag 10A has coinciding slit 21A.

[0131] In FIG. 6B, bag 10B has end seal 16B and bag skirt 19B in first and second lay-flat sides of bag 10B. First lay-flat side 17B of bag 10B has V-notch 20B, and second lay-flat side 18B of bag 10B has coinciding V-notch 21B.

[0132] In FIG. 6C, bag 10C has end seal 16C and bag skirt 19C in first and second lay-flat sides of bag 10C. First lay-flat side 17C of bag 10C has round notch 20C, and second lay-flat side 18C of bag 10C has coinciding round notch 21C.

[0133] In FIG. 6D, bag 10D has end seal 16D and bag skirt 19D in first and second lay-flat sides of bag 10D. First lay-flat side 17D of bag 10D has rectangular notch 20D, and second lay-flat side 18D of bag 10D has coinciding rectangular notch 21D.

[0134] In FIG. 6E, bag 10E has end seal 16E and bag skirt 19E in first and second lay-flat sides of bag 10E. First lay-flat side 17E of bag 10E has slit hole 20E, and second lay-flat side 18E of bag 10E has coinciding slit hole 21E.

[0135] In FIG. 6F, bag 10F has end seal 16F and bag skirt 19F in first and second lay-flat sides of bag 10F. First lay-flat side 17F of bag 10F has round hole 20F, and second lay-flat side 18F of bag 10F has coinciding round hole 21F.

[0136] In FIG. 6G, bag 10G has end seal 16G and bag skirt 19G in first and second lay-flat sides of bag 10G. First lay-flat side 17G of bag 10G has pointed oval hole 20G, and second lay-flat side 18G of bag 10G has coinciding pointed oval hole 21G.

[0137] In FIG. 6H, bag 10H has end seal 16H and bag skirt 19H in first and second lay-flat sides of bag 10H. First lay-flat side 17H of bag 10H has rectangular hole 20H, and second lay-flat side 18H of bag 10H has coinciding rectangular hole 21H.

[0138] In FIG. 6I, bag 10I has end seal 16I and bag skirt 19I in first and second lay-flat sides of bag 10I. First lay-flat side 17I of bag 10I has slit 20I and grip-assist hole 35I, and second lay-flat side 18I of bag 10I has coinciding slit 21I and coinciding grip-assist hole 36I.

[0139] In FIG. 6J, bag 10J has end seal 16J and bag skirt 19J in first and second lay-flat sides of bag 10J. First lay-flat side 17J of bag 10J has slit 20J and grip-assist holes 35J and 37J, and second lay-flat side 18J of bag 10J has coinciding slit 21J and coinciding grip-assist holes 36J and 38J.

[0140] In FIG. 6K, bag 10K has end seal 16K and bag skirt 19K in first and second lay-flat sides of bag 10K. First lay-flat side 17K of bag 10K has slit 20K and grip-assist tab 39K, and second lay-flat side 18K of bag 10K has coinciding slit 21K and coinciding grip-assist tab 40K.

[0141] In FIG. 6L, bag 10L has end seal 16L and bag skirt 19L in first and second lay-flat sides of bag 10L. First lay-flat side 17L of bag 10L has slit 20L and grip-assist tabs 39L and 41L, and second lay-flat side 18L of bag 10L has coinciding slit 21L and coinciding grip-assist tabs 40L and 42L.

[0142] FIGs. 6M, 6N, 6O, 6P, 6Q, 6R, 6S, 6T, 6U, 6V, 6W, 6X, 6Y, 6Z, 6AA, 6BB, 6CC, 6DD, 6EE, and 6FF are enlarged detailed views of various alternative embodiments including tear initiator, with most of these embodiments further including a grip assister. The grip assister is illustrated as a chadless-hole in FIG.s 6M, 6Q, 6U, 6BB, 6CC, and 6DD. The grip assister is illustrated as a hole with hanging chad in FIGs. 6N, 6O, 6P, 6R, 6S, 6T, 6V, 6W, 6X, 6Y, and 6FF.

[0143] It has been found that tear initiation can be generated with less force if the tear initiator is a slit angled relative to the side edge of the packaging article, i.e., into the packaging article, as illustrated in, for example, FIG. 6M. The slit can be angled from 1 to 45 degrees off of the machine direction, or angled from 3 to 30 degrees, or angled from 5 to 25 degrees, or angled from 10 to 20 degrees, or angled about 15 degrees.

[0144] A plurality of the heat-shrinkable end-seal bags of can be supplied individually in a container, or as a set of individual bags in shingled relationship on one or more tapes in accordance with U.S. Patent No. 4,113,139. Alternatively, a plurality of bags can be provided as a continuous strand of serrated bags, as illustrated in FIG.s 7A, 7B, and 7C. The continuous strands of bags in these figures are end-seal bags connected to one another in end-to-end, with a tear line of perforations being present so that bags can be torn off of the strand. FIG. 7A illustrates a portion of an elongate strip composed of a large number of end seal bags 65 made from a continuous seamless film tubing. Each end-seal bag has first side edge 67, second side edge 69, bottom seal 71, a bottom edge connected to top edge of adjoining bag along frangible tear line 73 formed by perforations through both lay-flat sides of the seamless film tubing. Each end-seal bag 65 is also provided with tear initiator 75 and grip assister 77, in the form of a hole through each lay-flat side of the bag. One or both of the holes can be made with a hanging chad therein, as described above.

[0145] FIG. 7B illustrates an alternative set of bags 65' also made from a continuous seamless film tubing. Each end-seal bag 65' has first side edge 67, second side edge 69, curved bottom seal 71', a curved bottom edge connected to a curved top edge of the adjoining bag along curved tear line 73' formed by perforations through both lay-flat sides of the seamless film tubing. Each end-seal bag 65' is also provided with tear initiator 75, and grip assister 77 in the form of a hole through each lay-flat side of the bag.

[0146] FIG. 7C illustrates an alternative set of bags 65" also made from a continuous seamless film tubing. Each end-seal bag 65" has first side edge 67, second side edge 69, curved bottom seal 71', and straight bottom edge connected to a straight top edge of the adjoining bag along straight tear line 73 formed by perforations through both lay-flat sides of the seamless film tubing. Each end-seal bag 65" is also provided with tear initiator 75, and grip assister 77 in the form of holes through each lay-flat side of the bag.

[0147] The combination of the straight tear line 73 and the curved bottom seal 71' in the strand of serrated bags illustrated in FIG. 7C, provide extra space for the tear initiators and manual grip assisters while at the same time providing a curved seal to better fit a variety of meat products to be packaged in the shrinkable bags. Otherwise, the tear initiators and the manual grip assisters require greater bag skirt length (e.g., the bags in FIG. 7A and 7B) to provide the same amount of space for the tear initiators and grip assisters. Moreover, straight tear line 73 provides bags that avoid the curvature at the open top end of the bag. Curved top edge of the packaging articles of a curved edge bag top as in the bags of FIG. 7B can cause problems on various commercial automated bag loaders that utilize pressurized air inflation to open the bag, as the pointed edge regions of the bags tend to fold inward. Moreover, the pointed edge of a curved

edge bag top may get out of the required alignment for use with suction cup style bag commercial bag opening devices.

[0148] Figure 8 illustrates a schematic of a preferred process for producing the multilayer heat-shrinkable film from which the packaging article can be made. In the process illustrated in Figure 8, solid polymer beads (not illustrated) are fed to a plurality of extruders 120 (for simplicity, only one extruder is illustrated). Inside extruders 120, the polymer beads are forwarded, melted, and degassed, following which the resulting bubble-free melt is forwarded into die head 122, and extruded through an annular die, resulting in tubing 124 which is 0.25 mm to 0.76 mm (10 to 30 mils) thick, more preferably 0.38 to 0.64 mm (15 to 25 mils) thick.

[0149] After cooling or quenching by water spray from cooling ring 126, tubing 124 is collapsed by pinch rolls 128, and is thereafter fed through irradiation vault 130 surrounded by shielding 132, where tubing 124 is irradiated with high energy electrons (i.e., ionizing radiation) from iron core transformer accelerator 134. Tubing 124 is guided through irradiation vault 130 on rolls 136. Preferably, tubing 124 is irradiated to a level of about 4.5 MR.

[0150] After irradiation, irradiated tubing 138 is directed through nip rolls 140, following which tubing 138 is slightly inflated, resulting in trapped bubble 142. However, at trapped bubble 142, the tubing is not significantly drawn longitudinally, as the surface speed of nip rolls 144 are about the same speed as nip rolls 140. Furthermore, irradiated tubing 138 is inflated only enough to provide a substantially circular tubing without significant transverse orientation, i.e., without stretching.

[0151] Slightly inflated, irradiated tubing 138 is passed through vacuum chamber 146, and thereafter forwarded through coating die 148. Second tubular film 150 is melt extruded from coating die 148 and coated onto slightly inflated, irradiated tube 138, to form two-ply tubular film 152. Second tubular film 150 preferably comprises an O₂-barrier layer, which does not pass through the ionizing radiation. Further details of the above-described coating step are generally as set forth in U.S. Patent No. 4,278,738, to BRAX et. al.,.

[0152] After irradiation and coating, two-ply tubing film 152 is wound up onto windup roll 154. Thereafter, windup roll 154 is removed and installed as unwind roll 156, on a second stage in the process of making the tubing film as ultimately desired. Two-ply tubular film 152, from unwind roll 156, is unwound and passed over guide roll 158, after which two-ply tubular film 152 passes into hot water bath tank 160 containing hot water 162. The now collapsed, irradiated, coated tubular film 152 is submersed in hot water 162 (having a temperature of about 99°C (210°F)) for a retention time of at least about 5 seconds, i.e., for a time period in order to bring the film up to the desired temperature for biaxial orientation. Thereafter, irradiated tubular film 152 is directed through nip rolls 164, and bubble 166 is blown, thereby transversely stretching tubular film 152. Furthermore, while being blown, i.e., transversely stretched, nip rolls 168 draw tubular film 152 in the longitudinal direction, as nip rolls 168 have a surface speed higher than the surface speed of nip rolls 164. As a result of the transverse stretching and longitudinal drawing, irradiated, coated biaxially-oriented blown tubing film 170 is produced, this blown tubing preferably having been both stretched in a ratio of from about 1:1.5 - 1:6, and drawn in a ratio of from about 1:1.5-1:6. More preferably, the stretching and drawing are each performed a ratio of from about 1:2 - 1:4. The result is a biaxial orientation of from about 1:2.25 - 1:36, more preferably, 1:4 - 1:16. While bubble 166 is maintained between pinch rolls 164 and 168, blown tubing film 170 is collapsed by rolls 172, and thereafter conveyed through nip rolls 168 and across guide roll 174, and then rolled onto wind-up roll 176. Idler roll 178 assures a good wind-up.

[0153] FIG. 9 illustrates a perspective view of package 50 made by placing a meat product into an end-seal bag having end seal 51, evacuating the atmosphere from within the bag, and sealing the bag closed with packing seal 55, and thereafter trimming off and discarding the excess bag length. Bag skirt 52 has slit 53 therein as the tear initiators for initiating manual opening of package 50. Slit 53 extends in the machine direction, toward end seal 51 from bag bottom edge 54.

[0154] FIG. 10 illustrates package 50' at an intermediate stage of the manual opening process, i.e., after having initiated tearing of the bag for a distance of about 25% of the length of the bag, revealing meat product 58. Linear, machine-direction tear 56 has been manually propagated through end seal 51 and down the length of the end-seal bag. Note that machine direction tear 56 is not terminated by being propagated to side edge 57 of package 50.

[0155] FIG. 11 illustrates package 50" at a final stage in the manual opening process, i.e., after having torn the end-seal bag for a distance corresponding with over 90% of its length, toward the opposite edge of the packaging article of the package, exposing enough of the length of meat product 58 that the product can be readily removed from package 50". Linear, machine-direction tear 56' has been manually propagated through end seal 51 and down the length of the end-seal bag.

[0156] FIG. 12 illustrates a perspective view of comparative package 60 after tearing has been initiated and propagated almost to completion, i.e., almost to termination at side edge 61, about 15 to 20 percent down the length of the package. Package 60 is representative of most heat-shrinkable bags in the marketplace today, which, if provided with a tear initiator in the bag skirt, undergo this type of "dog-leg" manual tear 62 initiation and propagation to side edge 61, whereby meat product 58 cannot be readily removed from torn package 60.

[0157] FIG. 13 illustrates a schematic of an alternative heat-shrinkable end-seal bag 10, in a lay-flat position. End-seal bag 10 comprises heat-shrinkable bag film 11, bag top edge 12 defining an open top, folded first side edge 13, folded second side edge 14, bottom edge 15, and end seal 16. End-seal bag 10 further has bag skirt 19 outward of end

seal 16. The end-seal bag has slit 20 that is a tear initiator in the first lay-flat side of the bag, and slit 21 that is a tear initiator in the second lay-flat side of the bag. The end-seal bag also has hole 120 that is a grip assister in the first lay-flat side of the bag, and hole 123 that is a grip assister in the second lay-flat side of the bag. The tear initiator and the grip assister are located near bag top edge 12. When a product is placed in the bag and the bag sealed closed so that it surrounds the product, the tear initiator and the grip assister will then be located in the excess bag length known as the "bag tail" or as the bag "header". Frequently, the bag tail provides more area for inclusion of the tear initiator and the grip assister than bag skirt 19.

[0158] FIG. 14 illustrates a schematic view of alternative side-seal bag 22 in lay-flat configuration. Side-seal bag 22 comprises top edge 24 defining an open top, folded bottom edge 25, first side seal 26, and second side seal 27, transverse bottom seal 34, first lay-flat side 28, second lay-flat side 29, first bag skirt 30, and second bag skirt 31, and third bag skirt 204. First bag skirt 30 is outward of first side seal 26, second bag skirt 31 is outward of second side seal 27, and third bag skirt 204 is outside of bottom seal 34. Third bag skirt 204 comprises first tear initiator 201 and first grip assister 203, each of which is present in both lay-flat sides of bag 22. First bag skirt 30 comprises second tear initiator 202 and second grip assister 204, each of which are present in both lay-flat sides of bag 22. After a product is placed in the bag, and the bag sealed closed, side-seal bag 22 can be opened by making a first tear propagated from first tear initiator 201, the tear being propagated for the full length of bag 22, thereby opening the bag for removal of the product. Thereafter, side-seal bag 22 can undergo a second tear propagated from second tear initiator 202, the second tear being propagated across the full remaining width of bag 22, enhancing the ease of removal of the product from the opened package.

[0159] FIG. 15 illustrates a schematic view of alternative side-seal bag 22' in lay-flat configuration. Bag 22' has top edge 24 defining an open top, folded bottom edge 25, first side seal 26, and second side seal 27, transverse bottom seal 34, first lay-flat side 28, second lay-flat side 29, first bag skirt 30, second bag skirt 31, and third bag skirt 204. First bag skirt 30 is outward of first side seal 26, second bag skirt 31 is outward of second side seal 27, and third bag skirt 204 is outside of bottom seal 34. Third bag skirt 204 comprises first tear initiator 201 and first grip assister 203, each of which is present in both lay-flat sides of bag 22. First bag skirt 30 comprises second tear initiator 206 and second grip assister 208, each of which are present in both lay-flat sides of bag 22'. After a product is placed in the bag, and the bag sealed closed, the package made from bag 22' can be opened by making a first tear propagated from first tear initiator 201, the tear being propagated for the full lengths of bag 22', thereby opening the bag for removal of the product. Thereafter, bag 22' can undergo a second tear propagated from second tear initiator 206, the second tear being propagated across the full remaining width of bag 22', thereby enhancing the ease of removal of the product from the opened package. Unlike bag 22 of FIG. 14, the order of which tear is made first is not important in the opening of bag 22'.

[0160] FIG. 16 illustrates a schematic view of alternative side-seal bag 22" in lay-flat configuration. Bag 22" has top edge 24 defining an open top, folded bottom edge 25, first side seal 26, and second side seal 27, transverse bottom seal 34, first lay-flat side 28, second lay-flat side 29, first bag skirt 30, second bag skirt 31, and third bag skirt 204. First bag skirt 30 is outward of first side seal 26, second bag skirt 31 is outward of second side seal 27, and third bag skirt 204 is outward of bottom seal 34. Near the top edge 24 of bag 22", in a region intended to be a bag tail after a product is placed into bag 22" and a seal made across bag 22" so that the product is fully enclosed within the bag, is first tear initiator 207 and first grip assister 209, each of which are present in both lay-flat sides of bag 22". First bag skirt 30 comprises second tear initiator 211 and second grip assister 213, each of which are present in both lay-flat sides of bag 22". After a product is placed in bag 22", and the bag sealed closed, the package made from bag 22" can be opened by making a first tear propagated from first tear initiator 207, the tear being propagated for the full lengths of bag 22", thereby opening the bag for removal of the product. Thereafter, bag 22" can undergo a second tear propagated from second tear initiator 211, the second tear being propagated across the full remaining width of bag 22", thereby enhancing the ease of removal of the product from the opened package.

[0161] FIG. 17 is a schematic of an apparatus for carrying out the process of placing tear initiators in the header region of a heat-shrinkable end-seal bag, with the tear initiators being made in the header during the packaging process. The tear initiators (and the optional grip assisters) can be made in the bag either before or after the product is placed into the packaging article, either before or after the bag is evacuated, and either before or after the heat seal is made to close the bag. Placing the tear initiators in the bag after the product is placed in the bag eliminates the potential for the tear initiator to cause the bag to tear during loading. Although the packaging article in FIG. 17 is an end-seal bag, the packaging article could be any packaging article in accordance with any one or more of the various aspects of the invention described above.

[0162] FIG. 17 illustrates a portion of vacuum chamber packaging machine 300, such as a series 8600 automated rotary chamber vacuum packaging machine from Cryovac, Inc. After end-seal bag 302 having product 304 therein is placed into the opened vacuum chamber, vacuum chamber lid 306 comes down to close the vacuum chamber and clamp across the top (header) portion of bag 302, so that bag 302 is clamped between chamber lid 306 and vacuum chamber base 308. For simplicity, only small portions of chamber lid 306 and chamber base 308 are illustrated in FIG. 17. For more detailed information on this machine, see U.S. Pat. No. 4,550,548.

[0163] Once bag 302 is clamped into position and chamber lid 306 closed, one or more holes are punched through

both sides of the header portion of bag 302 by the downward movement of piercing knife 310, which thereafter is retracted to the position illustrated. These holes allow atmosphere to readily evacuate bag 302 as the atmosphere is evacuated from the closed vacuum chamber. After atmospheric evacuation has been completed, seal seat 312 moves downward (i.e., into the position illustrated in FIG. 17) so that bag 302 is clamped between heat seal wires 314 and heat seal platen 316. Heat seal wires 314 are heated to produce a heat seal across bag 302, resulting in the closure of bag 302 and the formation of a packaged product. Shortly thereafter, tear-initiator knife 318 is activated downward and then retracted, with tear-initiator knife 318 piercing both sides of bag 302 to produce machine-direction tear initiators in each side of the header of bag 302. Optionally, a separate grip-assister knife (not illustrated, but preferably located alongside and spaced a short distance from knife 318) is activated downwardly and then retracted, so that it cuts through both sides of the header of bag 302, to form a grip assister in each side of bag 302. Cut-off knife 320 is then downwardly activated to cut off the excess length from the header of bag 302. Then the chamber is opened and the now easy-open packaged product is removed from the chamber.

[0164] While the process described above with respect to FIG. 17 could be used to make an easy open packaged product, alternatively the process could be carried out on vertical form fill and seal machines or on horizontal form fill and seal machines, to produce easy open packaged products. Typically, vertical and horizontal form fill and seal processes are not carried out under vacuum. Such equipment, packages, and processes are set forth in USPN 4,905,452, USPN 4,861,414, and USPN 4,768,411.

[0165] The tear initiators (and the optional grip assisters) can also be designed to facilitate automated opening, in addition to being designed to facilitate manual tearing to open the package. Automated tearing devices include hooks actuated by pneumatic actuators (air or hydraulic or electric), divergent hooks on chain conveyors, motorized hooks, and clamps in place of hooks.

[0166] FIG. 18 illustrates a schematic of packaged product 330 in which product 332 is packaged inside packaging article 334 having factory seal 336 and customer seal 338. Packaging article 334 includes header 340 with tear initiator 342 through each side of the package and with pairs of grip assisters 344 and 346, each pair being through both sides of the package, with one pair being on a first side of tear initiator 342, and the other pair being on the other side of tear initiator 342. In this manner, pairs of hooks or clamps can grip the package utilizing grip assisters 344 and 346 to thereafter automatically open packaging article 334. A robot, or another device that grips and tears the package open, or hanging the packaged product on hooks on diverging tracks, could be used to automatically open package 334.

[0167] FIG. 19 illustrates side-seal bag 350 having first side seal 352, second side seal 354, skirt sides 356 and 357 outward of first side seal 352, skirt sides 358 and 359 outward of second side seal 354, open top 360, and folded bottom edge 362. Skirt side 356 has a plurality of tear initiators 364 therein, and skirt side 357 has therein a plurality of tear initiators 366 (illustrated with dotted lines). The plurality of tear initiators 364 are positioned at intervals along skirt side 356, and the plurality of tear initiators 366 are positioned at intervals along skirt side 357. Each individual tear initiator 364 in skirt side 356 is paired with an individual tear initiator 366 in skirt side 357, so that paired sets of tear initiators 364 and 366 are provided. In the embodiment of FIG. 19, bag 350 is shown in lay-flat configuration, with each individual tear initiator 364 aligning directly over each individual tear initiator 366.

[0168] Upon packaging a product in bag 350 and sealing bag 350 closed and shrinking bag 350 around the product inside, a tearing force exerted at a paired set of individual tear initiators 364 and 366 simultaneously initiates two machine-direction tears, each tear passing through heat seal 352 and thereafter propagating across the film along a line traversing a portion of the film that corresponds with what was a single lay-flat side of bag 350 before the shrinking of the film around the product. The tears are propagated through skirt sides 356 and 357, through heat seal 352, across the package, through seal 354, and then through skirt sides 358 and 359, so that a portion of the film can be detached from the remainder of the film, in order to expose a portion of the product and/or allow the product to be removed from the package. Of course, if the film has been shrunk tightly around the product, the removal of a portion of the film leaves the remainder of the film wrapped tightly around the product, thereby preserving freshness. As is also apparent from FIG. 19, tear initiators 364 and 366 can be slits oriented perpendicular to seal 352. As such, tear initiators 364 and 366 are oriented directly in line with the machine direction in which the film was produced.

[0169] In FIG. 19, skirt sides 356 and 357 are each provided with a plurality of tear initiators so that upon packaging a product within bag 350 and shrinking the film around the product, two tears can be initiated from a first paired set of tear initiators 364 and 366, i.e., a pair of tear initiators close to either folded bottom edge 362 or the transverse heat seal (not illustrated) made across the top of bag 350 to close bag 350 after the product is placed into bag 350. The two tears can be propagated across the film in tears corresponding with the width of the package. Each tear is made across what was originally one lay-flat side of bag 350. The result of tearing all the way across the package is that a portion of the film making up the package is removed to expose a portion of the product, while leaving a remainder of the product covered by the remaining portion of the film making up the package. In this manner, most or substantially all of the unused portion of the product can remain covered by the film, with the remainder of the product thereby retaining greater freshness than if it is exposed to the environment, including handling.

[0170] If desired, the now-exposed end of the remainder of the product can be covered with a separate cover, such

as a separate piece of film, such as stretch film or the like. As more product is desired for consumption, the next pair of individual tear initiators in the sequence can be utilized to make another tear across the entirety of the package, and more product removed, and the process repeated, until all of the product is consumed.

[0171] FIG. 20 illustrates a portion of an end-seal bag 370 having end seal 372, first folded side edge 374, second folded side edge 376, bottom edge 378, skirt 379, a plurality of first tear initiators 380 in a first side of skirt 379, a plurality of second tear initiators 382 (illustrated with dotted lines) in a second side (not illustrated) of skirt 379, with the plurality of first tear initiators 380 being positioned at intervals along the first side of skirt 379, and the plurality of second tear initiators 382 being positioned at intervals along the second side of skirt 379. Each individual tear initiator 380 in the first side of skirt 379 is paired with an individual tear initiator 382 in the second side of skirt 379, to together provide a paired set of two tear initiators. When end-seal bag 370 is in the lay-flat configuration, each of the first tear initiators 380 aligns directly over a corresponding second tear initiator 382. After placing a product in the bag and sealing it closed under vacuum and shrinking the bag around the product, a manual tearing action at the location of a single pair of tear initiators 380 and 382 causes the simultaneous initiation of two machine-direction tears down the length of each lay-flat side of bag 350. In the embodiment of FIG. 20, end-seal bag 370 is showing in lay-flat configuration, with each individual tear initiator 384 aligning directly over each individual tear initiator 386. Each tear passes through heat seal 372 and thereafter propagates down the length of bag 370 along a line traversing a portion of the film that corresponds with what was a single lay-flat side of bag 370 before the shrinking of the film around the product. The tears thereafter pass through the top seal (not illustrated) as well as through the header (not illustrated) above the top seal, so that a portion of the film can be detached from the remainder of the film, exposing a portion of the product and/or allowing the product to be removed from the package. As in FIG. 19, in FIG. 20 skirt 379 is provided with a plurality of tear initiators for use in a manner analogous to the manner described above for FIG. 19.

[0172] FIG. 21 is an enlarged detailed view of a portion of side seal bag 390 having side seal 392 outward of which is skirt 391 having first tear initiator 396 on first side 394 and second tear initiator 400 on second side 398, with spot heat seals 402 and 404 at which first side 394 of skirt 391 is heat sealed to second side 398 of skirt 391. Those portions of the skirt 391 within spot seals 402 and 404 are heatset. Moreover, a small area of film surrounding the spot seals is also heatset, as the heat from the sealing operation generally radiates outward, heatsetting more film than just the bonded areas. After placing a product into bag 390 and evacuating the atmosphere from within bag 390 and sealing across the top of bag 390 to seal the product within the package, the packaged product is typically passed through a hot air tunnel to shrink the film around the product. Heatsetting reduces the tendency of skirt 391 to shrink during shrinking of the remainder of the film surrounding the product. Heatsetting also reduces the curling of skirt sides 394 and 398 during the shrinking of the film. The diminished curling and diminished shrink resulting from the heatsetting of portions of skirt 391 provides improved identification and utilization of tear initiators 396 and 400 by a consumer of the package.

[0173] FIG. 22 is an enlarged detailed view of a portion of side seal bag 406 having side seal 408 outward of which is skirt 410 having tear initiator 412 and skirt 414 having tear initiator 416, with spot heat seals 418 and 420 at which skirt 410 is heat sealed to skirt 414. As with the embodiment of FIG. 21, those portions of the films within spot seals 418 and 420 are heatset, as are small areas of film surrounding the spot seals. In addition, the embodiment of FIG. 22 has grip assisting holes having borders 422 and 424 in first skirt 410, and respective grip assisting holes having borders 426 and 428 in skirt 414. Grip assisting holes bounded by borders 422, 424, 426, and 428 provide locations that are easier to grip for the purpose of initiating tears from tear initiators 412 and 416.

[0174] FIG. 23 is an enlarged detailed view of a portion of side seal bag 430 having open top 431, folded bottom edge 433, side seal 432 outward of which is skirt 434 having a plurality of tear initiators 436, skirt 438 having a plurality of tear initiators 440, and a plurality of spot heat seals 442 and 444 on either side of each of tear initiators 436 and 440, at which skirt 434 is heat sealed to skirt 438. As with the embodiment of FIG. 21, those portions of the films within spot seals 442 and 444 are heatset, as are small areas of film surrounding spot seals 442 and 444. In addition, the embodiment of FIG. 23 has grip assisting holes having borders 446 on either side of each tear initiator 436 in first skirt 434, and respective grip assisting holes having borders 448 on either side of each tear initiator 440 in skirt 438. The embodiment of FIG. 23 provides multiple locations of paired tear initiators 436 and 440 so that portions of the package can be torn off, leaving a remainder of the film around the product in the bag. For purposes of simplicity, only two pairs of tear initiators are illustrated in FIG. 23.

[0175] FIG. 24 illustrates a perspective view of a portion of a comparative packaged product 450 made by placing a product into an end seal bag, after which the atmosphere is evacuated from the bag and the bag sealed closed with a heat seal made across the top of the bag (not illustrated), with the film having been shrunk tight against the product. The bag has a skirt (452) below end seal (454), with skirt (452) having two lay-flat sides, with each lay-flat side being provided with a tear initiator (456) therethrough. While the end seal bag is provided with tear initiators in the form of slits through each lay-flat side of the bag skirt, during shrinkage of the film the tear initiator slits take on the somewhat "pointed oval" shape of tear initiators 456, as illustrated in FIG. 24. The excess bag length has been trimmed off of the header (not illustrated) and the packaged product run through a shrink tunnel in which the film was heated and shrunk around the product. During shrinking of the film, skirt 452 undergoes substantially unrestrained free shrink and curling, thereby

partially or fully obscuring tear initiators from direct view, making it more difficult to find and use the tear initiators.

[0176] FIG. 25 illustrates a perspective view of a portion of a packaged product 460 also made using an end seal bag from which the atmosphere is evacuated and the bag sealed closed with a heat seal made across the top of the bag (not illustrated), with the film having been shrunk tight against the product. Skirt (462) extends below end seal (464), with skirt (462) having two lay-flat sides, with each lay-flat side being provided with a tear initiator (466 and 468, respectively). During the shrinking of the film, transverse shrinkage causes tear initiation slits to take on the somewhat pointed oval shape of tear initiators 466 and 468 of FIG. 25. Grip assisting holes defined by borders 470 and 474 are located on either side of tear initiator 466, and grip assisting holes defined by borders 472 and 476 are located on either side of tear initiator 468. The two lay-flat sides of skirt 462 are also heat sealed together at spot seals 478 and 480. In addition to providing a mechanical bond of the lay-flat sides to one another to resist curling, the film is heatset in the region of spot seals 470 and 472, and an area extending radially outward a short distance around each of spot seals 470 and 472 is also heatset. The heatsetting of these portions of skirt 462 reduces shrinking of the skirt during the shrinking of the film, causing skirt 462 to undergo less free shrink and curling than would occur without the heatsetting. As a result, it is apparent from FIG. 25 that tear initiators 466 and 468, as well as grip assisting holes defined by borders 470, 472, 474, and 476, are more readily identified and used by a consumer, due to less shrinkage and less curling, making it easier to find and use the tear initiators 466 and 468 than for the embodiment of FIG. 24.

[0177] FIG. 26 illustrates a perspective view of a portion of a packaged product 490 also made using an end seal bag from which the atmosphere is evacuated and the bag sealed closed with a heat seal made across the top of the bag (not illustrated), with the film having been shrunk tight against the product. As in the package of FIG. 25, packaged product 490 of FIG. 26 has skirt 492 extending below end seal (494), with skirt (492) having two lay-flat sides, each of which is provided with a tear initiator (496 and 498, respectively). Grip assisting holes defined by borders 500 and 502 are located on either side of tear initiator 496, and grip assisting holes defined by borders 504 and 506 are located on either side of tear initiator 498. The two lay-flat sides of skirt 462 are heat sealed together at four discrete spot seals: 508, 510, 512, and 514, each of which heatsets the film in the seal region as well as a region extending radially outward a short distance around each of the spot seals. The heatsetting of these portions of skirt 492 reduces shrinking of the skirt during the shrinking of the film, causing skirt 462 to undergo less free shrink and curling than would occur without the heatsetting. As a result, it is apparent from FIG. 26 that tear initiators 496 and 498, as well as grip assisting holes defined by borders 470, 472, 474, and 476, are even more readily apparent than in FIG. 25, making it still making it easier to find and use the tear initiators 466 and 468 than for the embodiment of FIG. 25.

[0178] FIG. 27 illustrates a perspective view of a portion of an alternative packaged product 520 also made using an end seal bag from which the atmosphere is evacuated and the bag sealed closed with a heat seal made across the top of the bag (not illustrated), with the film having been shrunk tight against the product. As in the package of FIG. 25, packaged product 520 of FIG. 27 has skirt 522 extending below end seal (524), with skirt (522) having two lay-flat sides, each of which is provided with a tear initiator (526 and 528, respectively). Grip assisting holes defined by borders 530 and 532 are located on either side of tear initiator 526, and grip assisting holes defined by borders 534 and 536 are located on either side of tear initiator 528. The two lay-flat sides of skirt 522 are heat sealed together at perimeter heat seal 538 that extends the full width of skirt 522 and is located near the bottom edge 540 of packaged product 520. Perimeter heat seal 540 heatsets the portion of the film in the seal region as well as a region extending outward a short in both directions from the seal itself.

[0179] The heatsetting of this portion of skirt 522 reduces shrinking of the skirt during the shrinking of the film, causing skirt 522 to undergo less free shrink and curling than would occur without the heatsetting. As a result, it is apparent from FIG. 27 that tear initiators 526 and 528, as well as grip assisting holes defined by borders 530, 532, 534, and 536, are in a configuration to be more easily seen by a consumer, and more readily used by a consumer. It also helps a consumer distinguish the design and intended use of the package. Less curling, together with the opening up of the tear initiation slits, makes it easier to place fingers through the grip assist holes. Less curling and the opening up of the tear initiation slits also makes it easier to utilize automated machinery to open the package. Heatsetting makes it easier to detect, find, and use tear initiators 526 and 528 as well as the grip assisting holes defined by borders 530, 532, 534, and 536. The heat setting of particular areas prevents shrink of the tab, makes them easier to grip, and allows the notches to open into an easily seen oval holes.

[0180] FIG. 28 illustrates a lay-flat schematic view of an alternative embodiment of a side-seal bag 550 having first side seal 552, second side seal 554, skirts 556 and 558 outward of first side seal 552, skirts 560 and 562 outward of second side seal 554, open top 564, and folded bottom edge 566. Skirt 556 has a plurality of first tear initiators 568 and skirt 558 has a plurality of second tear initiators (not illustrated), with the plurality of first tear initiators 568 being positioned at intervals along skirt 556, and the plurality of second tear initiators (not illustrated) being positioned at intervals along skirt 558. Each individual tear initiator 568 in skirt 556 is paired with an individual tear initiator (not illustrated) in skirt 558, to together provide a set of paired tear initiators. In FIG. 28, bag 550 is showing in lay-flat configuration, with each individual tear initiator 568 in skirt 556 being positioned directly over each individual tear initiator (not illustrated) in skirt 558. The film is heatset along the hatched perimeter area 570 of skirt 556 as well as a corresponding area (not illustrated)

of skirt 558. Moreover, the film is heatset at hatched areas 572 and 574 along each side of each tear initiator 568, as well as at corresponding areas (not illustrated) along each side of each corresponding tear initiator (not illustrated) in skirt 558. While heatset areas 570, 572, and 574 of skirt 556, as well as corresponding heatset areas (not illustrated) of skirt 558 can be heated only enough to reduce the shrink of the areas, heatset areas 570, 572, and 574 of skirt 556 and corresponding areas of skirt 558 can further be heat sealed to one another. The heatsetting (and also any heat sealing) results in reduced shrinkage of the heated regions, thereby making it easier to detect, find, and use tear initiators. In addition, skirts 556 and 558 can be provided with grip assisting holes (not illustrated) on one or both sides of the tear initiators.

Resins Utilized in the Examples

[0181] Unless otherwise indicated, the following listing of resins identifies the various resins utilized in Examples 1-35 below.

Resin code	Tradename	Generic Resin Name {additional information}	Density (g/cc)	Melt Index (dg/min)	Supplier
ION 1	Surlyn® 1702-1	Zinc neutralized ethylene methacrylic acid copolymer	0.940	14	DuPont
ION 2	Surlyn® 1650 SB	Zinc neutralized ethylene methacrylic acid copolymer + slip additive	0.950	1.55	DuPont
SSPE 1	Affinity® 1280G	Homogeneous ethylene/alpha-olefin copolymer	0.900	6.0	Dow
SSPE 2	Affinity® PL 1281G1	Homogeneous ethylene/octene copolymer	0.900 g/cc	6.0	Dow
SSPE3	Affinity® PL 1850G	Homogeneous ethylene/octene copolymer	0.902	3.0	Dow
SSPE4	Affinity® PF 1140G	Homogeneous ethylene/octene copolymer	0.8965g/cc	1.6	Dow
SSPE5	DPF 1150.03	Homogeneous Ethylene/octene copolymer	0.901	0.9	Dow
SSPE6	Exceed® 4518 PA	Homogeneous Ethylene/hexene copolymer	0.918	4.5	Exxon Mobil
VLDPE 1	XUS 61520.15L	Very low density polyethylene	0.903	0.5	Dow
VLDPE 2	Attane® 4203	Very low density polyethylene	0.905	0.80	Dow
VLDPE 3	Rexell® V3401	Very low density polyethylene	0.915	6.6	Huntsman
VLDPE 4	ECD 364	VLDPE (ethylene/hexene copolymer)	0.912	1.0	ExxonMobil
LLDPE 1	Dowlex® 2045.03	Linear Low Density Polyethylene	0.920	1.0	Dow
LLDPE 2	LL 3003.32	Heterogeneous Ethylene/hexene copolymer	0.9175	3.2	Exxon Mobil
HDPE	Fortiflex® T60-500-119	High density polyethylene	0.961	6.0	Ineos
Ion&Eva&Pb	Appel 72D799	Blend of ionomer, EVA, and polybutylene	0.932	3.7	DuPont

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(continued)

Resin code	Tradename	Generic Resin Name {additional information}	Density (g/cc)	Melt Index (dg/min)	Supplier
EVA&PP	Versify XUR- YM 2006268985	Blend of EVA and Polypropylene	0.89	3.0	Dow
RECLAIM	TO35B	Recycled multilayer film containing wide variety of polymers, including ionomer resin, ethylene homo- and co-polymers, propylene homo- and co-polymers, EVOH, polyamide, anhydride modified polymers, ionomer, antiblock, etc.	---	---	Sealed Air Corp
PP1	Inspire 112	Propylene homopolymer	0.9	0.4	Dow
PP2	Basell Pro-Fax PH835	Propylene homopolymer	0.902	34	Basell Polyolefins
PP3	PP3155	Propylene homopolymer	0.900	36	Exxon Mobil
PP4	Escorene® PP 3445	Propylene homopolymer	0.900	36.0	Exxon Mobil
PB	PB8640M	Butene homopolymer	0.908	1	Basell
					Polyolefins
ssPP	Eltex® P KS 409	Propylene/ethylene copolymer	0.900	5.5	Ineos
znPP	Escorene® PP9012E1	Propylene/ethylene copolymer	0.902	6.00	Ineos
EPC 1	Pro-Fas SA 861	Propylene/ethylene copolymer (single site catalyzed)	0.902	6.5	Lyondell -basell
Et-Pr TER	Vistalon 7800	Ethylene-propylene diene terpolymer	0.870	1.5	Exxon Mobil
MA-LLD 1	Tymor® 1228B	Maleic anhydride modified polyethylene {blended with linear low density polyethylene}	0.921	2.0	Rohm & Haas
MA-LLD 2	PX 3227	Maleic anhydride modified polyethylene {blended with linear low density polyethylene}	0.913	1.7	Equistar Division of Lyondell
MA-LLD 3	PX3236	Maleic anhydride modified polyethylene {blended with linear low density polyethylene}	0.922	2.00	Equistar Division of Lyondell
MA-EVA	Bynel® 3101	Acid/Acrylate Anhydride-Modified Ethylene/Vinyl Acetate Copolymer	0.943	3.2	DuPont
modPP	Admer® QB510A	Maleic anhydride modified polypropylene	0.900	3.2	Mitsui
modEVA	SPS-33C-3	Compounded modified EVA polymer blend	0.92	1.6	MSI Technology
Et-Norb 1	Topas® 9506X1	Ethylene norbornene copolymer	0.974	1.0	Topas Advanced Polymers Inc.

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(continued)

Resin code	Tradename	Generic Resin Name {additional information}	Density (g/cc)	Melt Index (dg/min)	Supplier
ET-Norb2	Topas® 8007 F-04	Ethylene norbornene copolymer	1.02	1.7	Topas Advance d Polymers Inc.
Nylon 1	Ultramid® B40	Polyamide 6	1.13	---	BASF
Nylon 2	Ultramid® B40LN01	Polyamide 6	1.14	---	BASF
Nylon 3	Ultramid® C33 01	Polyamide 6/66	1.13	---	BASF
Nylon 4	Grilamid XS 1392	Blend of Polyamide 6/12 and Polyamide 12	1.03	---	EMS-Grivory
EVA 1	Escorene® LD 713.93	Ethylene/vinyl acetate copolymer (14.4%VA)	0.933	3.5	Exxon Mobil
EVA 2	Escorene LD 318.92	Ethylene/vinyl acetate copolymer (8.7%VA)	0.93	2.0	Exxon Mobil
EVA 3	Escorene® LD 761.36	Ethylene/vinyl acetate copolymer (26.7%VA)	0.950	5.75	Exxon Mobil
EVA 4	Escorene® LD 705.MJ	Ethylene/vinyl acetate copolymer (12.8% VA)	0.935	0.4	Exxon Mobil
EVA 5	Escorene® LD 721.IK	Ethylene/vinyl acetate copolymer (18.5% VA)	0.942	2.55	Exxon Mobil
EVA 6	Elvax® 3175	Ethylene/vinyl acetate copolymer (28% VA)	0.950	6	DuPont
EVA 7	PE 1651	Ethylene/vinyl acetate copolymer (6.5% VA)	0.928	0.5	Flint Hills Resource s LP
EBA	SP 1802	Ethylene/butyl acrylate copolymer (22.5% BA)	0.928	6	Eastman Chemical
EVOH	Soarnok® ET3803	Hydrolyzed ethylene vinyl acetate copolymer (EVOH with 38 mol % ethylene)	1.17	3.2	Nippon Gohsei
PV dC	Saran® 806	Vinylidene chloride / methyl acrylate copolymer	1.69	---	Dow
Sty-But	Styrolux 656C	Styrene/butadiene copolymer	1.02	99	BASF
AOX	10555	Antioxidant in linear low density polyethylene	0.932	2.5	
SLIP 1	FSU 93E	Slip and antiblock in low density polyethylene	0.975	7.5	Schulma n
SLIP 2	1062 Ingenia	Slip masterbatch amide wax (erucamide) in linear low density polyethylene	0.92	2	Ingenia Polymers
WCC	11853	White color concentrate in linear low density polyethylene	1.513	2.90	Ampacet

(continued)

Resin code	Tradename	Generic Resin Name {additional information}	Density (g/cc)	Melt Index (dg/min)	Supplier
CCC	130374	Cream color concentrate in low density polyethylene	---	---	Ampacet
BCC	16417-81 blue	Blue color concentrate masterbatch	0.951	---	Colortec h
ABConc	18042 antiblock concentrate	Optical brightener in linear low density polyethylene	0.92	---	Teknor Color
procAID 1	100458	Processing aid: fluoropolymer in polyethylene	0.93	2.3	Ampacet
procAID2	IP 1121	Processing aid: fluoropolymer in linear low density polyethylene	0.92	2	Ampacet

Example 1 (working)

[0182] An end-seal bag approximately 178 to 203 mm (7 to 8 inches) wide (lay-flat) and approximately 16 inches long was made from a coextruded, multilayer, heat-shrinkable film produced utilizing the apparatus and process set forth in FIG. 8, described above. The multilayer film had a total of 7 layers, in the following order, with the thickness of each layer of the film shown in mils in the bottom row of each column representing a layer of the multilayer structure. The composition of each layer is provided in the second row, with each code corresponding with the composition in the resin table set forth above.

Example 1

[0183]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
80% SSPE1 20% LLDPE 2	70% VLDPE2 30% EVA1	100% EVA1	PVDC	100% EVA3	70% VLDPE1 30% EVA1	85% SSPE3 15% LLDPE 1
0.42 mil	0.76 mil	0.08 mil	0.18 mil	0.13 mil	0.25 mil	0.13 mils
1 mil = 0.0254 mm						

[0184] Both lay-flat sides of the skirt below the end-seal were manually slit (using scissors) about one to two inches from a side edge of the bag, the slit being in the machine direction, the slit extending from the bottom edge of the bag and across about 30 to 50 percent of the 38 mm (1.5 inch) wide bag skirt, to produce first and second coincident tear initiators. The bag was then used to package a simulated product, after which it was tested for linear tearing in the machine direction after shrinking by immersion in 85°C (185 °F) water. The simulated product was a simulated meat product, i.e., simulated by a sealed bag of water, the bag of water containing about 1300 milliliters of water in a heat-shrinkable bag having a lay-flat width of about 140 mm (5.5 inches) and a length of 229 mm (about 9 inches), this bag having been sealed closed with the water therein (and minimal air) and thereafter immersed in water at 91°C (195°F) and shrunk tightly around the water to result in a simulated product having a substantially round cross sectional area. The bag of water was placed into the heat-shrinkable end-seal bag being tested, with the bag and simulated product then being placed into a vacuum chamber, and the atmosphere evacuated. The bag was then sealed closed and the resulting packaged product removed from the vacuum chamber and immersed in 85°C (185°F) water for about 5 seconds, during which the bag shrunk tightly around the simulated product. After removal from the hot water, the bag was allowed to stand for a period of at least 5 minutes, and thereafter a manual tear was made by grasping the shrunken skirt portion of the article on either side of the tear initiators. The manual machine direction tear test results are set forth in the table

below, following the examples.

[0185] A plurality of side seal bags were produced using the film of Example 1. The bags had a lay-flat length of 343 mm (13.5 inches) and a lay-flat width of 159 mm (6.25 inches). Each of the skirts had a width of 25.4 mm (1 inch) Pairs of tear initiators were made at intervals of 38 mm (1.5 inches) down the full length of one of the skirts. Each of the tear initiators was a slit 16 mm (0.625 inch) long in the machine direction.

Example 2 (working)

[0186] An end-seal bag was made from a coextruded, multilayer, heat-shrinkable film produced utilizing the apparatus and process set forth in FIG. 8, described above. The multilayer film had a total of 7 layers, with the order, thickness, and composition being set forth in the table below in a manner corresponding with the description in Example 1, above. The end-seal bag was tear-tested as set forth in Example 1.

Example 2

[0187]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
80% SSPE2	70% VLDPE1	100%	PVDC	100%	70% VLDPE1	80% SSPE3
20% LLDPE 2	30% EVA1	EVA1		EVA3	30% EVA1	20% LLDPE 1
0.43 mil	0.78 mil	0.09 mil	0.18 mil	0.09 mil	0.26 mil	0.17 mils
1 mil = 0.0254 mm						

Example 3 (Comparative)

[0188] An end-seal bag was made from a coextruded, multilayer, heat-shrinkable film produced utilizing the apparatus and process set forth in FIG. 8, described above. The multilayer film had a total of 4 layers, with the order, thickness, and composition being set forth in the table below in a manner corresponding with the description in Example 1, above. The end-seal bag was tear-tested as set forth in Example 1.

Example 3 (comparative)

[0189]

Layer 1	Layer 2	Layer 3	Layer 4
100% VLDPE3	100% EVA2	100% PVDC	100% EVA 2
0.26 mil	1.26 mils	0.18 mil	0.6 mil
1 mil = 0.0254 mm			

Example 4 (Comparative)

[0190] An end-seal bag was made from a coextruded, multilayer, heat-shrinkable film produced utilizing the apparatus and process set forth in FIG. 8, described above. The multilayer film had a total of 7 layers, with the order, thickness, and composition being set forth in the table below in a manner corresponding with the description in Example 1, above. The end-seal bag was tear-tested as set forth in Example 1.

Example 4 (comparative)

[0191]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP1	80% VLDPE2 20% LLDPE1	100% EVA1	PVDC	100% EVA3	99% VLDPE2 1% AOX	85% SSPE3 15% LLDPE 1
0.44 mil	0.71 mil	0.09 mil	0.18 mil	0.09 mil	0.27 mil	0.18 mils
1 mil = 0.0254 mm						

Example 5 (Comparative)

[0192] An end-seal bag was made from a coextruded, multilayer, heat-shrinkable film produced utilizing the apparatus and process set forth in FIG. 8, described above. The multilayer film had a total of 7 layers, with the order, thickness, and composition being set forth in the table below in a manner corresponding with the description in Example 1, above. The end-seal bag was tear-tested as set forth in Example 1.

Example 5 (comparative)

[0193]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
80% SSPE2 20%	80% VLDPE1 20%	100% EVA1	PVDC	100% EVA3	80% VLDPE1 20%	80% SSPE3 20%
LLDPE 2	VLDPE4				VLDPE4	LLDPE 1
0.46 mil	1.11 mil	0.09 mil	0.18 mil	0.09 mil	0.28 mil	0.18 mils
1 mil = 0.0254 mm						

Example 6 (Comparative)

[0194] An end-seal bag was made from a coextruded, multilayer, heat-shrinkable film produced utilizing the apparatus and process set forth in FIG. 8, described above. The multilayer film had a total of 7 layers, with the order, thickness, and composition being set forth in the table below in a manner corresponding with the description in Example 1, above. The end-seal bag was tear-tested as set forth in Example 1.

Example 6 (comparative)

[0195]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP 2	90% SSPE5 10% Et-PrTER	100% EVA1	PVDC	100% EVA3	80% SSPE5 20% VLDPE1	100% SSPE3
0.49 mil	0.89 mil	0.1 mil	0.19 mil	0.1 mil	0.26 mil	0.18 mils
1 mil = 0.0254 mm						

Example 7 (Comparative)

[0196] An end-seal bag was made from a coextruded, multilayer, heat-shrinkable film produced utilizing the apparatus and process set forth in FIG. 8, described above. The multilayer film had a total of 7 layers, with the order, thickness, and composition being set forth in the table below in a manner corresponding with the description in Example 1, above. The end-seal bag was tear-tested as set forth in Example 1.

Example 7 (comparative)

[0197]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
100% ION 1	100% EVA1	100% EVA1	PVDC	100% EVA3	100% SSPE4	85% SSPE3 15% LLDPE1
0.32 mil	0.87 mil	0.16 mil	0.18 mil	0.08 mil	0.21 mil	0.12 mils
1 mil = 0.0254 mm						

Example 8 (Comparative)

[0198] An end-seal bag was made from a coextruded, multilayer, heat-shrinkable film produced utilizing the apparatus and process set forth in FIG. 8, described above. The multilayer film had a total of 4 layers, with the order, thickness, and composition being set forth in the table below in a manner corresponding with the description in Example 1, above.

Example 8

[0199]

Layer 1	Layer 2	Layer 3	Layer 4
100% SSPE6	84% LLDPE1 16%	85% EVA2 15%	85% EVA2 15%
	CCC	LLDPE1	LLDPE1
0.25 mil	1.09 mil	0.76 mil	0.25 mil
1 mil = 0.0254 mm			

Example 9 (Comparative)

[0200] An end-seal bag was made from a coextruded, multilayer, heat-shrinkable film produced utilizing the apparatus and process set forth in FIG. 8, described above. The multilayer film had a total of 6 layers, with the order, thickness, and composition being set forth in the table below in a manner corresponding with the description in Example 1, above.

Example 9

[0201]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6
100% SSPE6	100% VLDPE2	100% EVA2	100% EVA2	100% VLDPE2	85% EVA2 15%

(continued)

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6
					LLDPE1
0.31 mil	0.8 mil	0.09 mil	0.13 mil	0.4 mil	0.27 mils
1 mil = 0.0254 mm					

Example 10 (Comparative)

[0202] An end-seal bag was made from a coextruded, multilayer, heat-shrinkable film produced utilizing the apparatus and process set forth in FIG. 8, described above. The multilayer film had a total of 3 layers, with the order, thickness, and composition being set forth in the table below in a manner corresponding with the description in Example 1, above.

Example 10

[0203]

Layer 1	Layer 2	Layer 3
80% SSPE1 20% LLDPE2	100% EBA	85% SSPE3 15% LLDPE1
0.08 mil	1.84 mil	0.08 mil
1 mil = 0.0254 mm		

Example 11 (working)

[0204] An end-seal bag was made from a fully coextruded, multilayer, heat-shrinkable film produced utilizing the apparatus and process set forth in FIG. 8, described above, but without the extrusion coating step. The multilayer film had a total of 3 layers, with the order, thickness, and composition being set forth in the table below in a manner corresponding with the description in Example 1, above. The end-seal bag was tear-tested as set forth in Example 1.

Example 11 (working)

[0205]

Layer 1	Layer 2	Layer 3
100% EVA 6	75% VLDPE2 25%	75% VLDPE2 16.5%
	LLDPE1	LLDPE1 8.5% ABConc
0.68 mil	3.08 mil	1.24 mil
1 mil = 0.0254 mm		

Example 12 (working)

[0206] An end-seal bag marketed commercially by Curwood, Inc., under the name "Protite™ 34" was obtained from the marketplace. Analysis of the bag from which the multilayer film was made revealed the following layers, with the order, thickness, and composition being set forth in the table below. A small cut was made into the bag skirt, i.e., as

illustrated in FIG. 4A. The end-seal bag was tear-tested as set forth in Example 1.

Example 12 (working)

[0207]

Layer 1	Layer 2	Layer 3
Blend of EVA (3% vinyl acetate), LLDPE, and metallocene-catalyzed ethylene/alpha-olefin copolymer	Polyvinylidene chloride	Blend of EVA (3% vinyl acetate), LLDPE, and metallocene-catalyzed ethylene/alpha-olefin copolymer
1.53 mil	0.21 mil	0.74 mil
1 mil = 0.0254 mm		

Example 13 (comparative)

[0208] An end-seal bag marketed commercially by Curwood, Inc., under the name "Cleartite™ 52" was obtained from the marketplace. Analysis of the bag from which the multilayer film was made revealed the following layers, with the order, thickness, and composition being set forth in the table below. A small cut was made into the bag skirt, i.e., as illustrated in FIG. 4A. The end-seal bag was tear-tested as set forth in Example 1.

Example 13 (comparative)

[0209]

Layer 1	Layer 2	Layer 3
Blend of EVA (4% vinyl acetate), LLDPE, and metallocene-catalyzed ethylene/alpha-olefin copolymer	Polyvinylidene chloride	Blend of EVA (4% vinyl acetate), LLDPE, and metallocene-catalyzed ethylene/alpha-olefin copolymer
1.39 mil	0.23 mil	0.68 mil
1 mil = 0.0254 mm		

Example 14 (comparative)

[0210] An end-seal bag marketed commercially by Curwood, Inc., under the name "Perflex™ 64" was obtained from the marketplace. Analysis of the bag from which the multilayer film was made revealed the following layers, with the order, thickness, and composition being set forth in the table below. A small cut was made into the bag skirt, i.e., as illustrated in FIG. 4A. The end-seal bag was tear-tested as set forth in Example 1.

Example 14 (comparative)

[0211]

Layer 1	Layer 2	Layer 3
Blend of EVA (4% vinyl acetate), LLDPE, and metallocene-catalyzed ethylene/alpha-olefin copolymer	Polyvinylidene chloride	Blend of EVA (4% vinyl acetate), LLDPE, and metallocene-catalyzed ethylene/alpha-olefin copolymer
1.54 mil	0.19 mil	0.63 mil
1 mil = 0.0254 mm		

Example 15 (comparative)

[0212] An end-seal bag marketed commercially by Asahi Corporation, under the name "SN3" was obtained from the marketplace. Analysis of the bag from which the multilayer film was made revealed the following layers, with the order, thickness, and composition being set forth in the table below. A small cut was made into the bag skirt, i.e., as illustrated in FIG. 4A. The end-seal bag was tear-tested as set forth in Example 1.

Example 15 (comparative)**[0213]**

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5
Polyethylene blend	Ethylene/vinyl acetate copolymer, containing (15 wt % vinyl acetate mer)	Polyvinylidene chloride	Ethylene/vinyl acetate copolymer, containing (15 wt % vinyl acetate mer)	Low Density Polyethylene (possibly a blend)
0.39 mil	0.7	0.35 mil	0.66	0.63 mil
1 mil = 0.0254 mm				

Example 16 (working)

[0214] An end-seal bag marketed commercially by Pechiney Plastic Packaging, Inc., under the name "Clearshield™" was obtained from the marketplace. Analysis of the bag from which the multilayer film was made revealed the following layers, with the order, thickness, and composition being set forth in the table below. A small cut was made into the bag skirt, i.e., as illustrated in FIG. 4A. The end-seal bag was tear-tested as set forth in Example 1.

Example 16 (working)**[0215]**

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
Metallocene-catalyzed ethylene/alpha-olefin copolymer (possibly with LDPE or LLDPE)	100% Ethylene/methyl acrylate copolymer	Blend of polyamide 6 with polyamide 6I,6T	EVOH(27 mol % ethylene)	Blend of polyamide 6 with polyamide 6I,6T	100% Ethylene/methyl acrylate copolymer	Blend of low density polyethylene and linear low density polyethylene
1.58 mil	0.22 mil	0.9 mil	0.21 mil	0.85 mil	0.16 mil	0.57 mil
1 mil = 0.0254 mm						

Example 17 (working)

[0216] An end-seal bag was made from a coextruded, multilayer, heat-shrinkable film produced utilizing the apparatus and process set forth in FIG. 8, described above. The multilayer film had a total of 7 layers, with the order, thickness, and composition being set forth in the table below in a manner corresponding with the description in Example 1, above. The end-seal bag was tear-tested as set forth in Example 1.

Example 17 (working)**[0217]**

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	100% Ion&Eva&P B	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

[0218] An end-seal bag was made from the coextruded, multilayer, heat-shrinkable films of each of Examples 18 through 35, below, using the apparatus and process set forth in FIG. 5, described above. Each of the multilayer films had a total of 7 layers, with the order, thickness, and composition being set forth in the tables below in a manner corresponding with the description in Example 1, above. The end-seal bags were tear- tested as set forth in Example 1.

[0219] An end-seal bag was made from the fully coextruded, multilayer, heat-shrinkable films of each of Examples 36-42, below, using the apparatus and process set forth in FIG. 8, described above, except that all layers were extruded from die head 122, and no extrusion coating was employed. Each of the multilayer films of Examples 36-42 had the layer order, thickness, and composition set forth in the corresponding table below. The end-seal bags were tear- tested as set forth in Example 1.

[0220] Ten bags made from the film of Example 40 were filled with water and clipped. Before filling some of the bags with water, the header of the bags were spot sealed. The bags were placed in a smokehouse for 12 hours at 91°C (195°F). After 12 hours, one of the bags had experienced a seal failure. Some bags had 2 spot seals and some had 4 spot seals. Spot seals improved the appearance of the header by preventing extreme curling of the header. The 4 spot seal bags had better appearance overall, making it easier to see the holes and slit of the header.

Example 18 (working)

[0221]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	100% EVA&PP	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 19 (working)

[0222]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	75% EVA2 25% modEVA	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

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Example 20(working)

[0223]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	100% Et-Norb2	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mil ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 21 (working)

[0224]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	100% Et-Norb1	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 22 (comparative)

[0225]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	100% Sty-But	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 23 (working)

[0226]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	100% PP1	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1

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(continued)

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 24 (working):

[0227]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	70% Sty-But 30% EVA5	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 25 (working)

[0228]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	70% Sty-But 30% EVA2	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 26 (working)

[0229]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	70% VLDPE2 30% ET-Norb2	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 27 (working)

[0230]

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Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	70% ssPP 30% SSPE3	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 28 (working)

[0231]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	70% ssPP 30% EVA2	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 29 (working)

[0232]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	80% SSPE3 20% WCC	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 30 (working)

[0233]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	100% ION 2	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

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Example 31 working)

[0234]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	100% EVA6	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 32 (working)

[0235]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	100% PB	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 33 (working)

[0236]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	85% SSPE1 15% RECLAIM	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 34 (working)

[0237]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	70% SSPE1 30% RECLAIM	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1

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(continued)

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 35

[0238]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6	Layer 7
90% SSPE1 10% SLIP2	55% SSPE1 45% RECLAIM	50% EVA4 50% LLDPE1	100% PVdC	100% EVA3	80% VLDPE1 20% VLDPE4	80% SSPE3 20% LLDPE1
3.0 mil ^t	3.7 mil ^t	11.4 mil ^t	2.2 mil ^t	1 mil ^t	1.5 mils ^t	1.5 ^t
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process						

Example 36

[0239]

Layer 1	Layer 2	Layer 3	Layer 4	Layer 5
SSPE6	70% VLDPE4 30% EVA1	EVA2	70% VLDPE4 30% EVA1	85% EVA2 15% LLDPE 1
3.5	9	0.22	4.5	3
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process				

Example 37

[0240]

Layer 1	Layer 2	Layer 3
EPC 1	70% VLDPE4 30% EVA1	80% EVA-7 20% HDPE
5	12	5.5
1 mil = 0.0254 mm ^t thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process		

Example 38

[0241]

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Layer 1	Layer 2	Layer 3
98% EPC1 2% BCC	70% VLDPE4 30% EVA1	80% EVA-7 20% HDPE
5	12	5.5
1 mil = 0.0254 mm tthickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process		

Example 39

[0242]

Layer 1	Layer 2	Layer 3
EPC-1	70% VLDPE4 28% EVA1 2%BCC	80% EVA-7 20% HDPE
5	12	3.5
1 mil = 0.0254 mm tthickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process		

Example 40

[0243]

Layer 1	Layer 2	Layer 3	Layer 4
Nylon 3	MALLD-2	70% VLDPE4 30% EVA1	80% EVA-7 20% HDPE
2.00	1.00	10.00	3.50
1 mil = 0.0254 mm tthickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process			

Example 41

[0244]

Layer 1	Layer 2	Layer 3	Layer 4
98% Nylon 3 2%BCC	MALLD-2	70% VLDPE4	80% EVA-7
		30% EVA1	20% HDPE

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(continued)

Layer 1	Layer 2	Layer 3	Layer 4
2	1	10	3.5
1 mil = 0.0254 mm ¹ thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process			

Example 42

[0245]

Layer 1	Layer 2	Layer 3	Layer 4
Nylon 3	MALLD-2	70% VLDPE4 28% EVA1 2%BCC	80% EVA-7 20% HDPE
2	1	10	3.5
1 mil = 0.0254 mm ¹ thickness in table represents thickness of extrudate before solid state orientation at trapped bubble stage of process			

[0246] A seamless film tubing of each of the films of Examples 1-35 is cut and sealed to form an end-seal bag. A small cut was made in the bag skirt, about 25.4 to 50.8 mm (1 to 2 inches) from the folded bag side edge. The bag skirt had a width of about 38 mm (1.5 inches). A product was placed in the bag, and the bag was sealed closed and shrunk around the product. The resulting end-seal bags exhibit the following characteristics.

Table: Results of Bag Testing

Bag of Example No.	Total Film Gauge (mils) 1 mil = 0.0254 mm	Free Shrink at 85°C (185°F) (% MD/%TD)	Straight, Full Length Manual MD Tear after shrinking in water at 85°C (185°F)	LD Tear Propagation Max Load (gmf, i.e., grams force)	LD Tear Propagation Energy to Break (gmf-in)	LD Tear Resistance Max Load (gmf)	Peak Load Impact Strength per mil, via ASTM D 3763-95A (N/mil) 1 N/mil = 40 N/mm
1	2.0	32/45	Yes (94.4%)*	31	---	545	98
2	2.0	35/51	Yes (90.5%)*	23	31	598	114*
3	2.3	---	No (5%)*	22	36	673	54.9*
4	1.96	---	No (0%)*	31	39	566	102.6*
5	2.4	---	No (0%)*	54	58	791	100* 114.3* 137.2*
6	2.2	---	No (0%)*	61	68	625	138.7* 104.5*
7	1.9	---	No (0%)*	28	34	659	102*
8	2.35	17/28	---	24.8	---	---	113*
9	2.0	26/42	---	---	---	---	110*

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(continued)

	Bag of Example No.	Total Film Gauge (mils) 1 mil = 0.0254 mm	Free Shrinkat 85°C (185°F) (% MD/ %TD)	Straight, Full Length Manual MD Tear after shrinking in water at 85°C (185°F)	LD Tear Propagation Max Load (gmf, i.e., grams force)	LD Tear Propagation Energy to Break (gmf- in)	LD Tear Resistanc e Max Load (gmf)	Peak Load Impact Strength per mil, via ASTM D 3763-95A (N/mil) 1 N/mil = 40 N/mm
5								
10	10	2.0	---	---	---	---	---	---
	11	5.0	---	Yes	50	86	1470	105*
	12	2.18	32/40	Yes	20	38	840	116.3
15	13	2.03	35/39	No	22	35	732	73.9
	14	2.18	22/30*	No	23	44	732	---
	15	2.47	50/50	No	279	330	685	71.9
	16	4.6		Yes	284	440	3110	155.0
20	17	2.42	24/36	Yes (100%)**	35	---	747	---
	18	2.48	19/36	Yes (100%)**	205	---	797	---
	19	2.48	20/35	Yes (100%)**	23	---	817	---
25	20	---	---	Yes	---	---	---	---
	21	2.56	23/33	Yes (100%)**	21	30	676	---
	22	2.53	24/36	Yes (100%)**	40	---	726	---
	23	2.53	20/33	Yes	21	29	724	---
30				(100%)**				
	24	2.5	23/34	Yes (100%)**	32	47	848	---
	25	2.5	22/34	Yes (100%)**	22	35	707	---
35	26	2.51	24/32	Yes (100%)**	20	27	723	---
	27	2.39	18/32	Yes (100%)**	13	23	843	---
	28	2.36	15/34	Yes (100%)**	21	---	820	---
	29	2.39	17/34	Yes (100%)**	17	30	643	---
40	30	2.29	---	Yes (100%)**	71.0	81	551	---
	31	2.31	---	Yes (100%)**	15.3	---	557	---
	32	2.18	---	Yes (100%)**	113.0	140	693	---
45	33	2.55	---	Yes (100%)**	55.0	50	427	---
	34	2.41	---	Yes (100%)**	57.3	55	477	---
	35	2.45	---	Yes (100%)**	40.2	46	638	---
50	36	2.0	26/37	Yes**** (100%)	-	-	-	-
	37	2.34	14/26	Yes**** (100%)	-	-	-	-
55	38	2.4	19/32	Yes**** (100%)	-	-	-	-
	39	2.4	19/29	Yes**** (100%)	-	-	-	-

(continued)

Bag of Example No.	Total Film Gauge (mils) 1 mil = 0.0254 mm	Free Shrinkat 85°C (185°F) (% MD/%TD)	Straight, Full Length Manual MD Tear after shrinking in water at 85°C (185°F)	LD Tear Propagation Max Load (gmf, i.e., grams force)	LD Tear Propagation Energy to Break (gmf-in)	LD Tear Resistance Max Load (gmf)	Peak Load Impact Strength per mil, via ASTM D 3763-95A (N/mil) 1 N/mil = 40 N/mm
40	2.4	17/33	Yes**** (100%)	-	-	-	-
41	2.4	19/32	Yes**** (100%)	-	-	-	-
42	2.4	19/28	Yes**** (100%)	-	-	-	-
* impact strength tested on different sample of film with same designation ** test results based on tearing 5 samples *** test results based on tearing 20 samples **** test results based on tearing 10 samples							

[0247] The various preferred features in preferred embodiments of the invention as set forth above are useful in combination with one another. Any of the various preferred film compositions (e.g., blend of ethylene/hexene copolymer and ethylene/vinyl acetate copolymer) are preferred in combination with any one or more of the various preferred film properties (e.g., thickness of from 0.038 to 0.127 mm (1.5 to 5 mils), peak load impact strength of from 50 to 250 Newtons, etc.) and/or in combination with any one or more preferred types of packaging articles (e.g., end-seal bag, etc).

Claims

1. A heat-shrinkable packaging article comprising a heat-shrinkable multilayer film having an inside seal layer heat sealed to itself at a heat seal, the article having a first side and a second side, the article having a skirt or header outward of the heat seal, the skirt or header comprising an article edge and a pair of tear initiators, the pair of tear initiators having a first tear initiator and a second tear initiator, the first tear initiator of the pair being in the first side of the article, and the second tear initiator of the pair being in the second side of the article, the article being capable of having a manually-initiated, manually-propagated first tear in the first side of the article, and a manually-initiated and manually-propagated second tear in the second side of the article, the first tear and the second tear each being capable of being propagated in a machine direction from the pair of first and second tear initiators, with each tear being propagated in the machine direction through the heat seal and down the length of the article, or across the article, with each tear being capable of being manually propagated in the machine direction through and to an opposite article edge, so that upon using the multilayer film to make a packaged product by placing a product inside the article with the article being sealed closed around the product so that a package is formed, and thereafter shrinking the film around the product, the resulting package can be manually opened, and the product readily removed from the package, by manually initiating machine-direction tears from the first and second tear initiators, with the tears being manually propagated through the seal and toward the opposite edge of the article, with the multilayer film exhibiting a Peak Load Impact Strength of at least 50 Newtons per mil measured using ASTM D 3763-95A, with at least one layer of the multilayer film containing at least one incompatible polymer blend selected from the group consisting of:

(A) a blend of from 80 to 40 weight percent ethylene homopolymer and/or ethylene/alpha-olefin copolymer with from 20 to 60 weight percent ethylene/unsaturated ester copolymer having an unsaturated ester content of at least 10 weight percent;

(B) a blend of ionomer resin with ethylene/unsaturated ester copolymer, and/or polybutylene, and/or propylene homopolymer and/or propylene copolymer;

(C) a blend of homogeneous ethylene/alpha-olefin copolymer with recycled polymer blend comprising ethylene homopolymer, propylene homopolymer, ethylene copolymer, propylene copolymer, polyamide, ethylene/vinyl

alcohol copolymer, ionomer resin, anhydride-modified ethylene/alpha-olefin copolymer, and/or antiblock;

(D) a blend of from 10 to 75 weight percent ethylene/unsaturated ester copolymer with from 90 to 15 weight percent polypropylene and/or propylene/ethylene copolymer, and/or polybutylene, and/or modified ethylene/alpha-olefin copolymer, and/or styrene homopolymer, and/or styrene/butadiene copolymer;

(E) a blend of ethylene/norbornene copolymer with ethylene/unsaturated ester copolymer and/or polypropylene and/or polybutylene;

(F) a blend of from 90 to 15 weight percent ethylene/alpha-olefin copolymer with from 10 to 75 weight percent polypropylene and/or polybutylene and/or ethylene/norbornene;

(G) a blend of from 90 to 25 weight percent homogeneous propylene homopolymer and/or homogeneous propylene copolymer with from 10 to 75 weight percent homogeneous ethylene/alpha-olefin copolymer and/or ethylene/unsaturated ester copolymer;

(H) a blend of propylene homopolymer and/or propylene/ethylene copolymer and/or polybutylene with ethylene/methyl acrylate copolymer and/or ethylene/acrylic acid copolymer and/or ethylene/butyl acrylate copolymer;

(I) a blend of polyamide with polystyrene and/or ethylene/alpha-olefin copolymer and/or ethylene/vinyl acetate copolymer and/or styrene/butadiene copolymer; and

(J) a blend of polyamide 6 and polyamide 616T; and

wherein at least a portion of the skirt or header is heatset with a remainder of the film remaining heat-shrinkable, so that upon forming the package and shrinking the film around the product, the shrinkage and curl of the skirt or header is reduced, and wherein the heat-shrinkable packaging article does not comprise a patch thereon.

2. The heat-shrinkable article according to claim 1, wherein the header or skirt further comprises at least one grip assister for assisting grip of the multilayer film during manual tearing.
3. The heat-shrinkable article according to Claim 1, wherein a portion of the skirt or header on the first side of the article is heatset, and a corresponding portion of the skirt or header on the second side of the article is also heatset, preferably wherein the article is an end-seal bag and the first and second tear initiators are present in the bag skirt, and a heat seal is present within the heatset portion of the first and second sides of the article, more preferably wherein the first tear initiator is aligned over the second tear initiator, and the heat seal present within the heatset portion is a perimeter seal, and the skirt further comprise a first grip assister between the pair of tear initiators and a first end of the skirt, and a second grip assister between the pair of tear initiators and a second end of the skirt.
4. The heat-shrinkable article according to Claim 1, wherein a first portion of a first side of the skirt or header is spot sealed to the second side of the skirt or header at a first spot seal, and a second portion of the first side of the skirt or header is spot sealed to the second side of the skirt or header at a second spot seal.
5. The heat-shrinkable article according to Claim 1, wherein the heat-set portions of the first and second sides of the skirt or header comprise a perimeter seal in the skirt or header, preferably wherein the first tear initiator aligns directly over the second tear initiator, and the skirt or header further comprises a first spot seal within 25.4 mm (1 inch) of the first and second tear initiators and a first end of the skirt, and a second spot seal within 25.4 mm (1 inch) of the first and second tear initiators and a second end of the skirt or header.
6. The heat-shrinkable article according to claim 5, wherein the header or skirt further comprise a first grip assister between the first spot seal and the first end of the header or skirt, and a second grip assister between the first and second tear initiator and a second end of the header or skirt.
7. The heat-shrinkable article according to Claim 5, wherein the article is a side seal bag or pouch having a skirt comprising a plurality of pairs of first and second tear initiators, with each first tear initiator being aligned directly over the second tear initiator with which it is paired, preferably (a) wherein the article is a side-seal bag having a skirt that comprises, for each pair of first and second tear initiators, a first spot seal within 25.4 mm (1 inch) of the pair of tear initiators, the first spot seal being between the pair of tear initiators and a first end of the skirt, and a second spot seal within 25.4 mm (1 inch) of the pair of tear initiators, the second spot seal being between the pair of tear initiators and the a second end of the skirt, or (b) wherein the multilayer film has an oxygen transmission rate of at least 50 cc/m² day at stp and 0% relative humidity, or (c) wherein the multilayer film has a non-symmetrical polymeric layer arrangement.
8. The heat-shrinkable packaging article of claim 1, wherein the skirt or header comprises a plurality of the pair of tear initiators, each pair of tear initiators having a first tear initiator and a second tear initiator, the first tear initiator being

in the first side of the article, and the second tear initiator being in the second side of the article, each pair of tear initiators being at a location for generating a manually-initiated, manually-propagated first tear in the first side of the article, and a manually-initiated and manually-propagated second tear in the second side of the article, the first tear and the second tear each being capable of being propagated in a machine direction from the respective first and second tear initiators, with each tear being capable of being propagated in the machine direction through the heat seal and down the length of the article, or across the article, with each tear being capable of being manually propagated in the machine direction through and to an opposite article edge, so that upon using the multilayer film to make a packaged product by providing a product inside the article with the article being sealed closed around the product so that a package is formed, and thereafter shrinking the film around the product, the resulting package can be manually opened, with tearing from one or more of the pairs of tear initiators allowing a portion of the package to be removed from the packaged product so that an uncovered portion of the product can be separated from a remainder of the product, leaving a remainder of the package around at least a portion of the remainder of the product, by initiating first and second machine-direction tears from at least one pair of tear initiators, with the tears being propagated through the seal and toward the opposite edge of the article.

9. The heat-shrinkable packaging article according to Claim 8, wherein the packaging article is a lay-flat, side-seal bag made from a seamless tubing, the side-seal bag having an open top, a folded bottom edge, and first and second side seals with respective first and second bag skirts outward of respective first and second side seals, with the plurality of pairs of tear initiators being spaced apart along the first bag skirt, with each tear being capable of being manually propagated across the full width of the side-seal bag through both side seals and through second skirt.

10. The heat-shrinkable packaging article according to Claim 9, wherein at least a portion of a first side of the skirt or header is heat sealed to the second side of the skirt or header in at least one heat seal, preferably either (a) wherein the first side of the skirt or header is heat sealed to the second side of the skirt or header in a plurality of spot seals, or (b) wherein the first side of the skirt or header is heat sealed to the second side of the skirt or header in a heat seal along an outer edge of the skirt or header.

11. The heat-shrinkable packaging article according to Claim 9, wherein the plurality of pairs of tear initiators are located at intervals of from 25 mm to 76 mm (1 to 3 inches).

12. The heat-shrinkable packaging article according to Claim 8, wherein each of the first tear initiators is coincident or substantially coincident with the second tear initiator with which it is paired, and each of the first tear initiators is a slit through the first side of the article, and each of the second tear initiators is a slit through the second side of the article, and each of the slits is oriented in the machine direction, preferably wherein each of the slits is oriented within 20 degrees of the machine direction.

13. The heat-shrinkable packaging article according to Claim 8, wherein the multilayer film has been biaxially oriented in the solid state and has a total free shrink, as measured by ASTM D 2732, of from 20 percent to 105 percent at 85°C (185°F), or wherein the heat-shrinkable multilayer film exhibits a Peak Load Impact Strength, determined using ASTM D 3763-95A, of from 2000 to 10000 N/mm (50 to 250 Newtons per mil), and the multilayer film has a total thickness, before shrinking, of from 0.038 mm (1.5 mils) to 0.13 mm (5 mils), or wherein the multilayer film comprises an O₂-barrier layer and the multilayer film exhibits an oxygen transmission rate of from 1 to 20 cc/m² day atm at 23°C and 100% relative humidity.

14. The heat-shrinkable packaging article according to Claim 8, wherein the multilayer film comprises:

- (A) a first layer that is an outer food-contact layer and that also serves as a seal layer, the first layer comprising a blend of homogeneous ethylene/alpha-olefin copolymer and linear low density polyethylene;
- (B) a second layer comprising a blend of heterogeneous ethylene/alpha-olefin copolymer and ethylene/vinyl acetate copolymer;
- (C) a third layer comprising ethylene/vinyl acetate copolymer;
- (D) a fourth layer comprising polyvinylidene chloride;
- (E) a fifth layer comprising ethylene/vinyl acetate copolymer;
- (F) a sixth layer comprising a blend of heterogeneous ethylene/alpha-olefin copolymer and ethylene/vinyl acetate copolymer; and
- (G) a seventh layer comprising a blend of homogeneous ethylene/alpha-olefin copolymer and linear low density polyethylene; and

wherein the layers are present in the order of first / second / third / fourth / fifth / sixth / seventh.

Patentansprüche

1. Wärmeschrumpfbarer Verpackungsartikel, der Folgendes umfasst: eine wärmeschrumpfbare Mehrschichtfolie mit einer inneren Dichtungsschicht, die an einem Heißsiegel mit sich selbst heißversiegelt ist, wobei der Artikel eine erste Seite und eine zweite Seite aufweist, wobei der Artikel eine Schürze oder einen Kopfteil außerhalb der Heißsiegelung aufweist, wobei die Schürze oder der Kopfteil eine Artikelkante und ein Paar Aufreißinitiatoren umfasst, wobei das Paar Aufreißinitiatoren einen ersten Aufreißinitiator und einen zweiten Aufreißinitiator aufweist, wobei der erste Aufreißinitiator des Paares in der ersten Seite des Artikels angeordnet ist und der zweite Aufreißinitiator des Paares in der zweiten Seite des Artikels angeordnet ist, wobei der Artikel in der Lage ist, einen manuell eingeleiteten, manuell ausgebreiteten ersten Riss in der ersten Seite des Artikels und einen manuell eingeleiteten und manuell ausgebreiteten zweiten Riss in der zweiten Seite des Artikels aufzuweisen, wobei der erste Riss und der zweite Riss jeweils in der Lage sind, sich in einer Maschinenrichtung von dem Paar von ersten und zweiten Aufreißinitiatoren auszubreiten, wobei jeder Riss in der Maschinenrichtung durch die Heißsiegelung und die Länge des Artikels entlang oder über den Artikel hinweg ausgebreitet wird, wobei jeder Riss in Maschinenrichtung durch und zu einer gegenüberliegenden Artikelkante manuell ausgebreitet werden kann, so dass bei Verwendung der Mehrschichtfolie ein verpacktes Produkt erzeugt wird, indem ein Produkt in dem Artikel angeordnet wird, wobei der Artikel um das Produkt herum versiegelt wird, so dass eine Verpackung gebildet wird, und danach die Folie um das Produkt herum geschrumpft wird, wobei die daraus resultierende Packung manuell geöffnet und das Produkt leicht aus der Verpackung entnommen werden kann, indem von dem ersten und dem zweiten Aufreißinitiator manuell Risse in Maschinenrichtung eingeleitet werden, wobei die Risse durch die Dichtung und in Richtung der gegenüberliegenden Kante des Artikels manuell ausgebreitet werden, wobei die Mehrschichtfolie eine Spitzenlastschlagfestigkeit von mindestens 50 Newton pro mil gemessen unter Verwendung von ASTM D 3763-95A aufweist, wobei mindestens eine Schicht der Mehrschichtfolie mindestens eine inkompatible Polymermischung umfasst, die aus der Gruppe ausgewählt wird, die aus Folgendem besteht:

(A) einer Mischung aus 80 bis 40 Gew.-% Ethylenhomopolymer und/oder Ethylen/alpha-Olefin-Copolymer mit 20 bis 60 Gew.-% Ethylen/ungesättigtem Ester-Copolymer mit einem ungesättigten Estergehalt von mindestens 10 Gew.-%;

(B) einer Mischung aus Ionomerharz mit Ethylen/ungesättigtem Ester-Copolymer und/oder Polybutylen und/oder Propylenhomopolymer und/oder Propylen-Copolymer;

(C) einer Mischung aus homogenem Ethylen/alpha-Olefin-Copolymer mit einer recycelten Polymermischung, die Folgendes umfasst: Ethylenhomopolymer, Propylenhomopolymer, Ethylen-Copolymer, Propylen-Copolymer, Polyamid, Ethylen/Vinylalkohol-Copolymer, Ionomerharz, anhydrid-modifiziertes Ethylen/alpha-Olefin-Copolymer, und/oder Antiblockmittel;

(D) einer Mischung aus 10 bis 75 Gew.-% Ethylen/ungesättigtem Ester-Copolymer mit 90 bis 15 Gew.-% Polypropylen und/oder Propylen/Ethylen-Copolymer und/oder Polybutylen und/oder modifiziertes Ethylen/alpha-Olefin-Copolymer und/oder Styrolhomopolymer und/oder Styrol/Butadien-Copolymer;

(E) einer Mischung aus Ethylen/Norbomen-Copolymer mit Ethylen/ungesättigtem Ester-Copolymer und/oder Polypropylen und/oder Polybutylen;

(F) einer Mischung aus 90 bis 15 Gew.-% Ethylen/alpha-Olefin-Copolymer mit 10 bis 75 Gew.-% Polypropylen und/oder Polybutylen und/oder Ethylen/Norbomen;

(G) einer Mischung aus 90 bis 25 Gew.-% homogenem Propylenhomopolymer und/oder homogenem Propylen-Copolymer mit 10 bis 75 Gew.-% homogenem Ethylen/alpha-Olefin-Copolymer und/oder Ethylen/ungesättigtem Ester-Copolymer;

(H) einer Mischung aus Propylenhomopolymer und/oder Propylen/Ethylen-Copolymer und/oder Polybutylen mit Ethylen/Methylacrylat-Copolymer und/oder Ethylen/Acrylsäure-Copolymer und/oder Ethylen/Butylacrylat-Copolymer;

(I) einer Mischung aus Polyamid mit Polystyrol und/oder Ethylen/alpha-Olefin-Copolymer und/oder Ethylen/Vinylacetat-Copolymer und/oder Styrol/Butadien-Copolymer; und

(J) einer Mischung aus Polyamid 6 und Polyamid 6I6T; und

wobei mindestens ein Abschnitt der Schürze oder des Kopfteils mit einem Rest der Folie, der wärmeschrumpfbar bleibt, wärmegehärtet wird, so dass beim Bilden der Verpackung und Schrumpfen der Folie um das Produkt die Schrumpfung und Krümmung der Schürze oder des Kopfteils verringert wird und wobei der wärmeschrumpfbare Verpackungsartikel keinen Aufkleber darauf aufweist.

2. Wärmeschrumpfbarer Artikel nach Anspruch 1, wobei der Kopfteil oder die Schürze ferner mindestens eine Greifhilfe umfasst, um den Griff der Mehrschichtfolie während des manuellen Aufreißens zu unterstützen.

- 5 3. Wärmeschrumpfbarer Artikel nach Anspruch 1, wobei ein Abschnitt der Schürze oder des Kopfteils auf der ersten Seite des Artikels wärmegehärtet wird und ein entsprechender Abschnitt der Schürze oder des Kopfteils auf der zweiten Seite des Artikels vorzugsweise ebenfalls wärmegehärtet wird, wobei der Artikel ein Enddichtungsbeutel ist und der erste und der zweite Aufreißinitiator in der Beutelschürze vorhanden sind und eine Heißsiegelung innerhalb des wärmegehärteten Abschnitts der ersten und zweiten Seite des Artikels vorhanden ist, bevorzugter wobei der erste Aufreißinitiator über dem zweiten Aufreißinitiator ausgerichtet ist und die in dem wärmegehärteten Abschnitt vorhandene Heißsiegelung eine Umfangsdichtung ist, und wobei die Schürze ferner eine erste Greifhilfe zwischen dem Paar Aufreißinitiatoren und einem ersten Ende der Schürze und eine zweite Greifhilfe zwischen dem Paar Aufreißinitiatoren und einem zweiten Ende der Schürze umfasst.

- 10 4. Wärmeschrumpfbarer Artikel nach Anspruch 1, wobei ein erster Abschnitt einer ersten Seite der Schürze oder des Kopfteils an der zweiten Seite der Schürze oder des Kopfteils an einer ersten Punktdichtung punktversiegelt ist und ein zweiter Abschnitt der ersten Seite der Schürze oder des Kopfteils an der zweiten Seite der Schürze oder des Kopfteils an einer zweiten Punktdichtung punktversiegelt ist.

- 15 5. Wärmeschrumpfbarer Artikel nach Anspruch 1, wobei die wärmegehärteten Abschnitte der ersten und zweiten Seite der Schürze oder des Kopfteils eine Umfangsdichtung in der Schürze oder dem Kopfteil umfassen, vorzugsweise wobei der erste Aufreißinitiator direkt über dem zweiten Aufreißinitiator ausgerichtet ist und die Schürze oder der Kopfteil ferner eine erste Punktdichtung innerhalb von 25,4 mm (1 Zoll) des ersten und zweiten Aufreißinitiators und eines ersten Endes der Schürze und eine zweite Punktdichtung innerhalb von 25,4 mm (1 Zoll) des ersten und zweiten Aufreißinitiators und eines zweiten Endes der Schürze oder des Kopfteils umfasst.

- 20 6. Wärmeschrumpfbarer Artikel nach Anspruch 5, wobei der Kopfteil oder die Schürze ferner eine erste Greifhilfe zwischen der ersten Punktdichtung und dem ersten Ende des Kopfteils oder der Schürze und eine zweite Greifhilfe zwischen dem ersten und zweiten Aufreißinitiator und einem zweiten Ende des Kopfteils oder der Schürze umfasst.

- 25 7. Wärmeschrumpfbarer Artikel nach Anspruch 5, wobei der Artikel ein/eine Seitendichtungsbeutel oder -tasche ist, der/die eine Schürze aufweist, die eine Vielzahl von Paaren von ersten und zweiten Aufreißinitiatoren umfasst, wobei jeder erste Aufreißinitiator direkt über dem zweiten Aufreißinitiator ausgerichtet ist, mit dem er gepaart ist, vorzugsweise (a) wobei der Artikel ein Seitendichtungsbeutel mit einer Schürze ist, die für jedes Paar von ersten und zweiten Aufreißinitiatoren Folgendes umfasst: eine erste Punktdichtung innerhalb von 25,4 mm (1 Zoll) des Paares von Aufreißinitiatoren, wobei die erste Punktdichtung zwischen dem Paar Aufreißinitiatoren und einem ersten Ende der Schürze angeordnet ist, und eine zweite Punktdichtung innerhalb von 25,4 mm (1 Zoll) des Paares von Aufreißinitiatoren, wobei die zweite Punktdichtung zwischen dem Paar Aufreißinitiatoren und dem zweiten Ende der Schürze angeordnet ist, oder (b) wobei die Mehrschichtfolie eine Sauerstoffdurchlässigkeit von mindestens 50 cm³/m² pro Tag bei STP und 0 % relativer Feuchtigkeit aufweist oder (c) wobei die Mehrschichtfolie eine nicht-symmetrische Polymerschichtanordnung aufweist.

- 30 8. Wärmeschrumpfbarer Verpackungsartikel nach Anspruch 1, wobei die Schürze oder der Kopfteil eine Vielzahl des Paares von Aufreißinitiatoren umfasst, wobei jedes Paar Aufreißinitiatoren einen ersten Aufreißinitiator und einen zweiten Aufreißinitiator aufweist, wobei der erste Aufreißinitiator in der ersten Seite des Artikels angeordnet ist und der zweite Aufreißinitiator in der zweiten Seite des Artikels angeordnet ist, wobei jedes Paar Aufreißinitiatoren an einer Stelle zum Erzeugen eines manuell eingeleiteten, manuell ausgebreiteten ersten Risses in der ersten Seite des Artikels angeordnet ist und einen manuell eingeleiteten und manuell ausgebreiteten zweiten Riss in der zweiten Seite des Artikels aufweist, wobei der erste Riss und der zweite Riss jeweils in der Lage sind, sich in einer Maschinenrichtung der jeweiligen ersten und zweiten Aufreißinitiatoren auszubreiten, wobei jeder Riss in der Maschinenrichtung durch die Heißsiegelung und die Länge des Artikels entlang oder über den Artikel hinweg ausgebreitet werden kann, wobei jeder Riss in Maschinenrichtung durch und zu einer gegenüberliegenden Artikelkante manuell ausgebreitet werden kann, so dass bei Verwendung der Mehrschichtfolie ein verpacktes Produkt erzeugt wird, indem ein Produkt in dem Artikel bereitgestellt wird, wobei der Artikel um das Produkt herum versiegelt wird, so dass eine Verpackung gebildet wird, und danach die Folie um das Produkt herum geschrumpft wird, die resultierende Verpackung manuell geöffnet werden kann, indem an einem oder mehreren der Paare von Aufreißinitiatoren gerissen wird, die es ermöglichen, dass ein Teil der Verpackung von dem verpackten Produkt entfernt wird, so dass ein unbedeckter Abschnitt des Produktes von einem Rest des Produktes getrennt werden kann, wobei ein Rest der Verpackung um mindestens einem Abschnitt des Restes des Produktes verbleibt, indem erste und zweite Risse in
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Maschinenrichtung von mindestens einem Paar Aufreißinitiatoren eingeleitet werden, wobei die Risse durch die Dichtung und in Richtung der gegenüberliegenden Kante des Artikels ausgebreitet werden.

9. Wärmeschrumpfbarer Verpackungsartikel nach Anspruch 8, wobei der Verpackungsartikel ein flacher Seitendichtungsbeutel ist, der aus einem nahtlosen Schlauch hergestellt ist, wobei der Seitendichtungsbeutel eine offene Oberseite, eine gefaltete untere Kante und erste und zweite Seitenabdichtungen mit entsprechenden ersten und zweiten Beutelschürzen außerhalb der jeweiligen ersten und zweiten Seitendichtungen aufweist, wobei die Vielzahl von Paaren von Aufreißinitiatoren entlang des ersten Beutelschürze beabstandet ist, wobei jeder Riss manuell über die gesamte Breite des Seitendichtungsbeutels durch beide Seitenabdichtungen und durch die zweite Schürze ausgebreitet werden kann.

10. Wärmeschrumpfbarer Verpackungsartikel nach Anspruch 9, wobei ein mindestens ein Abschnitt einer ersten Seite der Schürze oder des Kopfteils an der zweiten Seite der Schürze oder des Kopfteils in mindestens einer Wärmedichtung wärmeversiegelt ist, vorzugsweise entweder (a) wobei die erste Seite der Schürze oder des Kopfteils an der zweiten Seite der Schürze oder des Kopfteils in einer Vielzahl von Punktdichtungen wärmeversiegelt ist oder (b) wobei die erste Seite der Schürze oder des Kopfteils an der zweiten Seite der Schürze oder des Kopfteils in einer Wärmedichtung entlang einer Außenkante der Schürze oder des Kopfteils wärmeversiegelt ist.

11. Wärmeschrumpfbarer Verpackungsartikel nach Anspruch 9, wobei die Vielzahl von Aufreißinitiatoren in Abständen von 25 mm bis 76 mm (1 bis 3 Zoll) angeordnet ist.

12. Wärmeschrumpfbarer Verpackungsartikel nach Anspruch 8, wobei jeder der ersten Aufreißinitiatoren mit dem zweiten Aufreißinitiator, mit dem er gepaart ist, zusammenfällt oder im Wesentlichen zusammenfällt und jeder der ersten Aufreißinitiatoren ein Schlitz durch die erste Seite des Artikels ist und jeder der zweiten Aufreißinitiatoren ein Schlitz durch die zweite Seite des Artikels ist und jeder der Schlitze vorzugsweise in Maschinenrichtung orientiert ist, wobei jeder der Schlitze innerhalb von 20 Grad der Maschinenrichtung orientiert ist.

13. Wärmeschrumpfbarer Verpackungsartikel nach Anspruch 8, wobei die mehrschichtige Folie biaxial im festen Zustand orientiert ist und eine vollständig freie Schrumpfung, gemessen nach ASTM D 2732, von 20 % bis 105 % bei 85 °C (185 ° F) aufweist, oder wobei die wärmeschrumpfbare Mehrschichtfolie eine nach ASTM D 3763-95A bestimmte Spitzenlastschlagfestigkeit von 2000 bis 10.000 N/mm (50 bis 250 Newton pro mil) aufweist und die Mehrschichtfolie eine Gesamtdicke, vor dem Schrumpfen, von 0,038 mm (1,5 mils) bis 0,13 mm (5 mils) aufweist oder wobei die Mehrschichtfolie eine O₂-Sperrschicht umfasst und die Mehrschichtfolie eine Sauerstoffdurchlässigkeit von 1 bis 20 cm³/m² pro Tag bei 23 °C und 100 % relativer Feuchtigkeit aufweist.

14. Wärmeschrumpfbarer Verpackungsartikel nach Anspruch 8, wobei die Mehrschichtfolie ferner Folgendes umfasst:

(A) eine erste Schicht, die eine äußere Nahrungsmittelkontaktschicht ist und die auch als eine Dichtungsschicht dient, wobei die erste Schicht eine Mischung aus homogenem Ethylen/alpha-Olefin-Copolymer und linearem Polyethylen niedriger Dichte umfasst;

(B) eine zweite Schicht, die eine Mischung aus heterogenem Ethylen/alpha-Olefin-Copolymer und Ethylen/Vinylacetat-Copolymer umfasst;

(C) eine dritte Schicht, die Ethylen/Vinylacetat-Copolymer umfasst;

(D) eine vierte Schicht, die Polyvinylidenchlorid umfasst;

(E) eine fünfte Schicht, die Ethylen/Vinylacetat-Copolymer umfasst;

(F) eine sechste Schicht, die eine Mischung aus heterogenem Ethylen/alpha-Olefin-Copolymer und Ethylen/Vinylacetat-Copolymer umfasst; und

(G) eine siebte Schicht, die eine Mischung aus homogenem Ethylen/alpha-Olefin-Copolymer und linearem Polyethylen niedriger Dichte umfasst; und

wobei die Schichten in der Reihenfolge der ersten/zweiten/dritten/vierten/fünften/ sechsten/siebten Schicht vorhanden sind.

Revendications

1. Article d'emballage thermo-rétractable comprenant un film multi-couche thermo-rétractable possédant une couche intérieure de scellage thermo-scellée sur elle-même à un thermo-scellage, l'article possédant un premier côté et

un second côté, l'article possédant une jupe ou une tête vers l'extérieur du thermo-scellage, la jupe ou tête comprenant un bord d'article et une paire d'initiateurs de déchirement, la paire d'initiateurs de déchirement possédant un premier initiateur de déchirement et un second initiateur de déchirement, le premier initiateur de déchirement de la paire étant dans le premier côté de l'article, et le second initiateur de déchirement de la paire étant dans le second côté de l'article, l'article étant capable de posséder un premier déchirement manuellement initié, manuellement étendu dans le premier côté de l'article, et un second déchirement manuellement initié et manuellement étendu dans le second côté de l'article, le premier déchirement et le second déchirement étant chacun capables d'être étendus dans un sens machine à partir de la paire de premier et second initiateurs de déchirement, chaque déchirement étant étendu dans le sens machine à travers le thermo-scellage et sur la longueur de l'article, ou à travers l'article, chaque déchirement étant capable d'être manuellement étendu dans le sens machine à travers et jusqu'à un bord d'article opposé, pour que, lors de l'utilisation du film multi-couche pour réaliser un produit emballé en plaçant un produit à l'intérieur de l'article avec l'article enfermé de façon scellée autour du produit pour qu'un emballage soit formé, et après cela en rétractant le film autour du produit, l'emballage résultant puisse être manuellement ouvert, et le produit facilement enlevé de l'emballage, en initiant manuellement des déchirements en sens machine à partir des premier et second initiateurs de déchirement, les déchirements étant manuellement étendus à travers le scellage et vers le bord opposé de l'article, le film multi-couche présentant une résistance à l'impact de pointe d'au moins 50 Newtons par millièbre de pouce mesurée en utilisant ASTM D 3763-95A, au moins une couche du film multi-couche contenant au moins un mélange de polymères incompatibles sélectionné parmi le groupe constitué de :

- (A) un mélange de 80 à 40 pour cent en poids d'homopolymère d'éthylène et/ou de copolymère d'éthylène/alpha-oléfine avec de 20 à 60 pour cent en poids de copolymère d'éthylène/ester insaturé possédant une teneur en ester insaturé d'au moins 10 pour cent en poids ;
- (B) un mélange de résine ionomère avec un copolymère d'éthylène/ester insaturé, et/ou polybutylène, et/ou homopolymère de propylène et/ou copolymère de propylène ;
- (C) un mélange de copolymère d'éthylène/alpha-oléfine homogène avec un mélange de polymère recyclé comprenant un homopolymère d'éthylène, homopolymère de propylène, copolymère d'éthylène, copolymère de propylène, polyamide, copolymère d'éthylène/alcool vinylique, une résine ionomère, un copolymère d'éthylène/alpha-oléfine modifié par anhydride, et/ou agent antibloquant ;
- (D) un mélange de 10 à 75 pour cent en poids de copolymère d'éthylène/ester insaturé avec de 90 à 15 pour cent en poids de polypropylène et/ou de propylène/copolymère d'éthylène, et/ou de polybutylène, et/ou de copolymère d'éthylène/alpha-oléfine modifié, et/ou d'homopolymère de styrène, et/ou de copolymère de styrène/butadiène ;
- (E) un mélange de copolymère d'éthylène/norbornène avec un copolymère d'éthylène/ester insaturé et/ou polypropylène et/ou polybutylène ;
- (F) un mélange de 90 à 15 pour cent en poids de copolymère d'éthylène/alpha-oléfine avec de 10 à 75 pour cent en poids de polypropylène et/ou de polybutylène et/ou d'éthylène/norbornène ;
- (G) un mélange de 90 à 25 pour cent en poids d'homopolymère de propylène homogène et/ou de copolymère de propylène homogène avec de 10 à 75 pour cent en poids de copolymère d'éthylène/alpha-oléfine homogène et/ou de copolymère d'éthylène/ester insaturé ;
- (H) un mélange d'homopolymère de propylène et/ou de propylène/copolymère d'éthylène et/ou de polybutylène avec un copolymère d'éthylène/acrylate de méthyle et/ou copolymère d'éthylène/acide acrylique et/ou copolymère d'éthylène/acrylate de butyle ;
- (I) un mélange de polyamide avec du polystyrène et/ou un copolymère d'éthylène/alpha-oléfine et/ou copolymère d'éthylène/acétate de vinyle et/ou copolymère de styrène/butadiène ; et
- (J) un mélange de polyamide 6 et de polyamide 6I6T ; et

dans lequel au moins une portion de la jupe ou tête est thermo-fixée avec un reste du film restant thermo-rétractible, pour que, lors de la formation de l'emballage et la rétraction du film autour du produit, les retrait et roulage de la jupe ou tête soient réduits, et dans lequel l'article d'emballage thermo-rétractible ne comprend pas de raccord sur celui-ci.

2. Article thermo-rétractable selon la revendication 1, dans lequel la tête ou jupe comprend en outre au moins une aide à la préhension pour aider la préhension du film multi-couche durant le déchirement manuel.

3. Article thermo-rétractable selon la revendication 1, dans lequel une portion de la jupe ou tête sur le premier côté de l'article est thermo-fixée, et une portion correspondante de la jupe ou tête sur le second côté de l'article est également thermo-fixée, de préférence dans lequel l'article est un sac à scellage terminal et les premier et second

initiateurs de déchirement sont présents dans la jupe de sac, et un thermo-scellage est présent à l'intérieur de la portion thermo-fixée des premier et second côtés de l'article, plus de préférence dans lequel le premier initiateur de déchirement est aligné au-dessus du second initiateur de déchirement, et le thermo-scellage présent à l'intérieur de la portion thermo-fixée est un scellage périmétrique, et la jupe comprend en outre une première aide à la pré-

5 4. Article thermo-rétractable selon la revendication 1, dans lequel une première portion d'un premier côté de la jupe ou tête est scellé par points sur le second côté de la jupe ou tête à un premier scellage par points, et une seconde
10 portion du premier côté de la jupe ou tête est scellée par points sur le second côté de la jupe ou tête à un second scellage par points.

15 5. Article thermo-rétractable selon la revendication 1, dans lequel les portions thermo-fixées des premier et second côtés de la jupe ou tête comprennent un scellage périmétrique dans la jupe ou tête, de préférence dans lequel le premier initiateur de déchirement s'aligne directement au-dessus du second initiateur de déchirement, et la jupe ou
20 tête comprend en outre un premier scellage par points au sein de 25,4 mm (1 pouce) des premier et second initiateurs de déchirement et d'une première extrémité de la jupe, et un second scellage par points au sein de 25,4 mm (1 pouce) des premier et second initiateurs de déchirement et d'une seconde extrémité de la jupe ou tête.

25 6. Article thermo-rétractable selon la revendication 5, dans lequel la tête ou jupe comprend en outre une première aide à la préhension entre le premier scellage par points et la première extrémité de la tête ou jupe, et une seconde
30 aide à la préhension entre les premier et second initiateur de déchirement et une seconde extrémité de la tête ou jupe.

35 7. Article thermo-rétractable selon la revendication 5, dans lequel l'article est un sac ou sachet à scellage latéral possédant une jupe comprenant une pluralité de paires de premier et second initiateurs de déchirement, chaque premier initiateur de déchirement étant aligné directement au-dessus du second initiateur de déchirement avec lequel est il est apparié, de préférence (a) dans lequel l'article est un sac à scellage latéral possédant une jupe qui comprend, pour chaque paire de premier et second initiateurs de déchirement, un premier scellage par points au sein de 25,4 mm (1 pouce) de la paire d'initiateurs de déchirement, le premier scellage par points étant entre la
40 paire d'initiateurs de déchirement et une première extrémité de la jupe, et un second scellage par points au sein de 25,4 mm (1 pouce) de la paire d'initiateurs de déchirement, le second scellage par points étant entre la paire d'initiateurs de déchirement et une seconde extrémité de la jupe, ou (b) dans lequel le film multi-couche possède un taux de transmission d'oxygène d'au moins 50 cc/m² par jour à TPN et 0 % d'humidité relative, ou (c) dans lequel le film multi-couche présente un agencement de couches polymériques non symétrique.

45 8. Article d'emballage thermo-rétractable selon la revendication 1, dans lequel la jupe ou tête comprend une pluralité de la paire d'initiateurs de déchirement, chaque paire d'initiateurs de déchirement possédant un premier initiateur de déchirement et un second initiateur de déchirement, le premier initiateur de déchirement étant dans le premier côté de l'article, et le second initiateur de déchirement étant dans le second côté de l'article, chaque paire d'initiateurs de déchirement étant à un emplacement pour générer un premier déchirement manuellement initié, manuellement étendu dans le premier côté de l'article, et un second déchirement manuellement initié et manuellement étendu dans le second côté de l'article, le premier déchirement et le second déchirement étant chacun capables d'être étendus dans un sens machine à partir des premier et second initiateurs de déchirement respectifs, chaque déchirement étant capable d'être étendu dans le sens machine à travers le thermo-scellage et sur la longueur de l'article, ou à travers l'article, chaque déchirement étant capable d'être manuellement étendu dans le sens machine à travers et jusqu'à un bord d'article opposé, pour que, lors de l'utilisation du film multi-couche pour réaliser un produit emballé en fournissant un produit à l'intérieur de l'article avec l'article enfermé de façon scellée autour du produit pour qu'un emballage soit formé, et après cela en rétractant le film autour du produit, l'emballage résultant puisse être manuellement ouvert, le déchirement d'une ou de plusieurs des paires d'initiateurs de déchirement permettant à une portion de l'emballage d'être enlevée du produit emballé pour qu'une portion découverte du produit puisse être séparée d'un reste du produit, laissant un reste de l'emballage autour d'au moins une portion du reste du produit, en initiant des premier et second déchirements en sens machine à partir d'au moins une paire d'initiateurs de déchirement, les déchirements étant étendus à travers le scellage et vers le bord opposé de l'article.

55 9. Article d'emballage thermo-rétractable selon la revendication 8, dans lequel l'article d'emballage est un sac à scellage latéral aplati réalisé à partir d'un tubage sans soudure, le sac à scellage latéral possédant un haut ouvert, un bord bas plié, et des premier et second scellages latéraux avec des première et seconde jupes de sac respectives vers l'extérieur de premier et second scellages latéraux respectifs, la pluralité de paires d'initiateurs de déchirement étant

espacées les unes des autres le long de la première jupe de sac, chaque déchirement étant capable d'être manuellement étendu sur la largeur entière du sac à scellage latéral à travers les deux scellages latéraux et à travers la seconde jupe.

5 10. Article d'emballage thermo-rétractable selon la revendication 9, dans lequel au moins une portion d'un premier côté de la jupe ou tête est thermo-scellée sur le second côté de la jupe ou tête en au moins un thermo-scellage, de préférence (a) dans lequel le premier côté de la jupe ou tête est thermo-scellé sur le second côté de la jupe ou tête en une pluralité de scellages par points, ou (b) dans lequel le premier côté de la jupe ou tête est thermo-scellé sur le second côté de la jupe ou tête en un thermo-scellage le long d'un bord extérieur de la jupe ou tête.

10 11. Article d'emballage thermo-rétractable selon la revendication 9, dans lequel la pluralité de paires d'initiateurs de déchirement sont situées à des intervalles de 25 mm à 76 mm (1 à 3 pouces).

15 12. Article d'emballage thermo-rétractable selon la revendication 8, dans lequel chacun des premier initiateurs de déchirement coïncide ou coïncide sensiblement avec le second initiateur de déchirement avec lequel il est apparié, et chacun des premier initiateurs de déchirement est une fente à travers le premier côté de l'article, et chacun des second initiateurs de déchirement est une fente à travers le second côté de l'article, et chacune des fentes est orientée dans le sens machine, de préférence dans lequel chacune des fentes est orientée au sein de 20 degrés du sens machine.

20 13. Article d'emballage thermo-rétractable selon la revendication 8, dans lequel le film multi-couche a été orienté biaxialement à l'état solide et présente un retrait libre total, tel que mesuré par ASTM D 2732, de 20 pour cent à 105 pour cent à 85°C (185°F), ou dans lequel le film multi-couche thermo-rétractable présente une résistance à l'impact de pointe, déterminée en utilisant ASTM D 3763-95A, de 2000 à 10000 N/mm (50 à 250 Newtons par millième de pouce), et le film multi-couche possède une épaisseur totale, avant rétraction, de 0,038 mm (1,5 millième de pouce) à 0,13 mm (5 millièmes de pouce), ou dans lequel le film multi-couche comprend une couche barrière à l'O₂ et le film multi-couche présente un taux de transmission d'oxygène de 1 à 20 cc/m² par jour par atm à 23°C et 100 % d'humidité relative.

30 14. Article d'emballage thermo-rétractable selon la revendication 8, dans lequel le film multi-couche comprend :

(A) une première couche qui est une couche extérieure de contact alimentaire et qui sert également de couche de scellage, la première couche comprenant un mélange de copolymère d'éthylène/alpha-oléfine homogène et de polyéthylène basse densité linéaire ;

35 (B) une deuxième couche comprenant un mélange de copolymère d'éthylène/alpha-oléfine hétérogène et de copolymère d'éthylène/acétate de vinyle ;

(C) une troisième couche comprenant un copolymère d'éthylène/acétate de vinyle ;

(D) une quatrième couche comprenant du chlorure de polyvinylidène ;

(E) une cinquième couche comprenant un copolymère d'éthylène/acétate de vinyle ;

40 (F) une sixième couche comprenant un mélange de copolymère d'éthylène/alpha-oléfine hétérogène et de copolymère d'éthylène/acétate de vinyle ; et

(G) une septième couche comprenant un mélange de copolymère d'éthylène/alpha-oléfine homogène et de polyéthylène basse densité linéaire ; et

45 dans lequel les couches sont présentes dans l'ordre de : première / deuxième / troisième / quatrième / cinquième / sixième / septième.

FIG. 1A

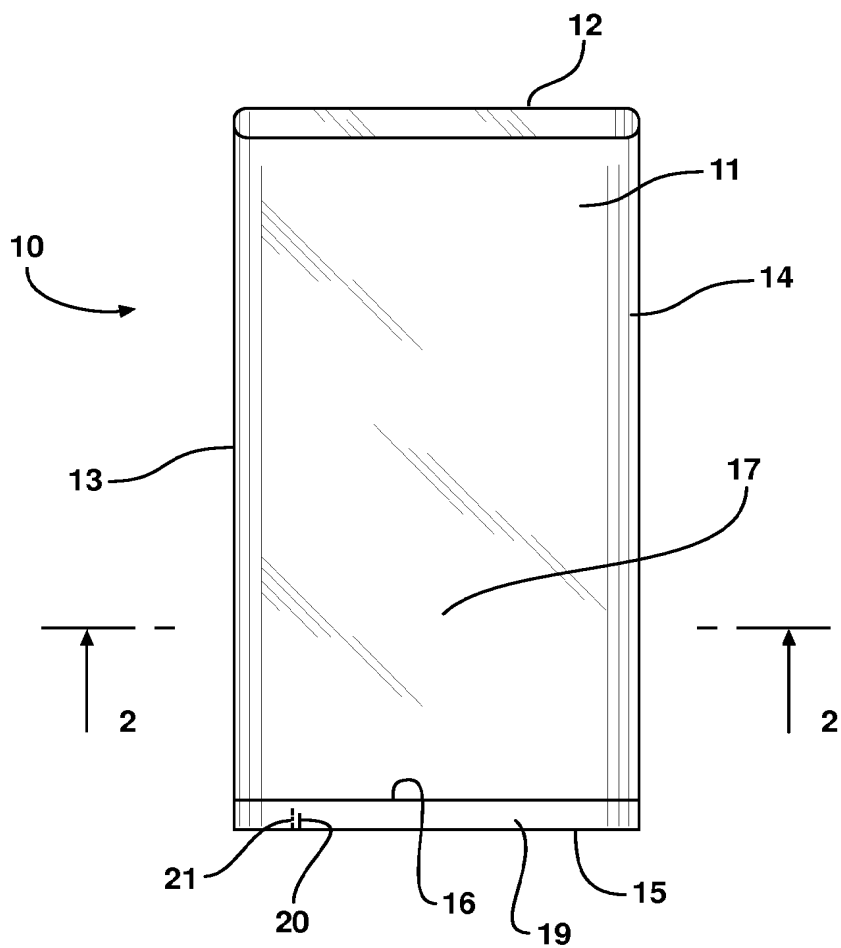


FIG. 2

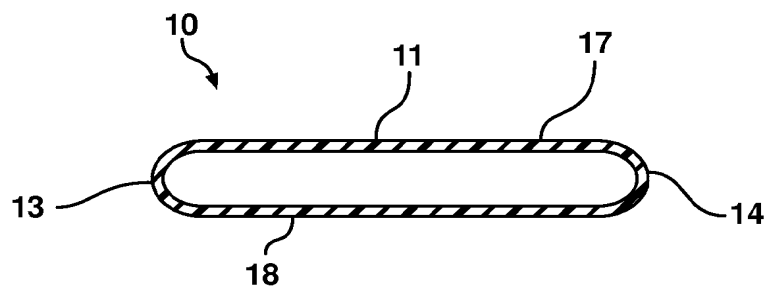


FIG. 1B

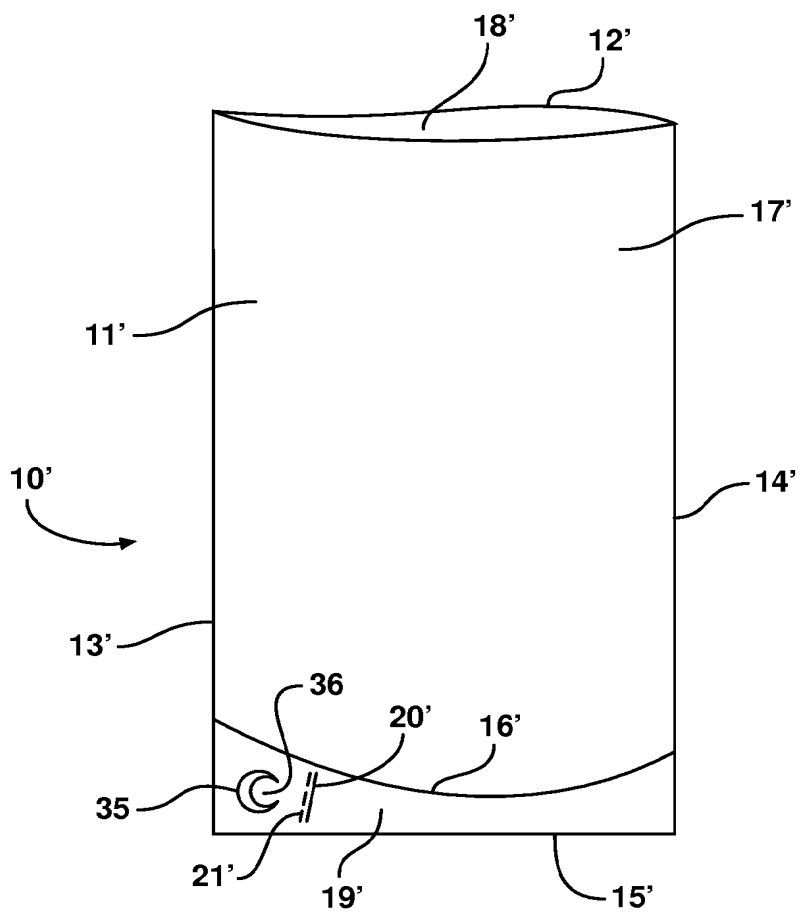


FIG. 1C

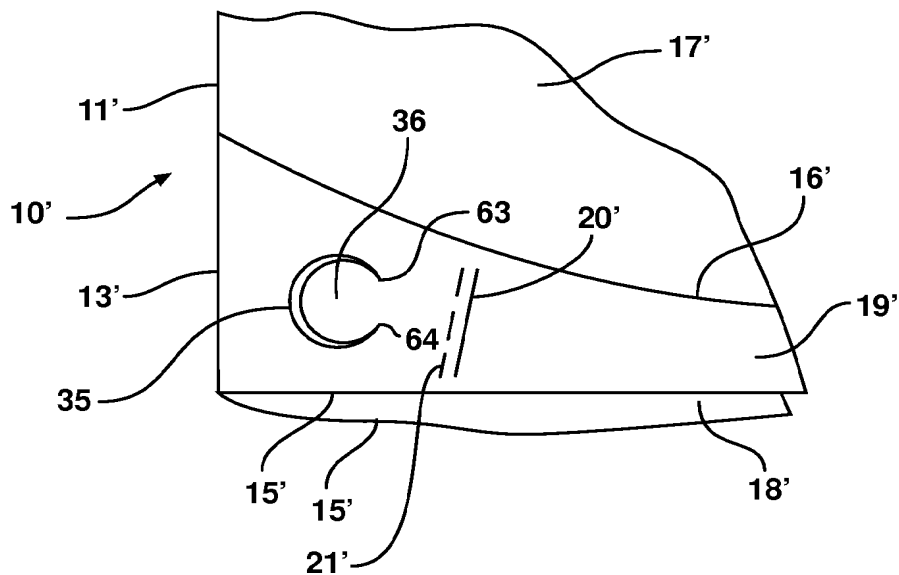


FIG. 1D

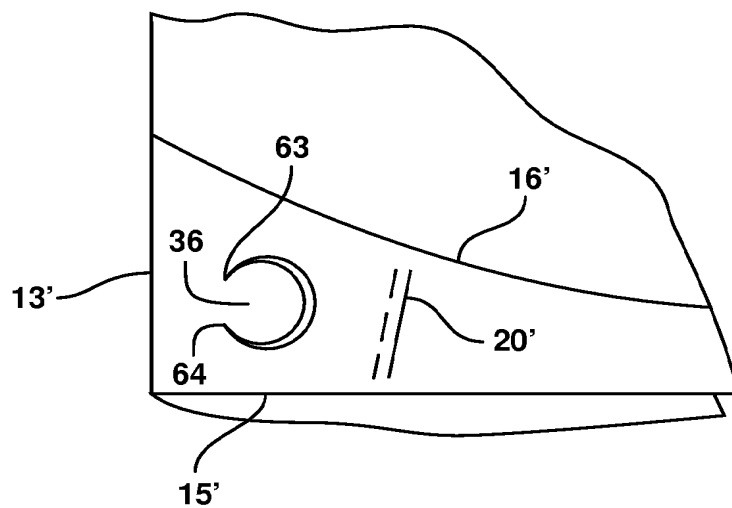


FIG. 1E

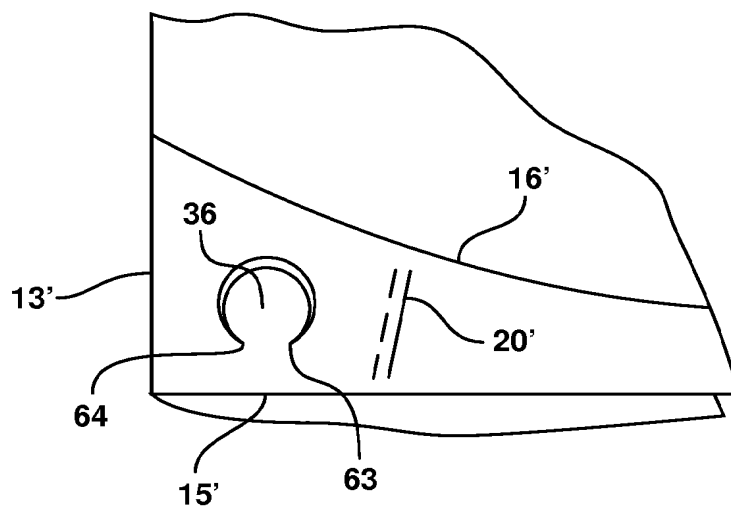


FIG. 1F

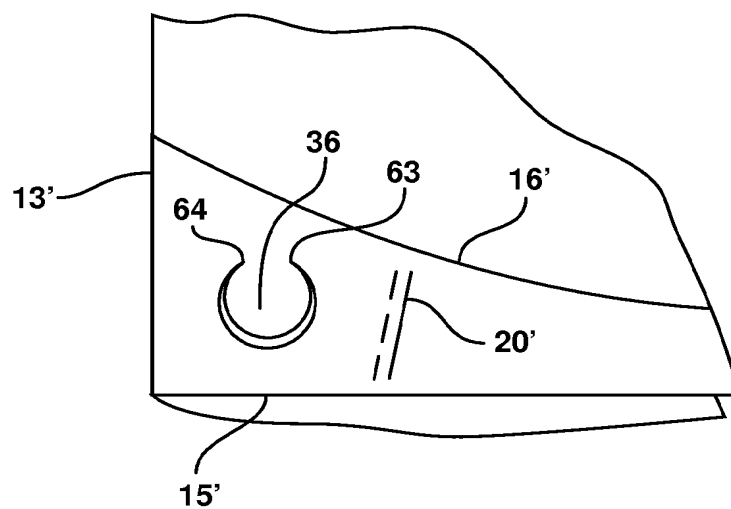


FIG. 3

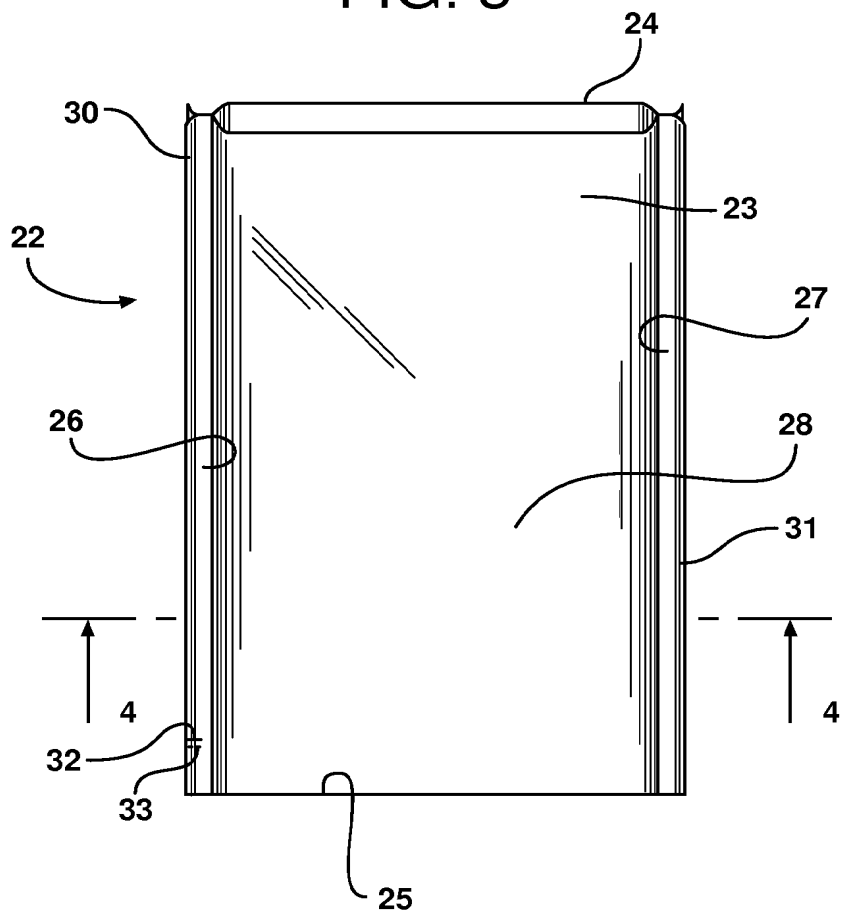


FIG. 4

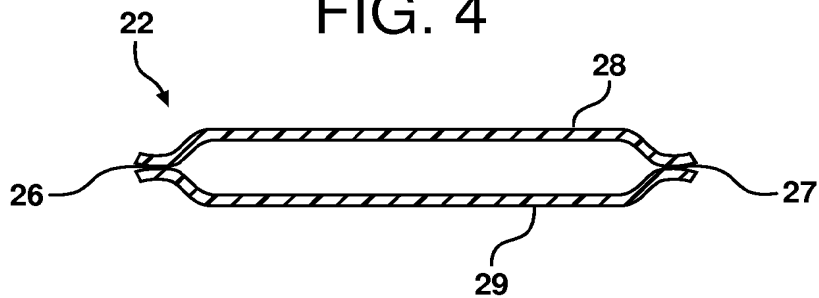


FIG. 5

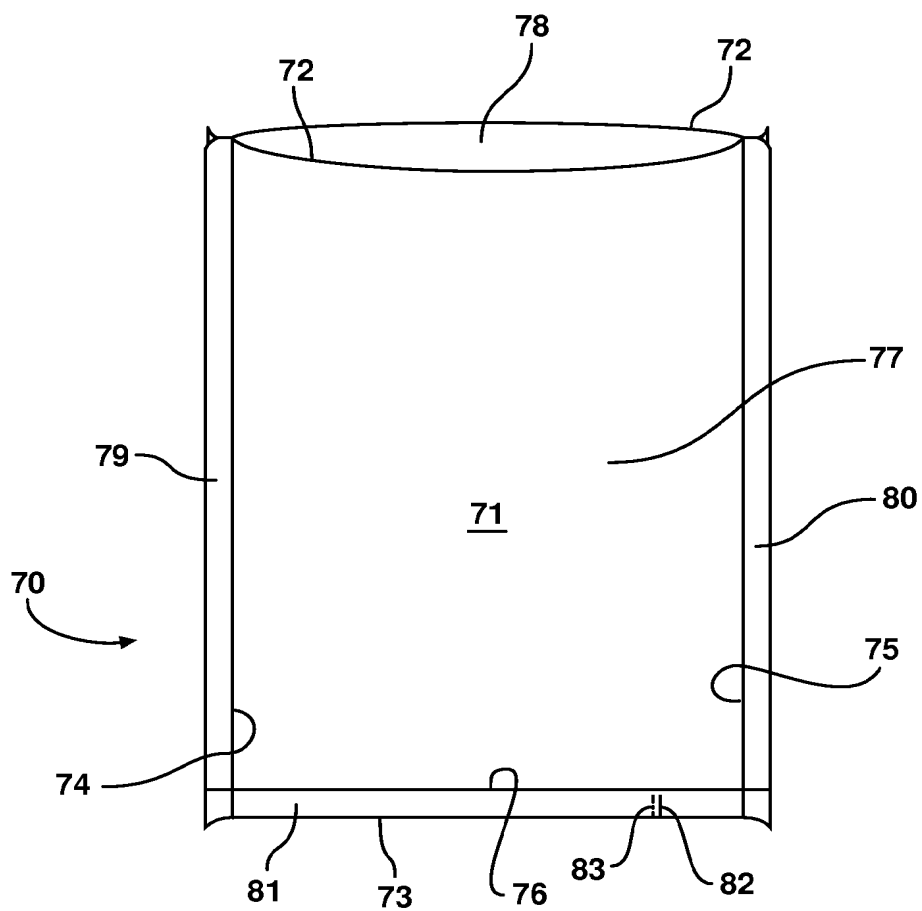


FIG. 6A

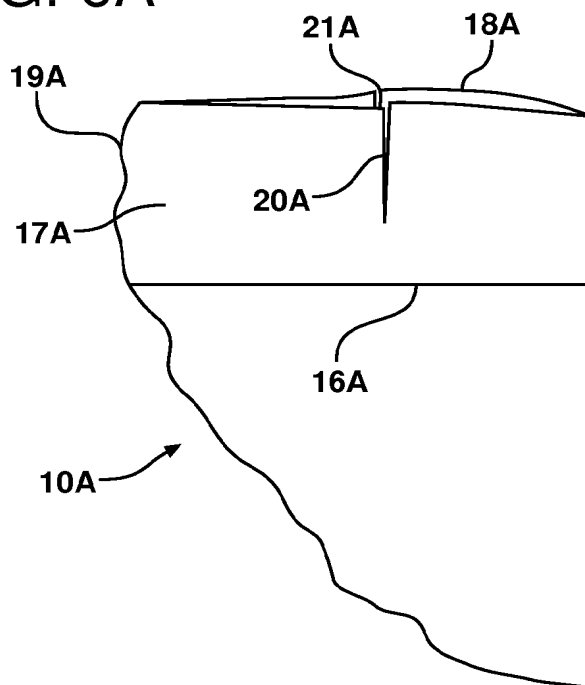


FIG. 6B

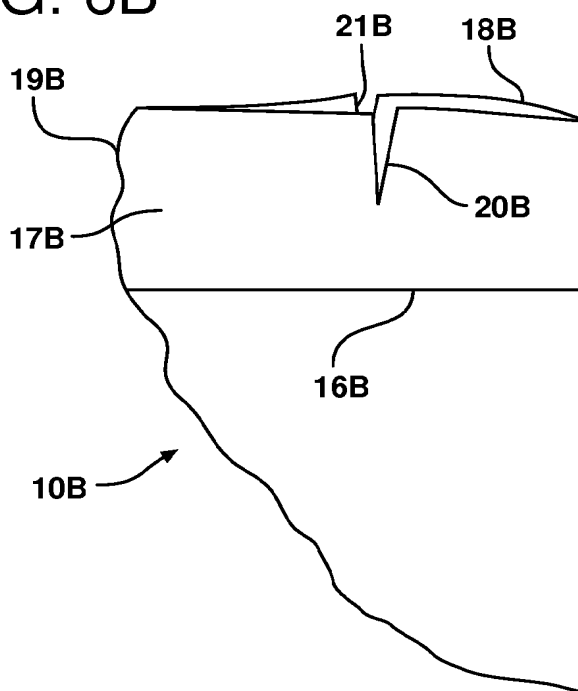


FIG. 6C

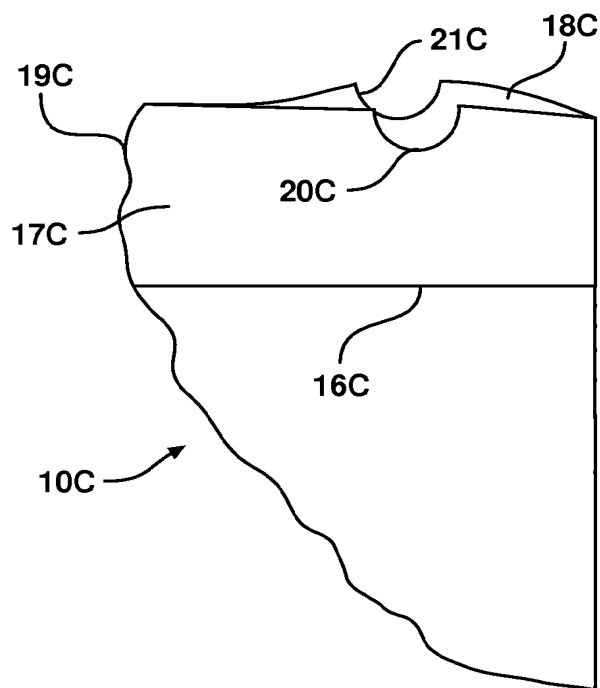


FIG. 6D

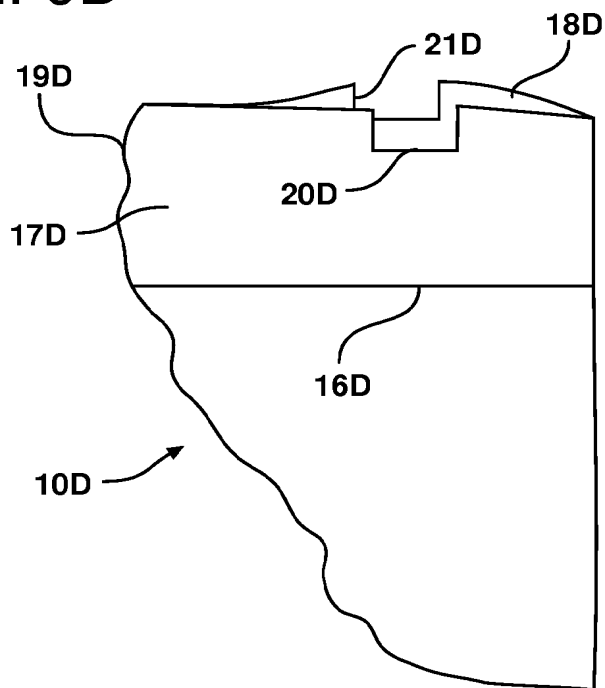


FIG. 6E

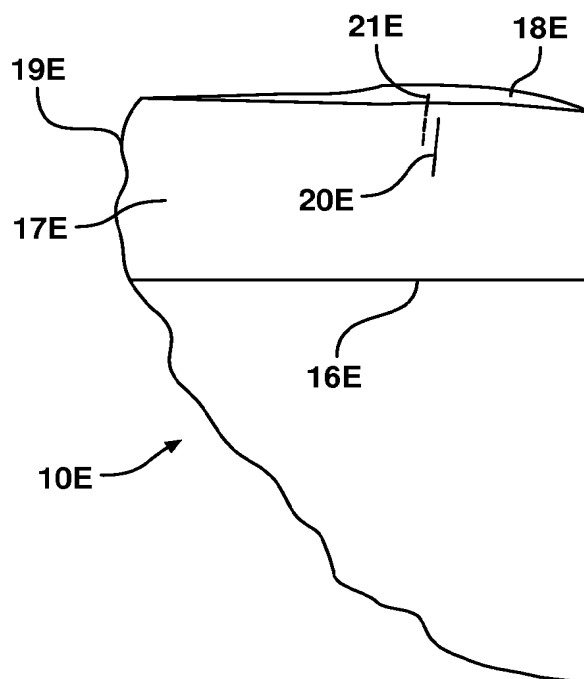


FIG. 6F

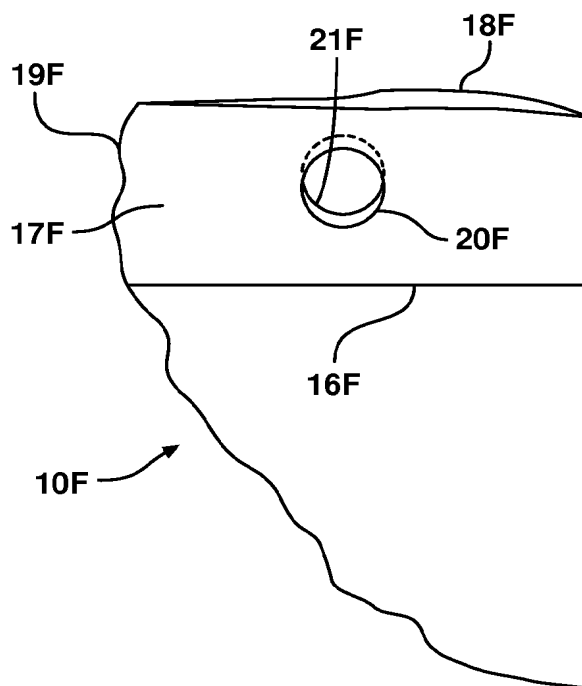


FIG. 6G

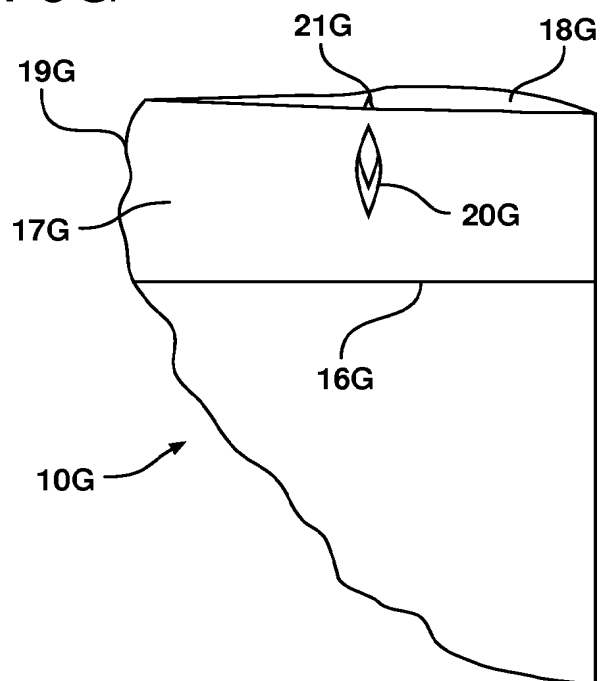


FIG. 6H

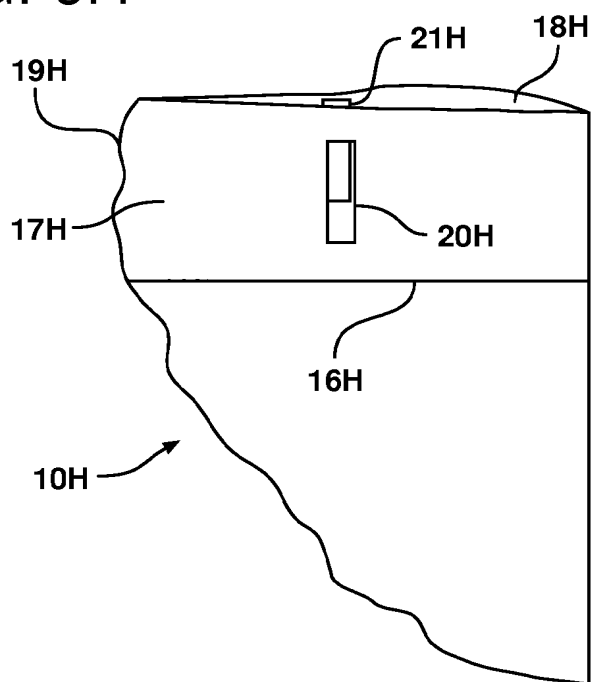


FIG. 6I

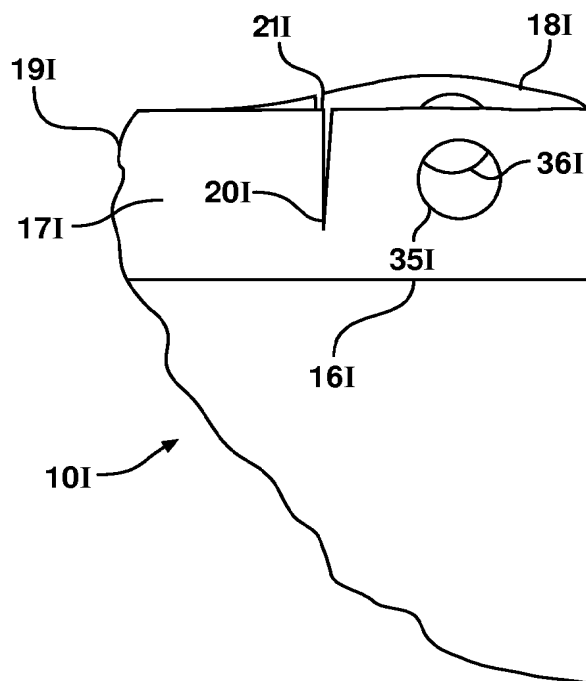


FIG. 6J

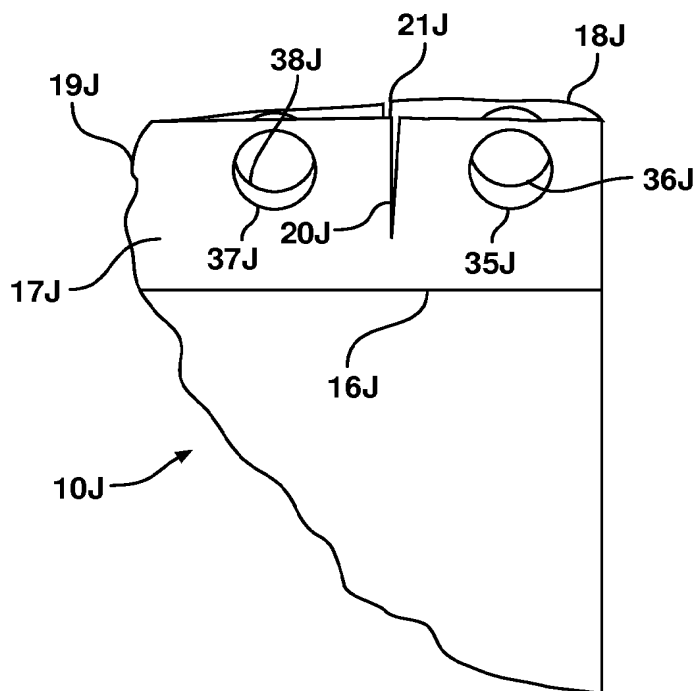


FIG. 6K

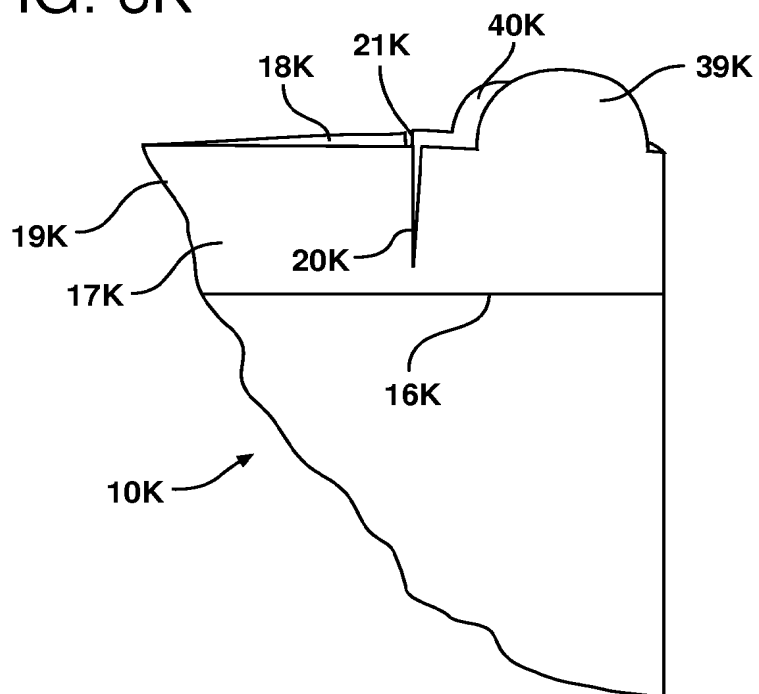


FIG. 6L

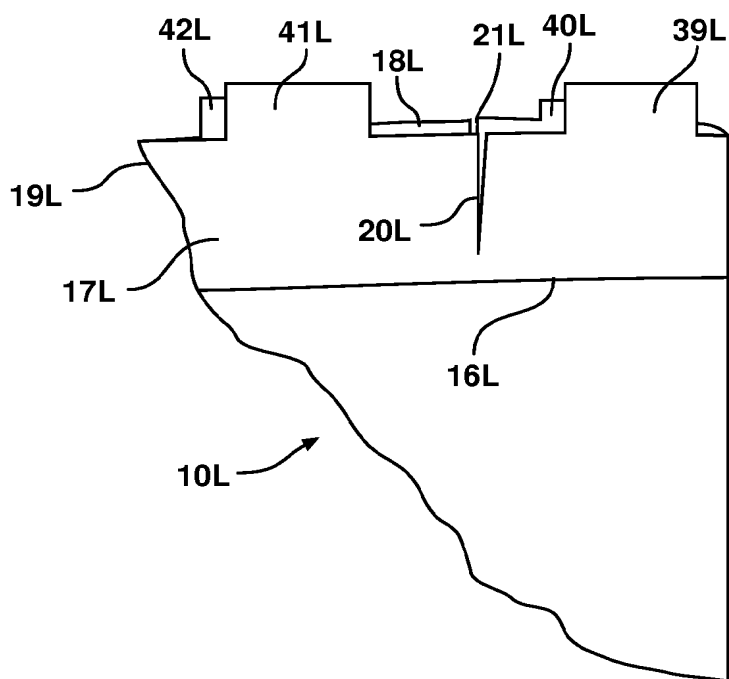


FIG. 6M

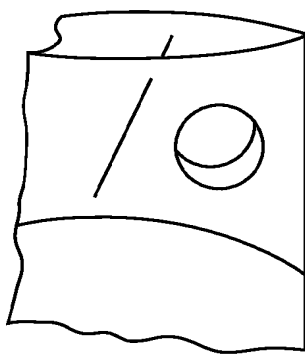


FIG. 6N

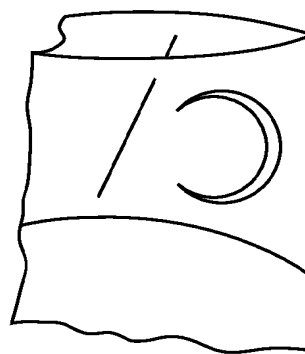


FIG. 6O

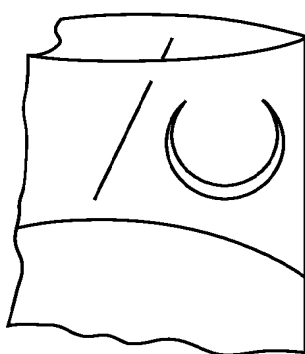


FIG. 6P

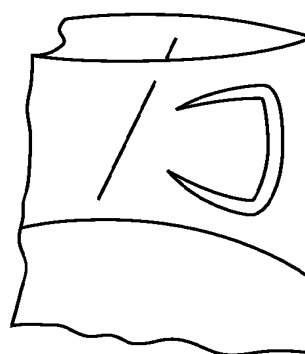


FIG. 6Q

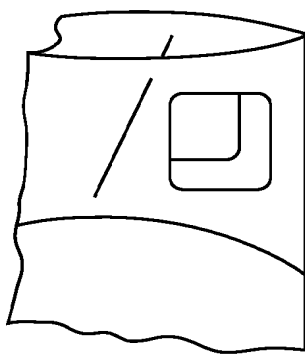


FIG. 6R

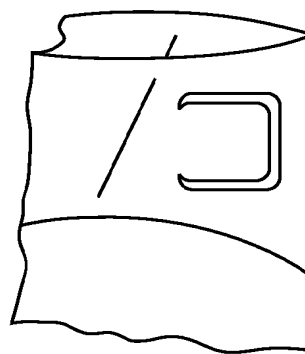


FIG. 6S

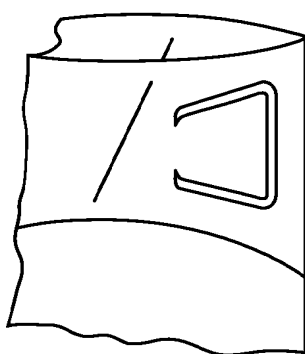


FIG. 6T

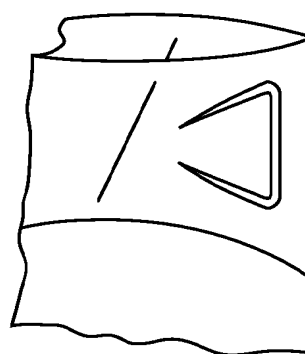


FIG. 6U

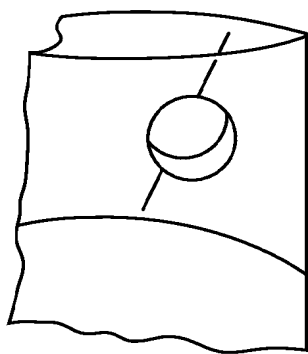


FIG. 6V

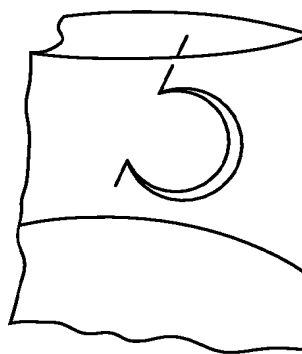


FIG. 6W

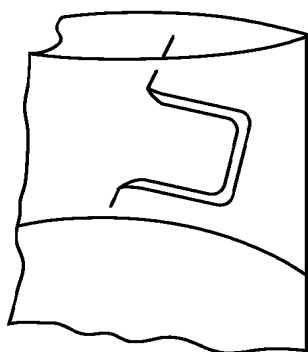


FIG. 6X

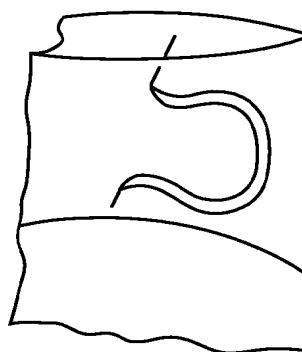


FIG. 6Y

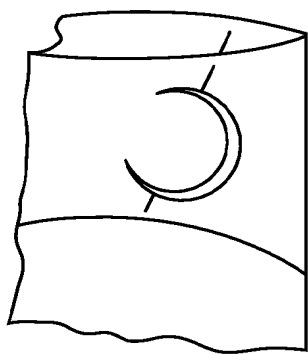


FIG. 6Z

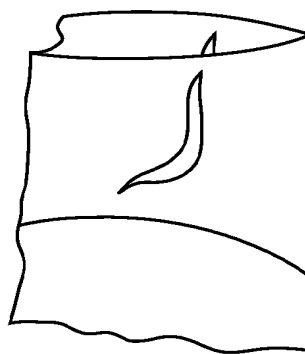


FIG. 6AA

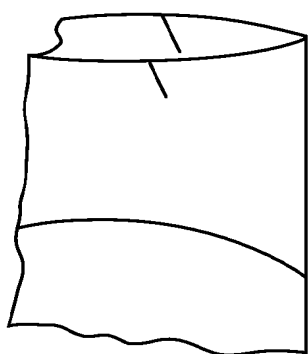


FIG. 6BB

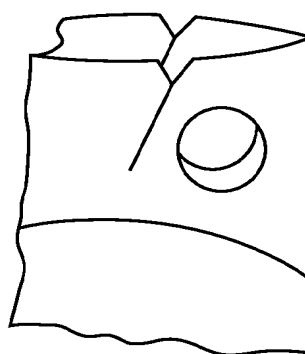


FIG. 6CC

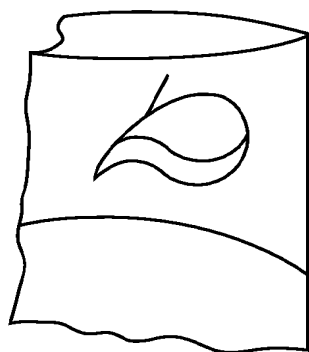


FIG. 6DD

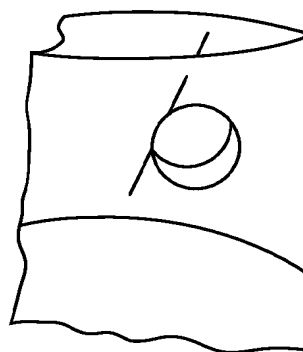


FIG. 6EE

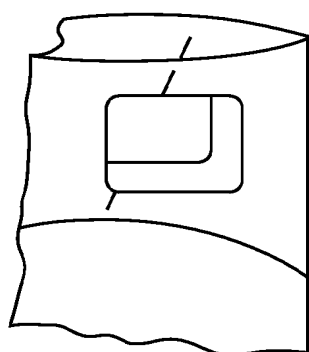


FIG. 6FF

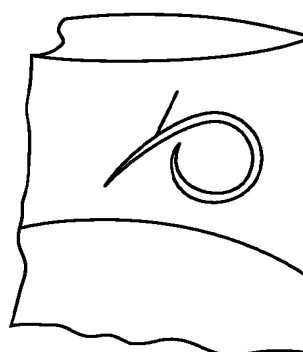


FIG. 7A

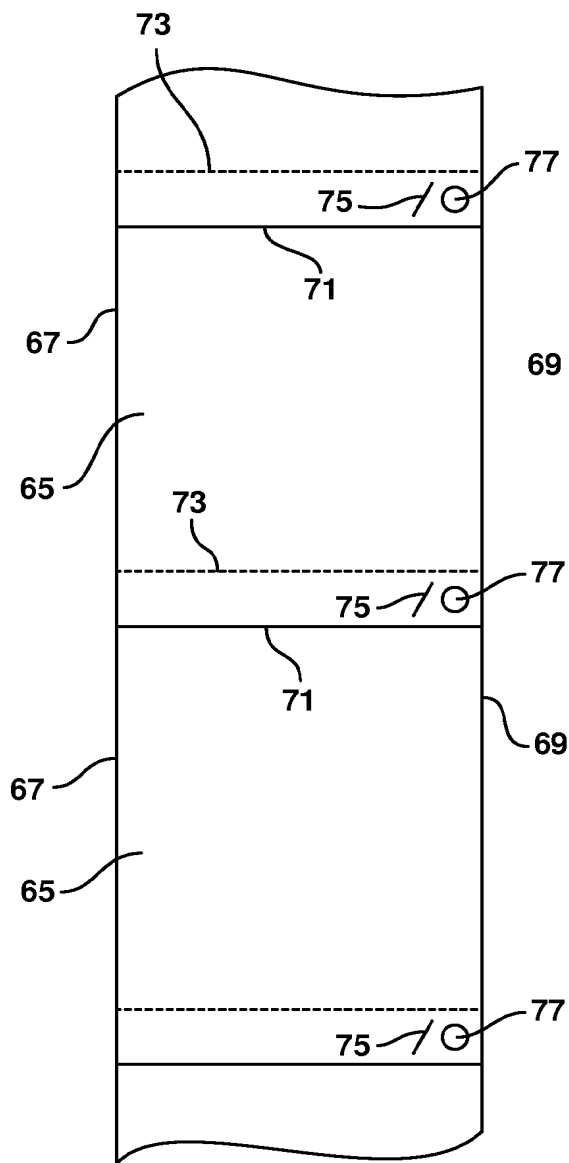


FIG. 7B

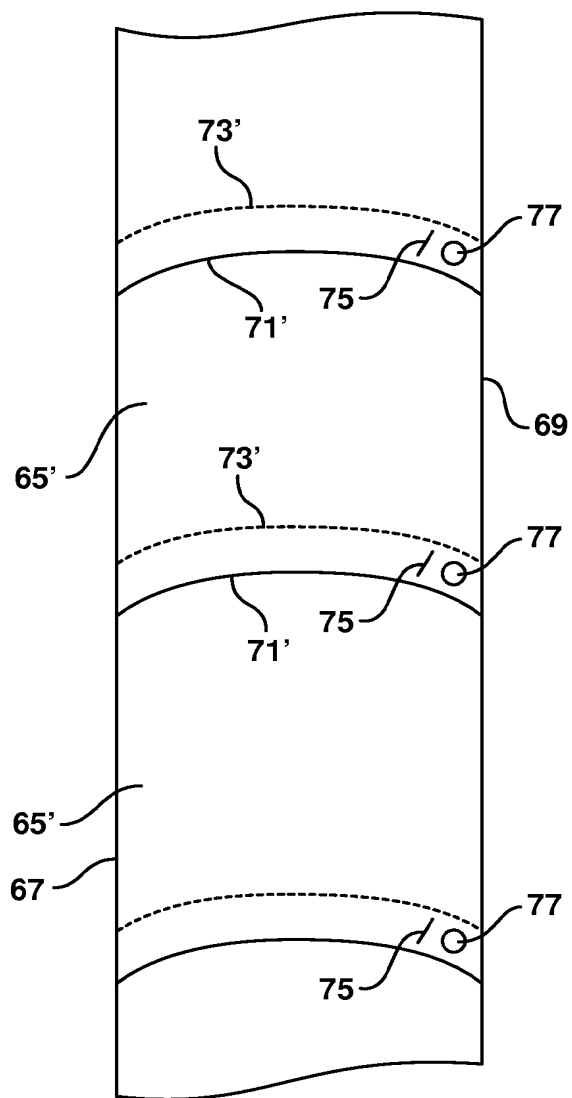


FIG. 7C

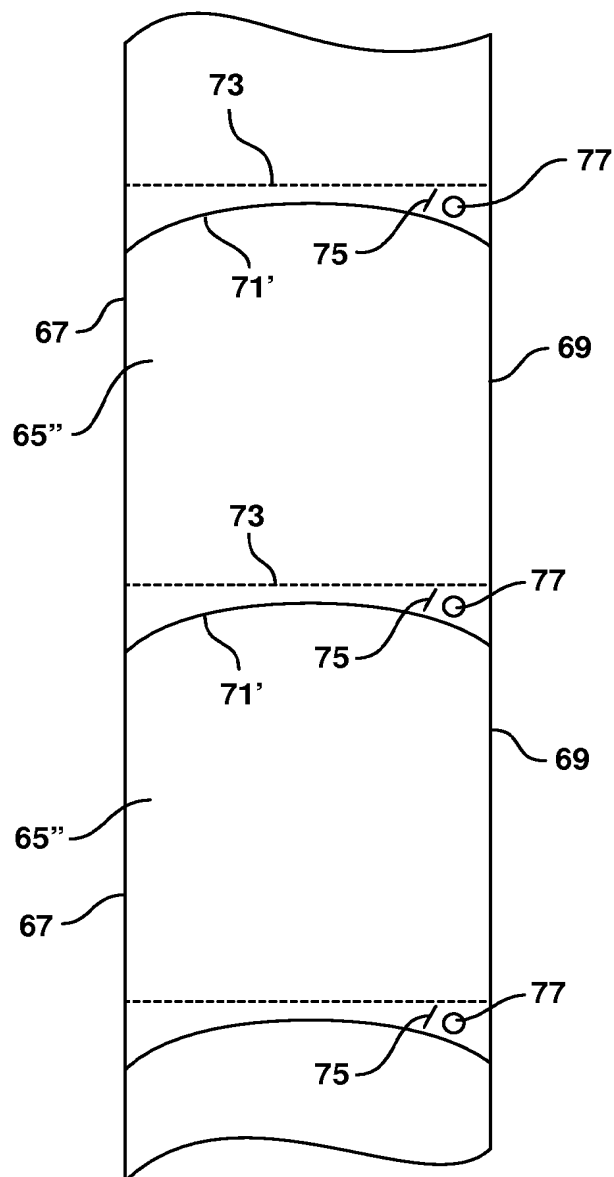


FIG. 8

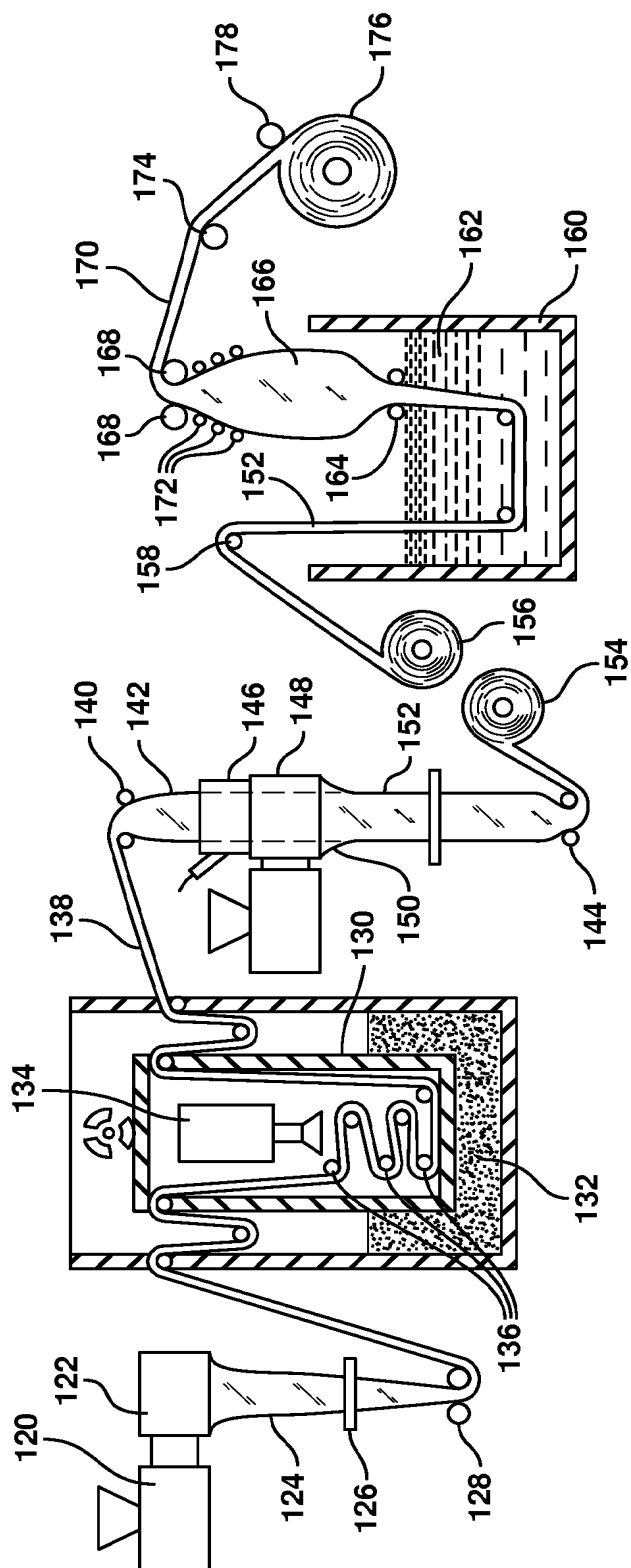


FIG. 9

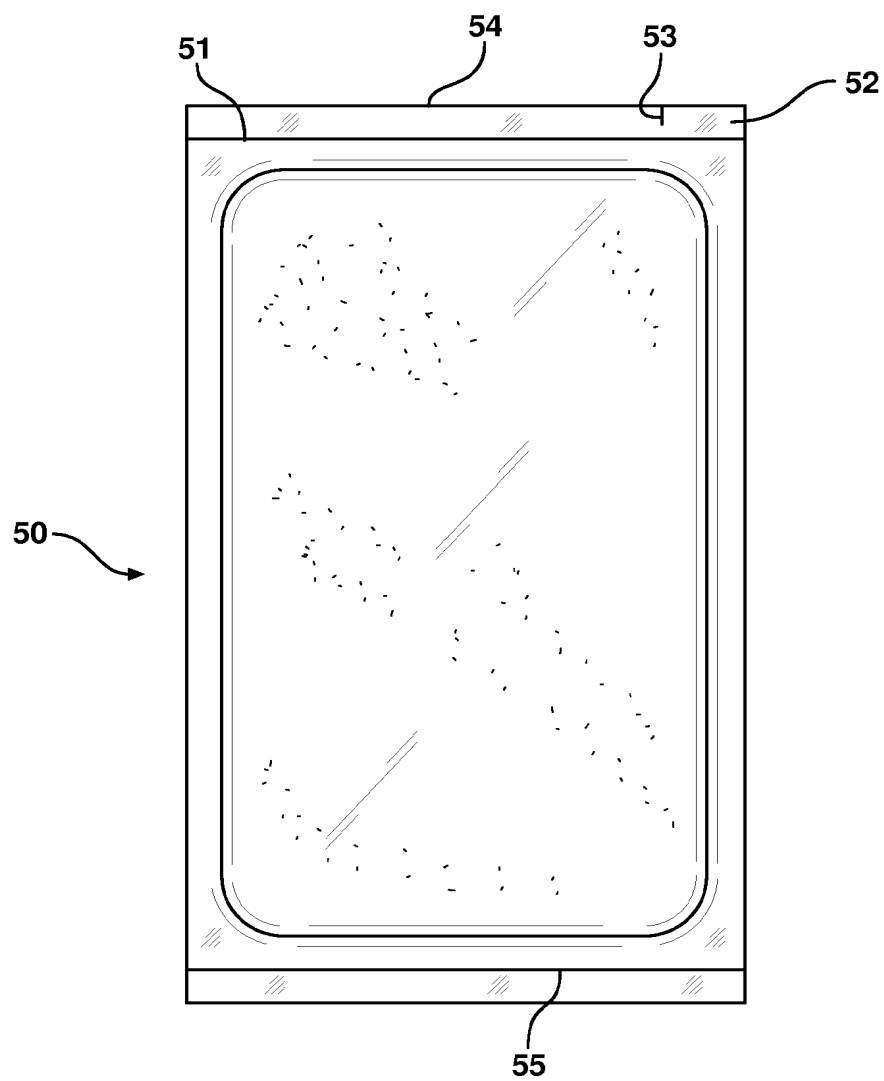


FIG. 10

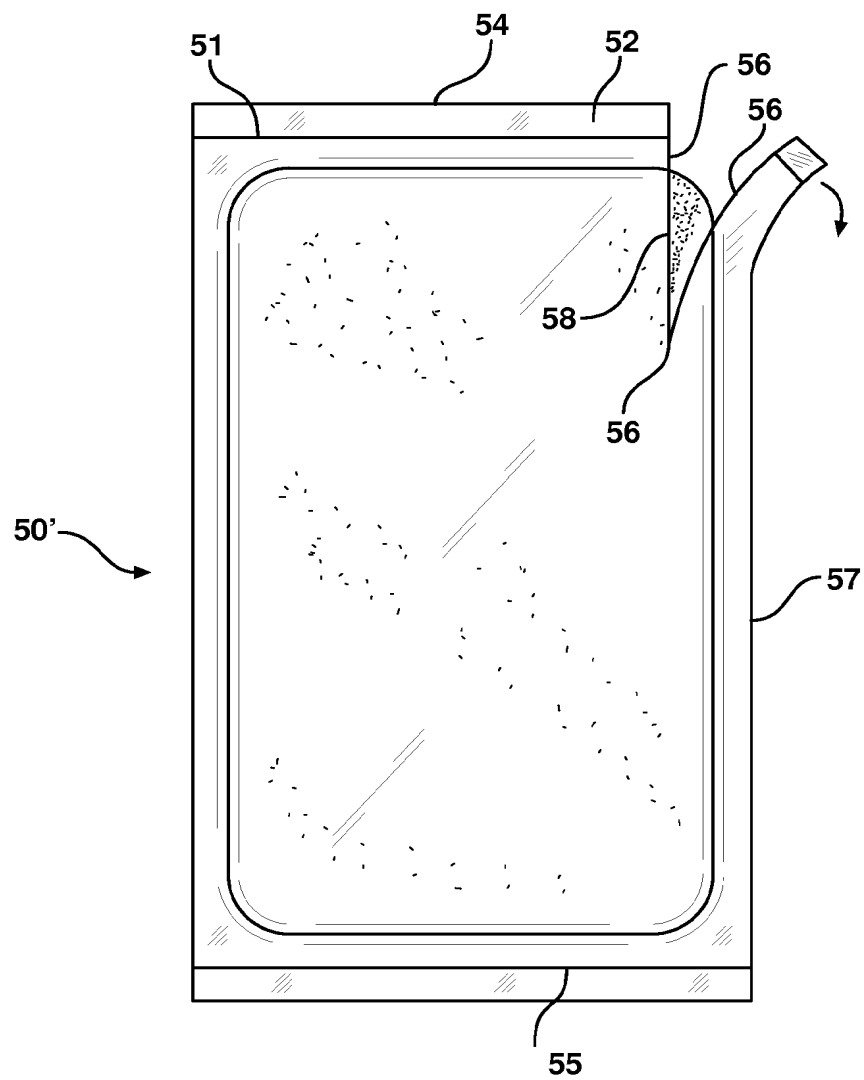


FIG. 11

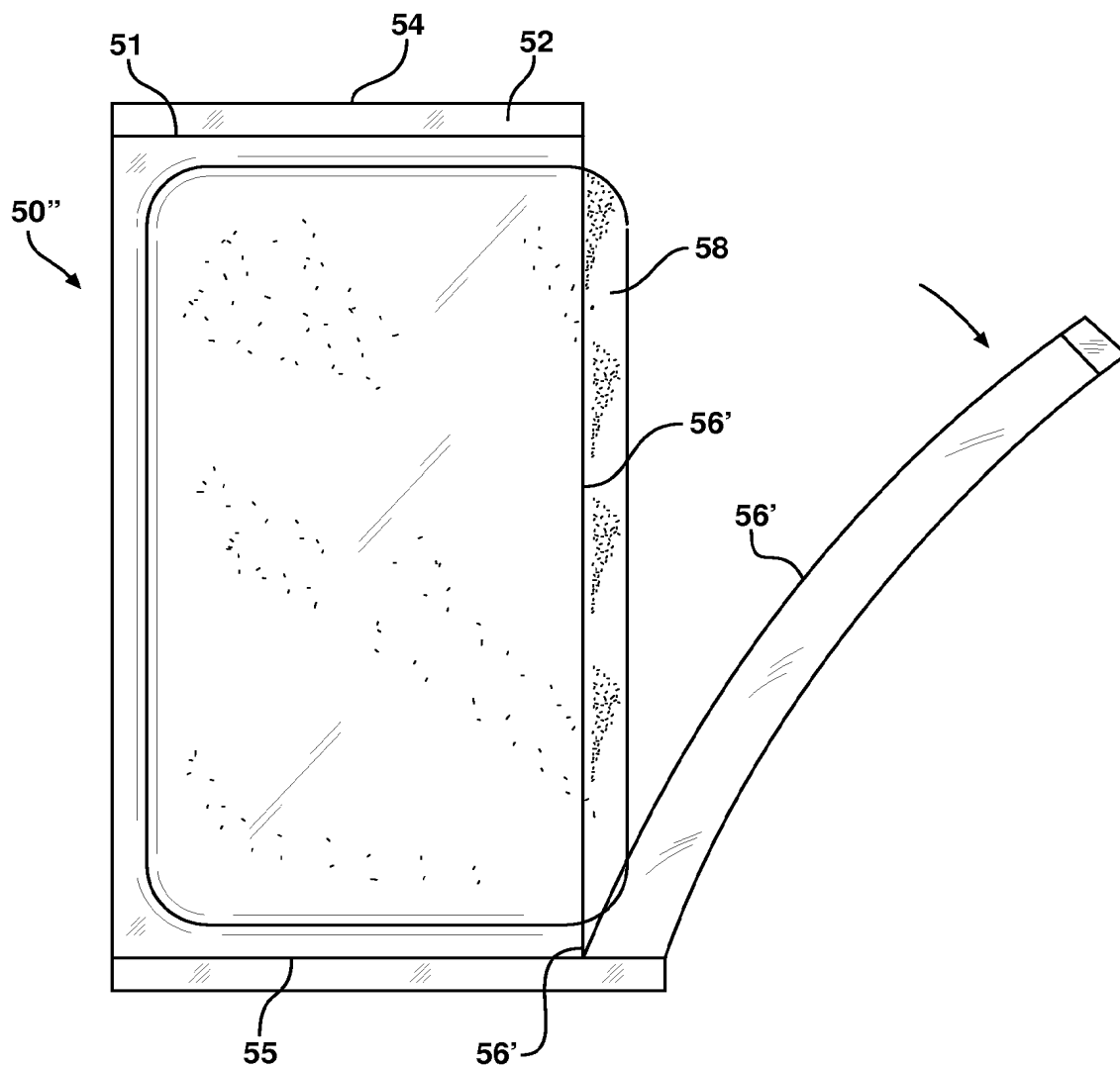


FIG. 12
(Comparative)

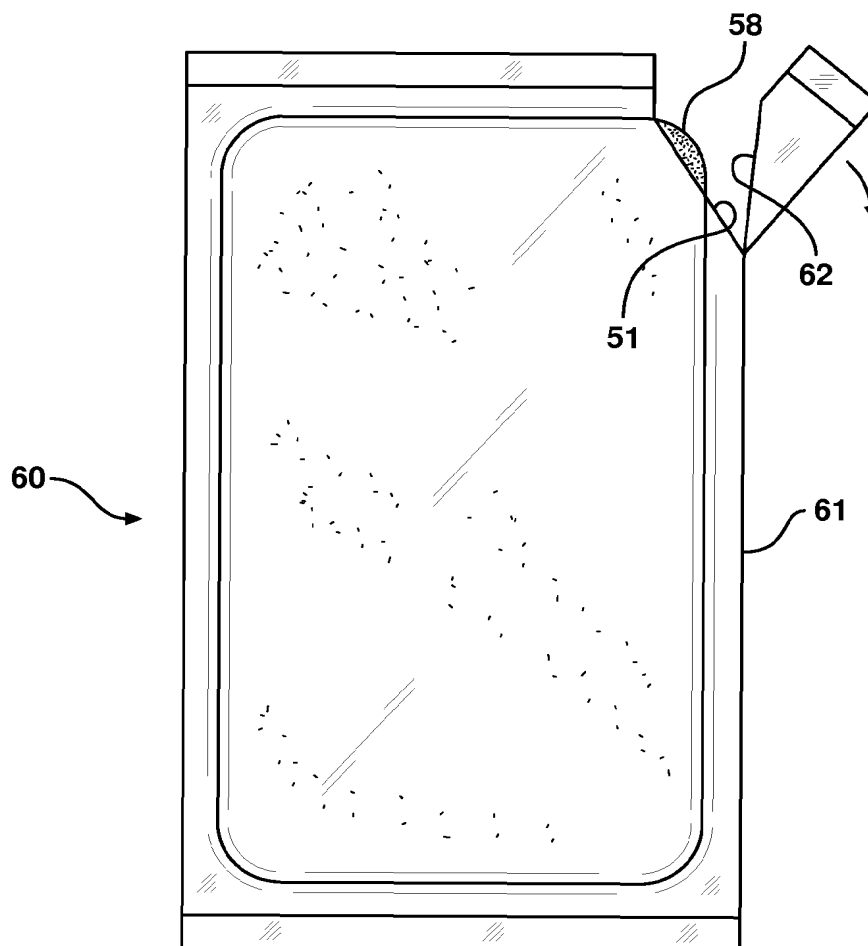


FIG. 13

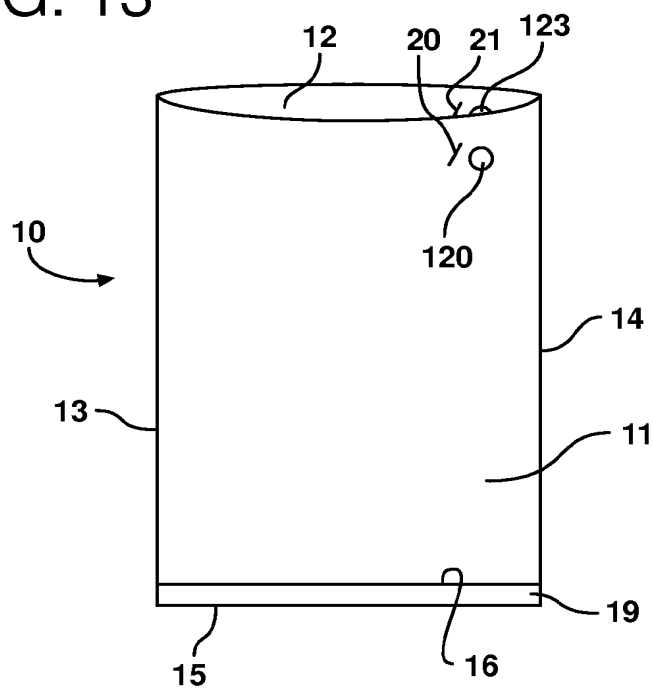


FIG. 14

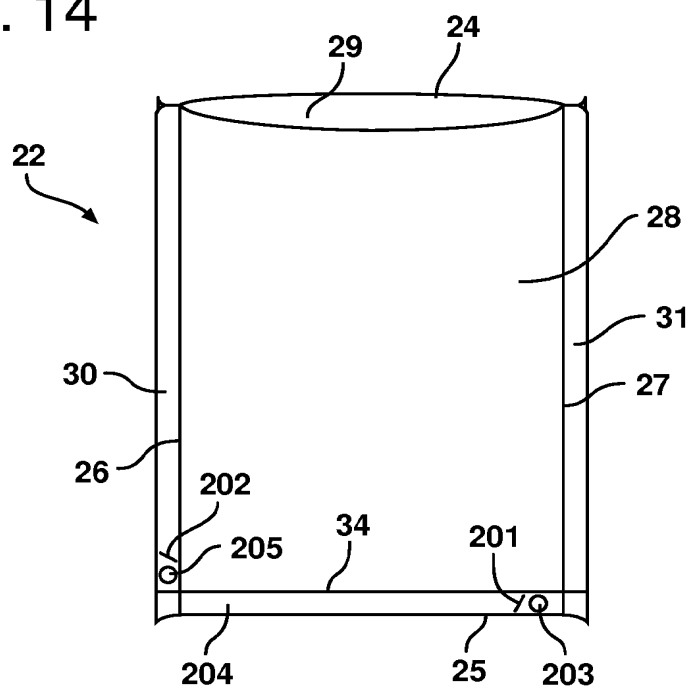


FIG. 15

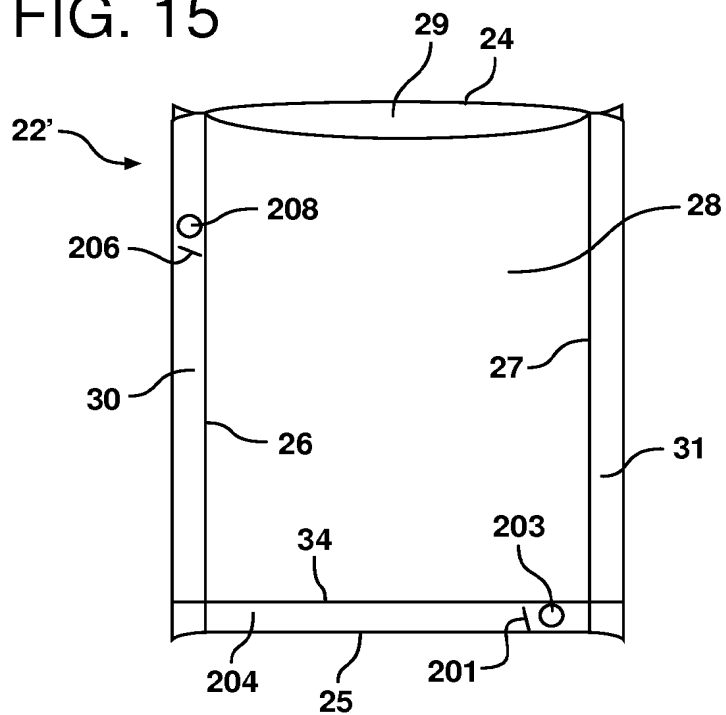


FIG. 16

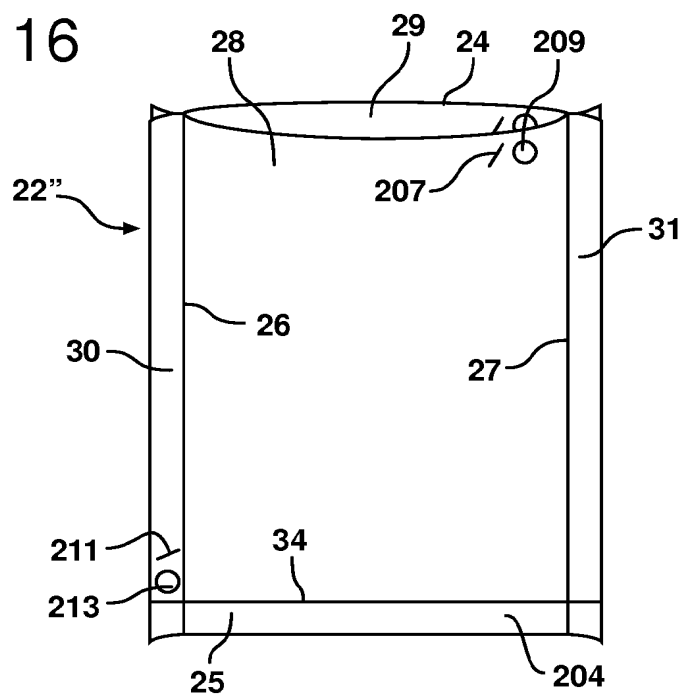


FIG. 17

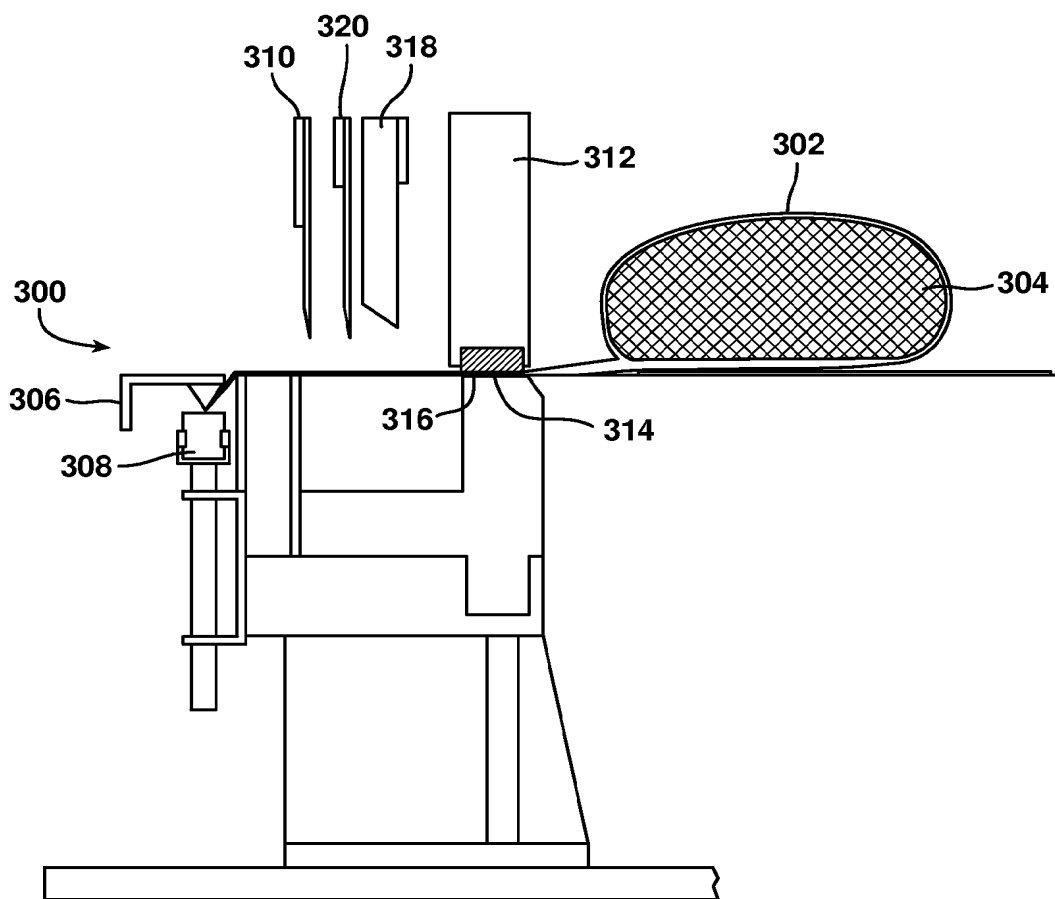


FIG. 18

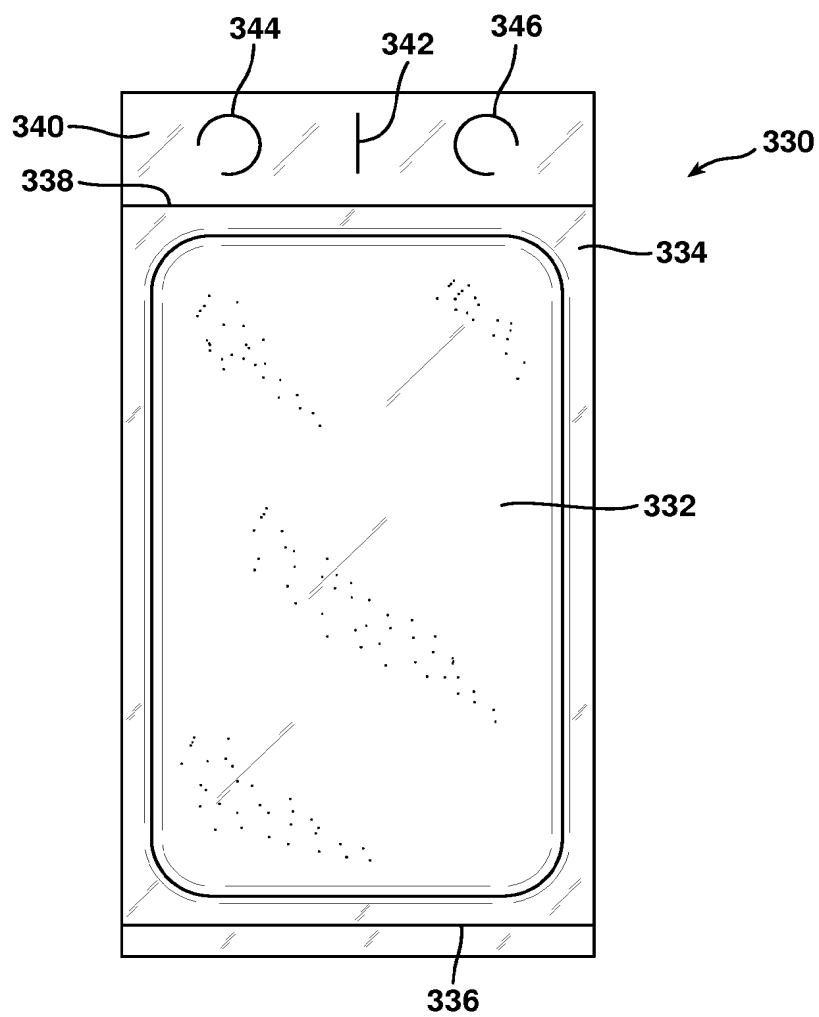


FIG. 19

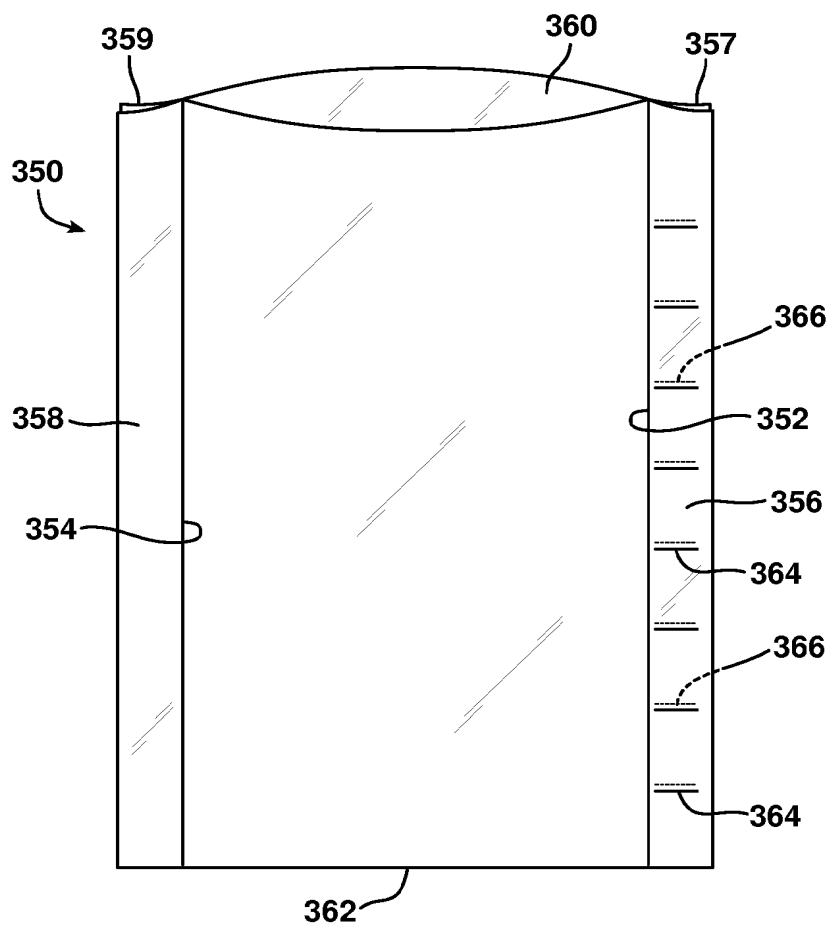


FIG. 20

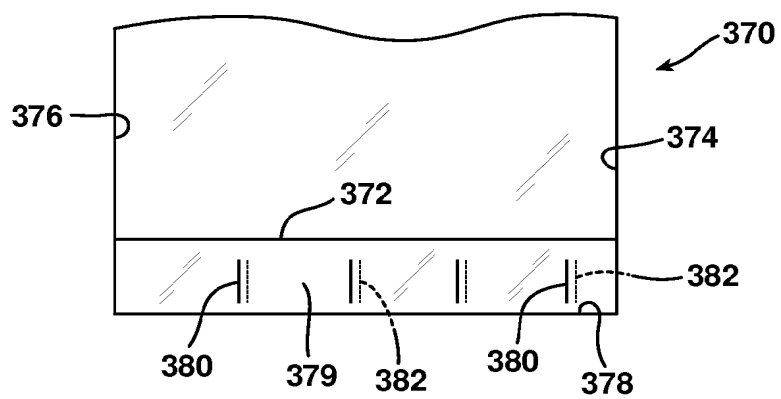


FIG. 21

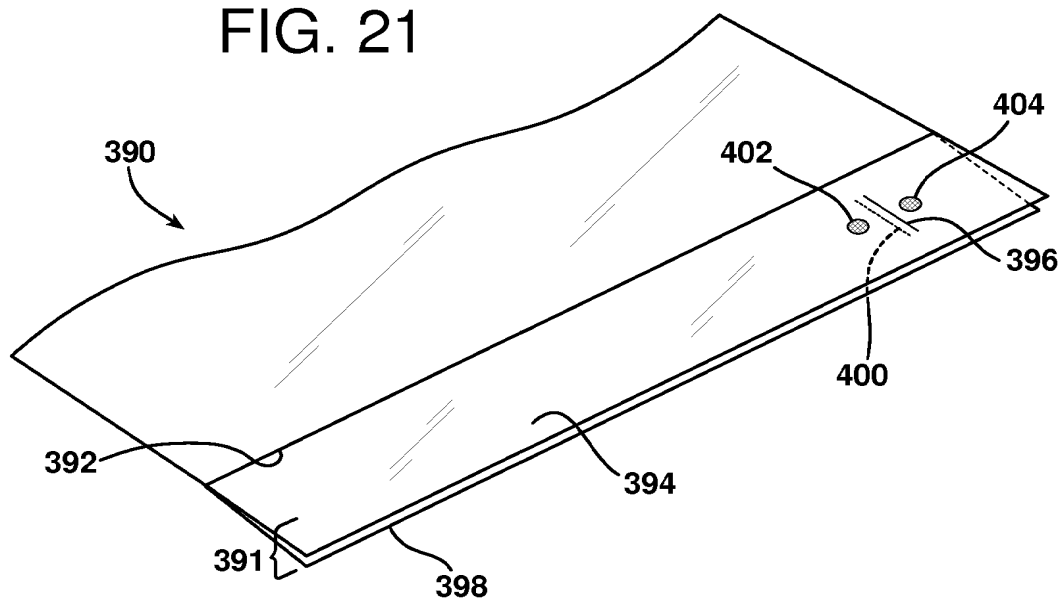


FIG. 22

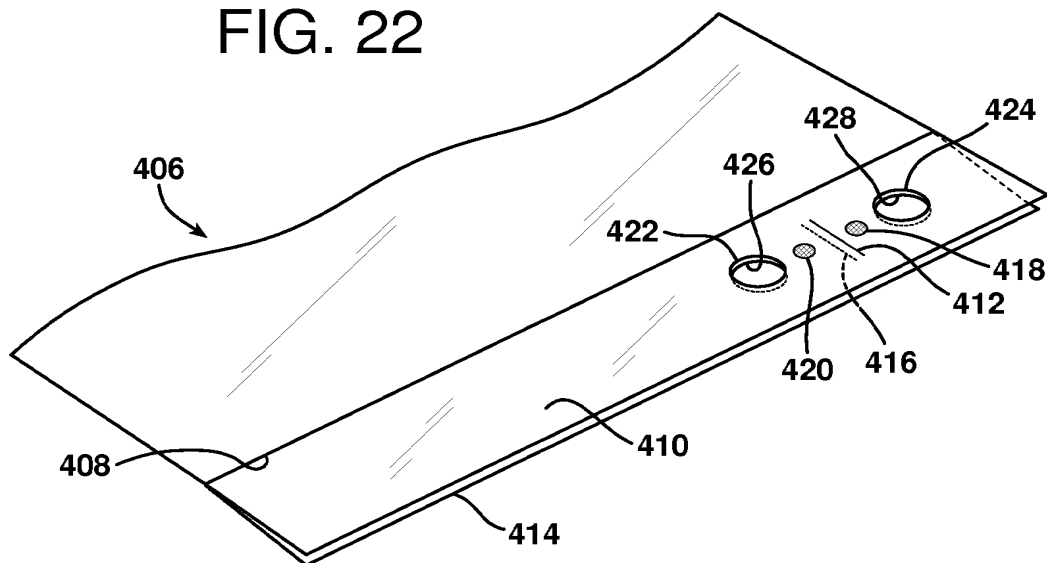


FIG. 23

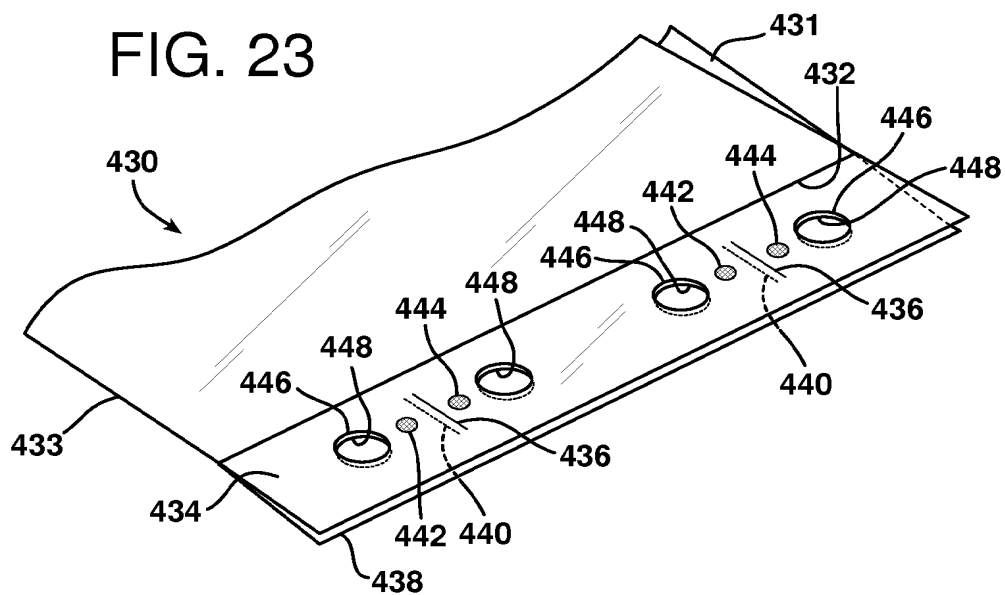


FIG. 24
(COMPARATIVE)

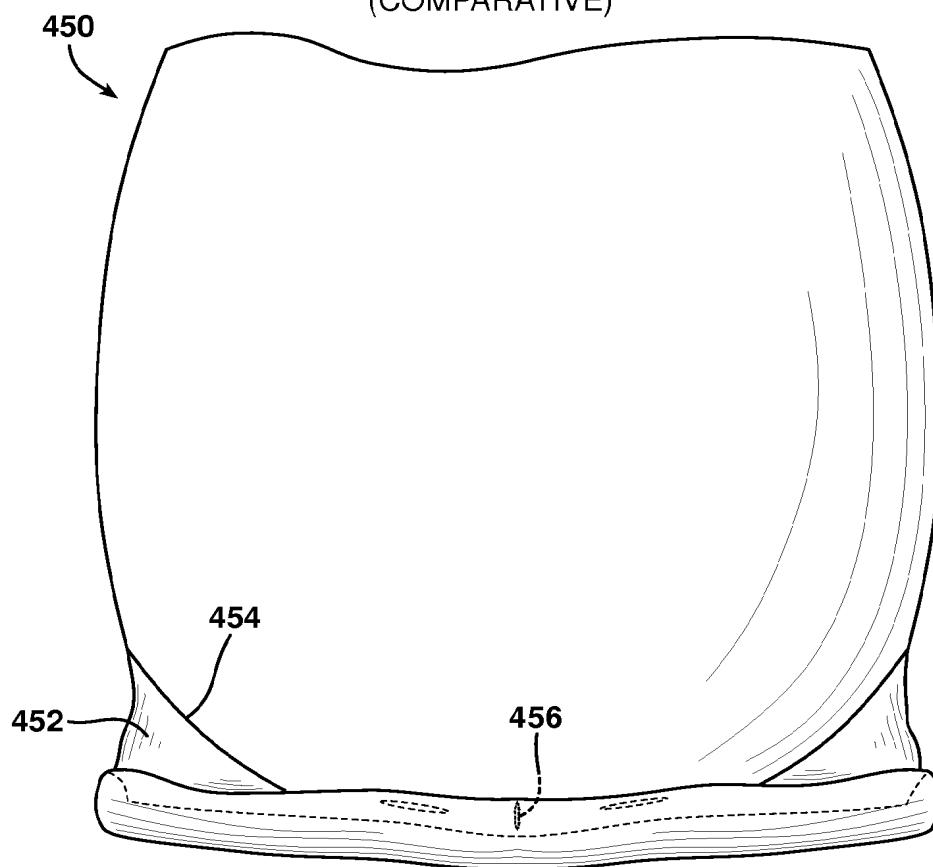


FIG. 25

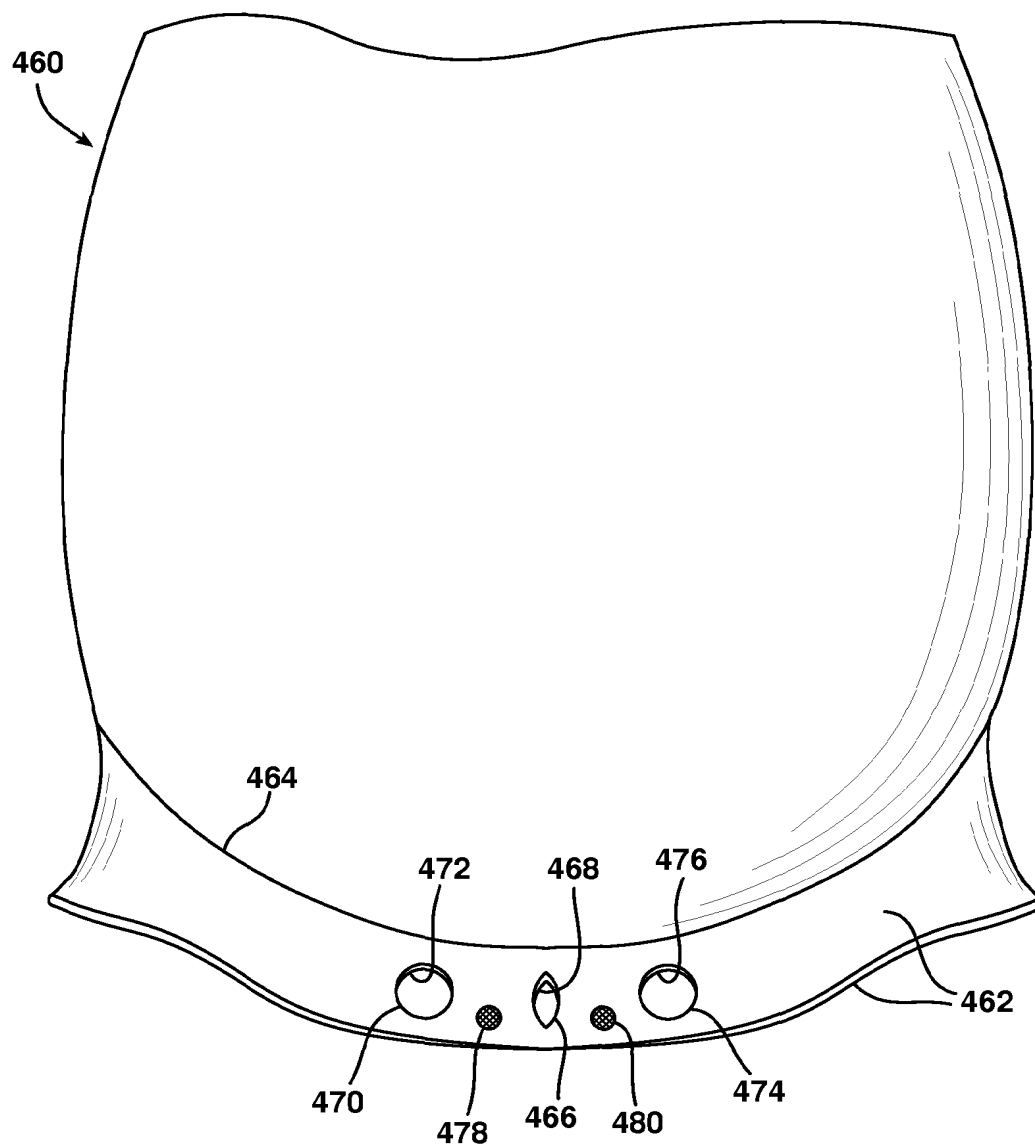


FIG. 26

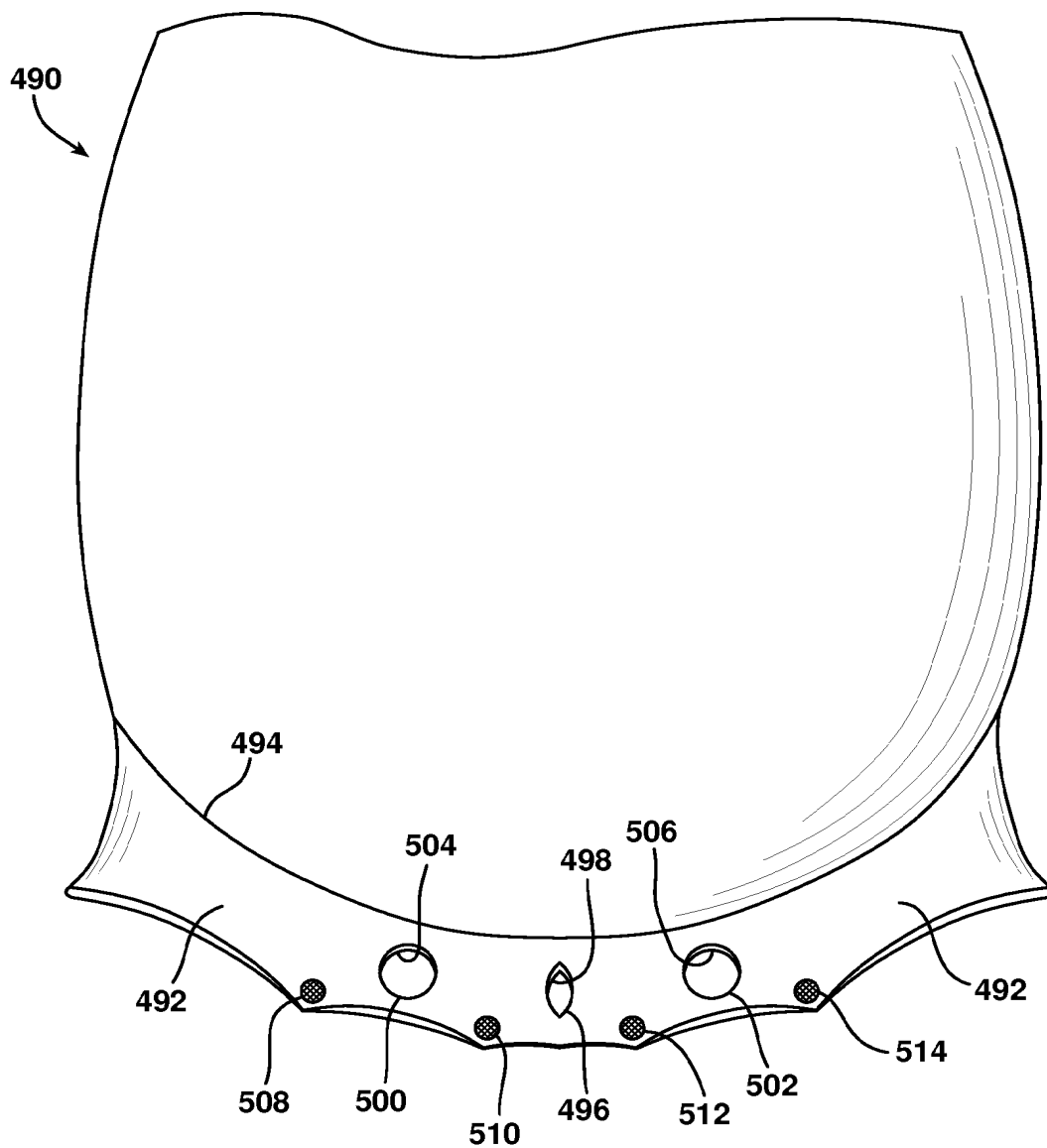


FIG. 27

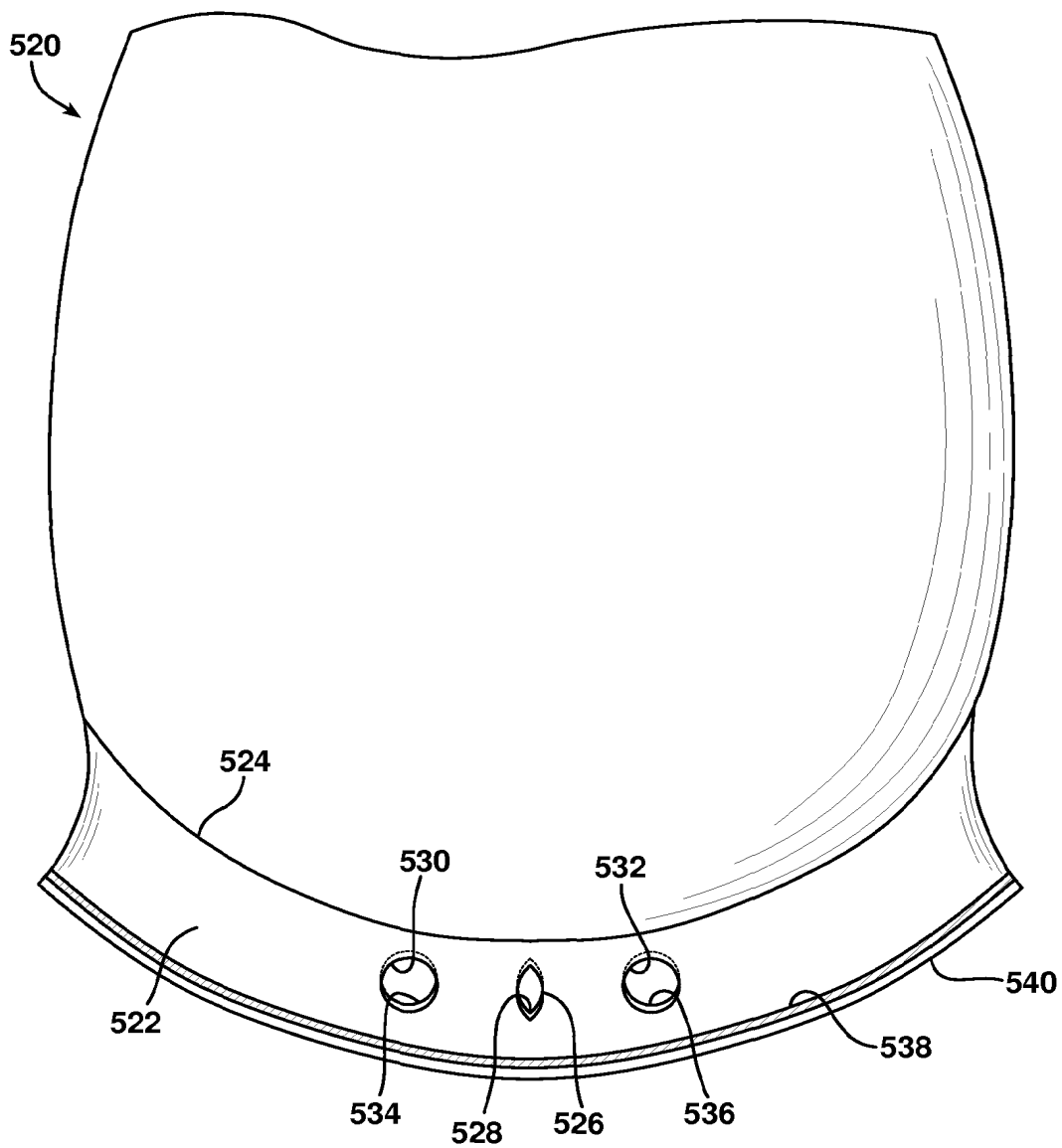
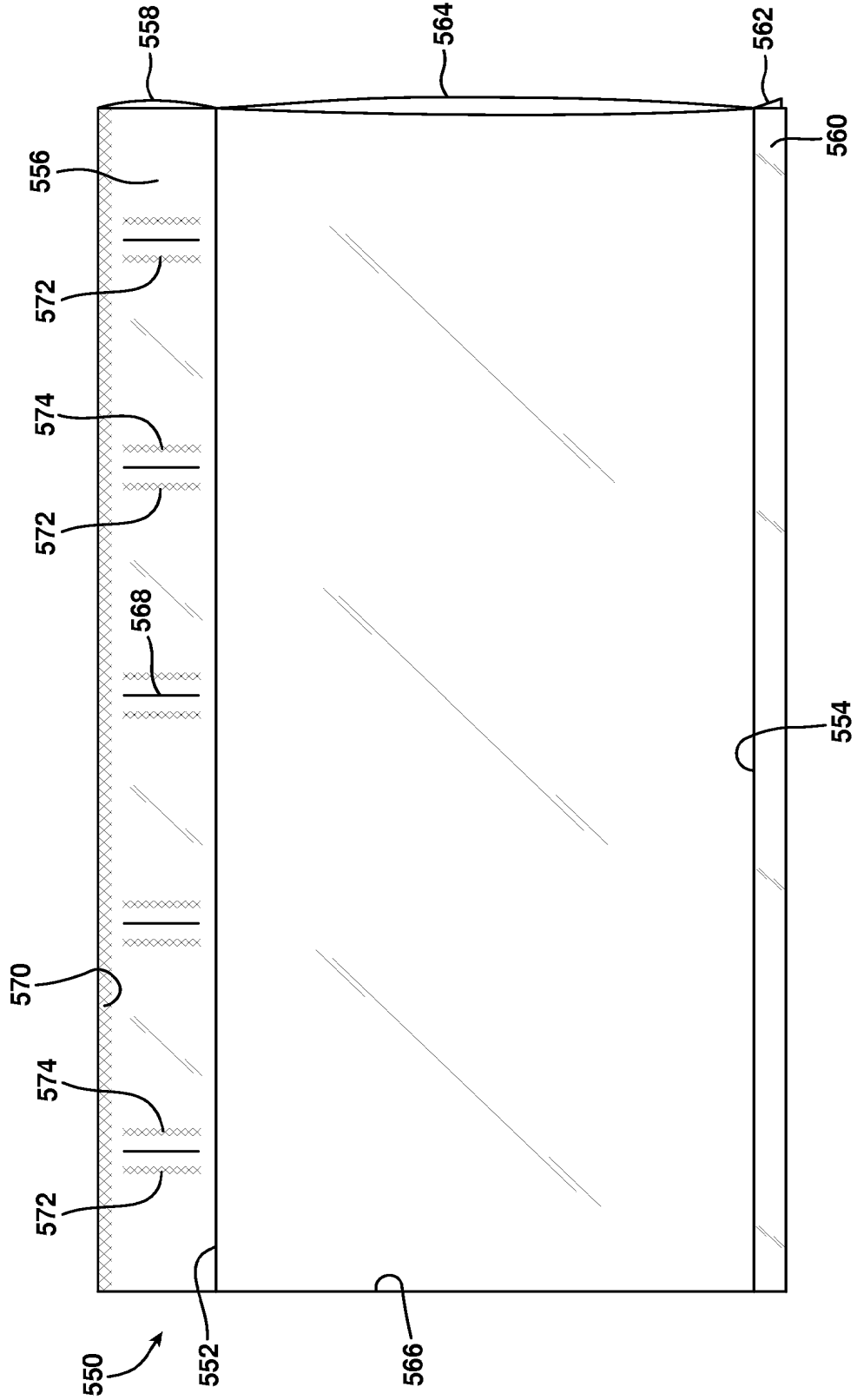


FIG. 28



REFERENCES CITED IN THE DESCRIPTION

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(19)



(11)

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(12)

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(21) Application number: **15155499.5**

(22) Date of filing: **18.02.2015**

(54) **Film and method for packaging a compressible product in a compressed state and packaged compressible product**

Folie und Verfahren zum Verpacken eines komprimierbaren Produkts in einem komprimierten Zustand und verpacktes, komprimierbares Produkt

Film et procédé d'emballage d'un produit compressible dans un état comprimé et ledit produit emballé

(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**

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US-A1- 2013 294 821

EP 2 907 769 B1

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Description**FIELD**

5 **[0001]** The present invention is in the field of packaging compressible products such as mineral wool products in a compressed state. The present invention provides a film and a method for packaging a compressible product in a compressed state. The present invention also relates to a packaged compressible product in a compressed state.

BACKGROUND

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[0002] Compressible products which are used in the building sector for thermal and acoustic insulation such as mineral wool products may be packaged at different stages in order to reduce the space such products occupy during storage and transport.

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[0003] Mineral wool products such as glass mineral wool and rock mineral wool products may be packaged at a first stage with a primary wrap film. A compressible product such as a mineral wool mat may be rolled up in a roll packer together with the primary film and may be closed by an adhesive at the end of the roll up process to have finally a packaged mineral wool roll. In this process, a polyolefin film may be used as primary packaging material. Mineral wool slabs are packed in a different way: a polyolefin film is generally applied to the upper and lower surface of the slab or a pile of slabs before compression. A single mineral wool slab or a pile of multiple slabs may be compressed and the lower and upper film may be sealed at the front and back to close the package. The mineral wool slab or pile of multiple mineral wool slabs is then released from compression and is limited in expansion due to the holding force of the film.

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[0004] During a secondary packaging stage, multiple previously packaged mineral wool rolls or slabs are compressed and pushed in a first and second sheet of film sealed at one end, and the package is closed by sealing the other end. The multiple mineral wool rolls or slabs are released from compression and are limited in expansion due to the holding force of the film. The obtained package is called a multipack. Sometimes, there is a tertiary packaging stage, where multiple multipacks are again compressed and pushed in a first and second sheet of film sealed at one end and the package is closed by sealing the other end. The multiple multipacks are released from compression and are limited in expansion due to the holding force of the film.

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[0005] In the packaging stages, typically a polyolefin film is used whereby the thickness of the film depends on multiple factors including the compression ratio of the compressible product such as the mineral wool product. The film has to withstand high forces due the expansion force of the packaged rolls or slabs which are trying to revert to their original state. The creep of a film, i.e., the tendency of the film to elongate, generally decreases when the thickness of the film increases. However, for economical reasons and in order to comply with ecological requirements, it is desirable to keep the film as thin as possible.

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[0006] Conventional non-oriented polyolefin films are used for packaging compressible products. For instance, EP 0908400 describes a mineral wool product compression-packaged in a film of polyethylene comprising high density polyethylene. However, these conventional non-oriented polyolefin films have high creep, i.e., high tendency to elongate, resulting in too high growing ratios of the packages. As a consequence, the compression ratios on the mineral wool are limited and rather thick films are to be used to compensate the poor creep properties.

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[0007] US 2002/0012807 relates to a heat-sealable polyester composition having an amorphous processing window ranging from a glass transition temperature in the range of about 40 °C to about 70 °C, to a peak crystallization temperature in the range of about 70 °C to about 150 °C. The composition preferably contains a mixture of poly(ethylene terephthalate) homopolymer or copolymer and poly(trimethylene terephthalate) homopolymer or copolymer, either as a physical blend or as a copolyester oligomer or polymer prepared from the respective monomers.

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[0008] The latest trend in packing mineral wool products is the use of machine direction oriented (MDO) films which can withstand high expansion forces in the machine direction. These existing MDO films have a low creep in the machine direction which leads to a very high tendency of the packaged product to stay in the compressed state. The existing MDO films have such low creep performance that even the thickness of the films can be reduced in comparison with the above mentioned conventional non-oriented polyolefin films. However, when using the existing MDO films for packaging a compressible product in a compressed state, a drawback of these films is their relatively poor heat sealing properties. For instance, sealing bars have to be well aligned and maintained with a lot of attention on a very regular basis, to get reasonable heat seals with these existing MDO films. But even when sealed on adapted sealing bars (e.g., Flexweld sealing bars from Qubiq), the heat seals of the mineral wool packages prepared with the existing MDO films are fragile and form the weak point of the packaged compressible product. Mineral wool packs prepared with the existing MDO films are frequently popping open due to the poor sealing behaviour of these films.

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[0009] US 2013/0294821 relates to a method for welding uniaxially oriented renewable raw materials and to a strap produced according to the method. The renewable raw material is preferably selected from the group of aliphatic polyesters, polyamide, aliphatic polyester amide, polyhydroxyalkanoate, polyvinyl alcohol, polyalkylenglycol, lignin or a co-

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polymer which contains at least one of the compounds, or it is selected from mixtures or derivatives thereof.

[0010] US 2003/0211298 relates to a multilayer, oriented, polymeric film and the method for its manufacture. The film comprises a first and second skin layers, and a core layer comprising isotactic polypropylene, a polymeric modifier, and a hydrocarbon resin. A method for making the film includes the steps of coextruding skin layers comprising heat sealable polymers and a core layer comprising isotactic polypropylene, a polymeric modifier, and a hydrocarbon resin; stretching the film in the machine direction, e.g., from about 4 to 7 times at low MDO temperatures; and stretching the film in the transverse direction, e.g., from about 6 to 11 times.

[0011] Key in packing compressible products such as mineral wool products in a compressed state is to compress these products to a high degree to get a package with limited volume which can be stored and transported in an economical way, while being able to withstand the expansion forces of the packaged compressible product in the compressed state.

[0012] In view thereof, there exists a need for further and/or improved films and methods for packaging compressible products in a compressed state and/or packaged compressible products which comply at least partly with the aforementioned requirements and solve at least to a certain extent the aforementioned problems.

SUMMARY

[0013] The present inventors have found machine direction oriented (MDO) films for packaging compressible products in a compressed state which allow storing and transporting the packaged compressible products in an efficient and hence economical way and at the same time provide improved environmental sustainability.

[0014] The present invention provides subject-matter as set forth in any one and all of the appended claims 1 to 15.

[0015] Hence, a first aspect of the present invention relates to a method for packaging a compressible product in a compressed state, comprising the step of sealing at least two parts of a polymeric MDO film which encloses at least part of the compressible product in the compressed state, characterised in that the seal has a seal elongation at failure of about 20% to about 100%, as measured in accordance with ASTM F88/F88M-09, wherein the MDO film has an elongation at break in the machine direction of about 100% to about 300%, as measured in accordance with ASTM D882, and the MDO film comprises from about 1% to about 90% by weight of one or more polymers selected from the group consisting of high density polyethylene (HDPE), medium density polyethylene (MDPE), polypropylene (PP), cyclic olefin copolymer (COC), and styrene butadiene copolymer (SBC), with % by weight relative to the total weight of the MDO film.

[0016] A further aspect relates to a compressible product in a compressed state packaged in a polymeric MDO film which encloses at least part of the compressible product, wherein at least two parts of the MDO film are sealed and characterised in that the seal has a seal elongation at failure of about 20% to about 100%, as measured in accordance with ASTM F88/F88M-09, wherein the MDO film has an elongation at break in the machine direction of about 100% to about 300%, as measured in accordance with ASTM D882, and the MDO film comprises from about 1% to about 90% by weight of one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC, with % by weight relative to the total weight of the MDO film.

[0017] A further aspect relates to a polymeric MDO film for packaging a compressible product in a compressed state, characterised in that the MDO film, when at least two parts of the MDO film are sealed, provides a seal with a seal elongation at failure of about 20% to about 100%, as measured in accordance with ASTM F88/F88M-09, wherein the MDO film has an elongation at break in the machine direction of about 100% to about 300%, as measured in accordance with ASTM D882, and the MDO film comprises from about 1% to about 90% by weight of one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC, with % by weight relative to the total weight of the MDO film.

[0018] Such an MDO film embodying the principles of the present invention has satisfying heat sealing properties. The present MDO film allows packaging a compressible product in a compressed state by sealing at least two parts of the MDO film without the need to regularly align the heat sealing bars on a packaging line. Furthermore, a seal prepared with the present MDO film is able to resist better the expansion forces of the compressed product during storage and/or transport of the packaged product. The present inventors also found that a seal prepared with the present MDO film better withstands movements and shocks associated with transporting the packaged product.

[0019] The above and further aspects and preferred embodiments of the invention are described in the following sections and in the appended claims. The subject-matter of appended claims is hereby specifically incorporated in this specification.

BRIEF DESCRIPTION OF FIGURES

[0020] Figure 1 represents a graph (heat seal curve) illustrating the seal strength (in N) versus the heat seal elongation (in %) of a seal prepared with an MDO film illustrating the principles of the present invention (full line) and of a seal prepared with an existing mono-oriented film according to the prior art (dashed line).

DETAILED DESCRIPTION

[0021] As used herein, the singular forms "a", "an", and "the" include both singular and plural referents unless the context clearly dictates otherwise.

[0022] The terms "comprising", "comprises" and "comprised of" as used herein are synonymous with "including", "includes" or "containing", "contains", and are inclusive or open-ended and do not exclude additional, non-recited members, elements or method steps. The terms also encompass "consisting of" and "consisting essentially of".

[0023] The recitation of numerical ranges by endpoints includes all numbers and fractions subsumed within the respective ranges, as well as the recited endpoints.

[0024] The term "about" as used herein when referring to a measurable value such as a parameter, an amount, a temporal duration, and the like, is meant to encompass variations of and from the specified value, such as variations of $\pm 10\%$ or less, preferably $\pm 5\%$ or less, more preferably $\pm 1\%$ or less, and still more preferably $\pm 0.1\%$ or less of and from the specified value, insofar such variations are appropriate to perform in the disclosed invention. It is to be understood that the value to which the modifier "about" refers is itself also specifically, and preferably, disclosed.

[0025] Whereas the term "one or more", such as one or more members of a group of members, is clear per se, by means of further exemplification, the term encompasses *inter alia* a reference to any one of said members, or to any two or more of said members, such as, e.g., any ≥ 3 , ≥ 4 , ≥ 5 , ≥ 6 or ≥ 7 etc. of said members, and up to all said members.

[0026] All documents cited in the present specification are hereby incorporated by reference in their entirety.

[0027] Unless otherwise specified, all terms used in disclosing the invention, including technical and scientific terms, have the meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. By means of further guidance, term definitions may be included to better appreciate the teaching of the present invention.

[0028] As noted, the present inventors have found that when using an MDO film for packaging a compressible product in a compressed state which gives a seal having a seal elongation of about 20% to about 100%, it is possible to get a package which is able to withstand better the expansion forces of the compressed product, and shocks and movements exerted on the packaged products during transportation thereof.

[0029] Accordingly, in a first aspect, the invention provides a method as recited in the appended claims for packaging a compressible product in a compressed state, comprising the step of sealing at least two parts of a polymeric MDO film which encloses at least part of the compressible product in the compressed state, characterised in that the seal has a seal elongation at failure of about 20% to about 100%, as measured in accordance with ASTM F88/F88M-09.

[0030] A related aspect provides the use of the MDO film as defined herein for packaging a compressible product in a compressed state.

[0031] The terms "packaging" and "packing" can be used interchangeably herein and refer to at least partly wrapping an item or set of items. The package may protect the item(s) during storage and/or transport.

[0032] In certain embodiments, the method comprises the step of sealing at least two parts of an MDO film which encloses at least part of a compressible product in a compressed state.

[0033] The term "sealing" refers to joining at least two items together so as to prevent them coming apart and/or to prevent anything passing between them. The recitation "sealing at least two parts of a polymeric MDO film", as used herein, comprises joining at least two parts of a polymeric MDO film together so as to prevent them coming apart. Advantageously, the sealing, preferably heat sealing, obviates the need to use an adhesive to bind the at least two items, such as the at least two parts of the polymeric MDO film, together.

[0034] The term "seal", as used herein, refers to the area or path where the at least two parts of the MDO film are joined together so as to prevent them coming apart. In certain preferred embodiments, the seal is a permanent seal. In case the seal is a permanent seal, the packaged product may be opened by cutting the MDO film as defined herein.

[0035] The sealing step may be performed by any method known in the art suitable for sealing MDO films such as heat sealing, ultrasonic sealing, or high frequency sealing.

[0036] The term "heat sealing" refers to the process of sealing at least two items, for instance sealing at least two parts of a polymeric MDO film, using heat, time, and pressure. The method of heat sealing utilizes a constantly heated die or sealing bar to apply heat to a specific contact area or path to heat seal or weld the items together. The terms "heat sealing" or "welding" may be used interchangeably herein.

[0037] The term "ultrasonic sealing" refers to the process of sealing at least two items, for instance sealing at least two parts of a polymeric MDO film, using high-frequency ultrasonic acoustic vibrations. The high-frequency ultrasonic acoustic vibrations are locally applied to the at least two items being held together under pressure to create a solid-state weld between the at least two items.

[0038] The term "high frequency sealing" refers to the process of sealing at least two items, for instance sealing at least two parts of a polymeric MDO film, by heating with high frequency electromagnetic waves. The terms "high frequency sealing", "dielectric sealing", or "radio frequency heat sealing" may be used interchangeably herein.

[0039] In order to allow sealing at least two parts of a polymeric MDO film, the MDO film as defined herein or the outer layer of the MDO film as defined herein may be made of a thermoplastic material, such as polyethylene or polypropylene.

[0040] The term "thermoplastic" generally refers to a polymer that becomes pliable or mouldable above a specific temperature, and returns to a solid state upon cooling.

[0041] In certain embodiments, the sealing may comprise heat sealing. In certain embodiments, the sealing is heat sealing. In certain embodiments, the parts of the MDO film may be sealed by heat sealing.

[0042] In certain embodiments, the parts of the MDO film may be sealed by heat sealing with heat sealing bars, hot air, or impulse heat sealers.

[0043] Heat sealing bars generally have heated tooling kept at a constant temperature (also known as direct contact thermal sealing). Heat sealing bars typically use one or more heated bars which contact the items to heat the interface and form a bond. The bars may have various configurations and can be covered with a release layer or utilize various slick interposer materials (i.e. Teflon films) to prevent sticking to the hot tooling. Suitable non-limiting examples of heat sealing bars are Flexweld (from Qubiq), Integrity Seal™ (from International Food Partners Ltd), and others.

[0044] Impulse heat sealers generally have heating elements (one or two) of Nichrome placed between a resilient synthetic rubber and a release surface of film or fabric. The heating elements are typically not continuously heated; heat is generated only when current flows. When the items are placed in the heat sealer, they are held in place by pressure. An electric current heats the heating element for a specified time to create the required temperature. The jaws hold the items in place after the heat is stopped, sometimes with cooling water; this allows the items to fuse before stress can be applied.

[0045] In certain embodiments, the method may comprise the step of sealing, preferably heat sealing, at least two parts of an MDO film which encloses at least part of a compressible product in a compressed state.

[0046] The recitation "an MDO film which encloses at least part of a compressible product", as used herein, is meant to encompass an MDO film which is provided at the outer surface of at least part of the compressible product. The terms "to enclose", "to cover", "to overlap with", or "to be provided at" may be used interchangeably herein.

[0047] In certain embodiments, the at least two parts of an MDO film may be parts of one (sheet of an) MDO film as defined herein. In certain embodiments, the at least two parts of an MDO film may be a part of a first (sheet of an) MDO film as defined herein and a part of a second (sheet of an) MDO film as defined herein.

[0048] In certain embodiments, the part of the MDO film which is to be sealed may be located or positioned at the end of the MDO film. Alternatively, in certain embodiments, the part of the MDO film which is to be sealed may be located or positioned within the MDO film, and during or after sealing the MDO film may be cut.

[0049] In certain embodiments, the sealing step may be part of any known method for compression packaging. In certain embodiments, the MDO film as defined herein may be applied (e.g., by enclosing at least part of the compressible product with the MDO film as defined herein) after compression, and sealed, preferably heat sealed, or the MDO film as defined herein may be applied (e.g., by enclosing at least part of the compressible product with the MDO film as defined herein) prior to compression and then sealed, preferably heat sealed, after compression.

[0050] In certain embodiments, the method may comprise the steps of: providing a compressible product in an uncompressed or partly compressed state, providing an MDO film as defined herein, enclosing at least part of the compressible product with the MDO film, compressing the compressible product to a compressed state, and sealing, preferably heat sealing, at least two parts of the MDO film which encloses at least part of the compressible product in the compressed state. Hereby, the MDO film as defined herein maintains or keeps the product in the compressed state.

[0051] In certain embodiments, the method may comprise the steps of: providing a compressible product in a compressed state, providing an MDO film as defined herein, enclosing at least part of the compressible product in the compressed state with the MDO film, and sealing, preferably heat sealing, at least two parts of the MDO film which encloses at least part of the compressible product in the compressed state. Hereby, the MDO film as defined herein maintains or keeps the product in the compressed state.

[0052] In certain embodiments, when the compressible product, such as a mineral wool product, is a slab (or plate) or a pile of slabs (or plates), one (sheet of the) MDO film as defined herein may enclose at least part of the upper and the lower surface of the slab (or plate) or pile of slabs (or plates), the compressible product may be compressed, and the (sheet of the) MDO film as defined herein may be sealed, preferably heat sealed.

[0053] Alternatively, in certain embodiments, when the compressible product, such as a mineral wool product, is a slab (or plate) or a pile of slabs (or plates), one (sheet of the) MDO film as defined herein (i.e., the upper or first sheet of MDO film) may enclose at least part of the upper surface of the slab (or plate) or pile of slabs (or plates) and another (sheet of the) MDO film as defined herein (i.e., the lower or second sheet of MDO film) may enclose at least part of the lower surface of the slab (or plate) or pile of slabs (or plates), the compressible product may be compressed, and the (sheets of the) MDO films as defined herein may be sealed, preferably heat sealed.

[0054] In certain embodiments, a first and second sheet of the MDO film as defined herein may be sealed, preferably heat sealed, simultaneously at one part, such as at a first part, of the first and second sheet of the MDO film as defined herein, and at another part, such as at a second part, of the first and second sheet of the MDO film as defined herein. In certain embodiments, a first and second sheet of the MDO film as defined herein may be sealed, preferably heat sealed, sequentially at one part, such as at a first part, of the first and second sheet of the MDO film as defined herein,

and at another part, such as at a second part, of the first and second sheet of the MDO film as defined herein.

[0055] In certain embodiments, a first and second sheet of the MDO film as defined herein may be sealed, preferably heat sealed, at one part, such as at a first part, of the first and second sheet of the MDO film as defined herein; a compressible product may be compressed in the sealed first and second sheet of the MDO film; and the package may be closed by sealing, preferably heat sealing, another part, such as a second part, of the first and second sheet of the MDO film as defined herein. This may happen during a primary packaging stage.

[0056] In certain embodiments, a first and second sheet of the MDO film as defined herein may be sealed, preferably heat sealed, at one part, such as at a first part, of the first and second sheet of the MDO film as defined herein; multiple packaged products, such as previously packaged mineral wool rolls or slabs, may be pushed and compressed in the sealed first and second sheet of the MDO film; and the package may be closed by sealing, preferably heat sealing, another part, such as a second part, of the first and second sheet of the MDO film as defined herein. This may happen during a secondary packaging stage.

[0057] In certain embodiments, a first and second sheet of the MDO film as defined herein may be sealed, preferably heat sealed, at one part, such as at a first part, of the first and second sheet of the MDO film as defined herein; multiple multipacks may be pushed and compressed in the sealed first and second sheet of the MDO film; and the package may be closed by sealing, preferably heat sealing, another part, such as a second part, of the first and second sheet of the MDO film as defined herein. This may happen during a tertiary packaging stage.

[0058] In certain embodiments, the MDO film as defined herein may be cut for instance during or after sealing. Cutting may be performed by a knife.

[0059] In certain embodiments, the MDO film as defined herein may be cut during sealing. In certain embodiments, a sealing station may comprise two sealing bars, i.e., a first sealing bar and a second sealing bar, and a knife between the first and second sealing bar. The sealing station may come down and the first sealing bar may seal the second part of a first package and at the same time the second sealing bar may seal the first part of the next or following package. At the same time, the knife which is in the middle of the two sealing bars may cut the MDO film as defined herein between the two seals.

[0060] In certain embodiments, the seal may have a seal elongation at failure of about 25% to about 100%, for instance, the seal may have a seal elongation at failure of about 25% to about 90%, of about 30% to about 90%, of about 35% to about 85%, of about 35% to about 80%, of about 35% to about 75%, of about 35% to about 70%, of about 35% to about 65%, of about 35% to about 60%, of about 35% to about 55%, of about 40% to about 80%, or of about 45% to about 75%, as measured in accordance with ASTM F88/F88M-09 as described herein. Such seal elongation at failure of about 25% to about 100% allows preparing a packaged compressible product in a compressed state which is able to resist the forces of the compressed product during storage and transportation thereof, and which is also able to withstand shocks and movements exerted on the packaged product during transportation thereof.

[0061] The term "seal elongation" or "seal elongation at failure", as used herein, refers to the percentage elongation at failure, as measured in accordance with the ASTM F88/F88M-09 standard, with tail holding technique A on a tensile testing machine. A sealed sample with a width of 15 mm is clamped between two grips with a distance of 50 mm and tested with a jaw separation speed of 250 mm/min. The tensile testing machine gives a curve of seal force versus grip travel. The mode of sample failure or test strip failure includes adhesive failure of the seal or adhesive peel; cohesive failure of the material; break or tear of material in seal area or at seal edge; delamination of surface layer(s) from substrate; elongation of material; and break or tear of material remote from seal (as illustrated in Fig. 4 of ASTM F88/F88M-09). Preferably, a sample to test the seal elongation is prepared in accordance with ASTM F2029-08, wherein the parts of the MDO film are sealed perpendicular to the machine direction of the film with a heat sealing equipment utilizing hot-bar jaws, and the conditions for heat sealing are set as follows: 1 sec. dwell time, 100 N sealing pressure, 5 mm jaw width and a sealing temperature of 160°C.

[0062] The seal elongation at failure generally refers to the percentage that a sealed film needs to be stretched between the grips of a tensile testing machine in order to observe failure. In order to determine the seal elongation at failure, the distance between the grips is gradually increased until the moment failure is determined. The seal elongation at failure may be calculated by dividing the extension of the sample at the moment of sample failure (i.e., grip travel at failure) by the initial length of the sample, and multiplying by 100.

[0063] The present method is used for packaging a compressible product in a compressed state.

[0064] The term "compressible product", as used herein, refers to any product or material which is capable of being compressed by the application of balanced inward (i.e., pushing or compressive) forces to different points on the product or material, and which is capable of reverting at least partly to its uncompressed state when the application of the balanced inward (i.e., pushing or compressive) forces is discontinued. The terms "product" or "material" may be used interchangeably herein.

[0065] The terms "compressible product in a compressed state" or "compressed product", as used herein, refer to a product or material wherein the size of the product or material is reduced in one or more directions, due to the application of balanced inward (i.e., pushing or compressive) forces to different points on the product or material. A compressible

product in a compressed state will exert balanced outward (i.e., pulling) forces on the material which keeps the compressible product in a compressed state. When the material which keeps the compressible product in a compressed state is removed, the compressible product will revert at least partly to its uncompressed or non-compressed state. For instance, a compressible product, such as a mineral wool product, in a compressed state will exert balanced outward (i.e., pulling) forces on the MDO film as defined herein (and by extension on the seal prepared by sealing the MDO film as defined herein) which keeps the compressible product in a compressed state. When the MDO film as defined herein is removed, the compressible product will revert at least partly to its uncompressed or non-compressed state.

[0066] In certain embodiments, the compressive forces on the product may be directed along one direction only (i.e., uniaxial compression), so that they act towards decreasing the length of the product along that direction. The compressive forces may also be applied in multiple directions; for example inwards along the edges of a plate or all over the side surface of a cylinder, so as to reduce its area (i.e., biaxial compression), or inwards over the entire surface of a body, so as to reduce its volume.

[0067] In certain embodiments, the length, area, or volume of a compressible product in a compressed state (e.g., due to the application of inward forces on the product) may be reduced by at least about 1% relative to (i.e., compared with) respective reference value(s) representing the length, area, or volume of the compressible product in an uncompressed state (e.g., without the application of any forces on the product). For example, the length, area, or volume of a compressible product in a compressed state (e.g., due to the application of inward forces on the product) may be reduced by at least about 5%, at least about 10%, at least about 15%, at least about 20%, at least about 25%, at least about 30%, at least about 35%, at least about 40%, at least about 45%, at least about 50%, at least about 55%, at least about 60%, at least about 65%, at least about 70%, at least about 75%, or at least about 80% relative to (i.e., compared with) respective reference value(s) representing the length, area, or volume of the compressible product in an uncompressed state (e.g., without the application of any inward forces on the product). Such reduction in the length, area, or volume of the compressible product advantageously allows to store and transport to compressible product in an efficient and hence, economical manner.

[0068] A further aspect relates to a compressible product in a compressed state packaged in a polymeric MDO film which encloses at least part of the compressible product, as recited in the appended claims, wherein at least two parts of the MDO film are sealed, and characterised in that the seal has a seal elongation at failure of about 20 % to about 100 %, as measured in accordance with ASTM F88/F88M-09.

[0069] The wordings "compressible product in a compressed state packaged in an MDO film", "packaged product", or "packaged compressible product" may be used interchangeably herein.

[0070] In certain embodiments, the packaged product may comprise a compressible product in a compressed state and a polymeric MDO film which encloses at least part of the compressible product in the compressed state, wherein at least two parts of the MDO film are sealed (so as to keep the compressible product in a compressed state), and characterised in that the seal has a seal elongation at failure of about 20% to about 100%, as measured in accordance with ASTM F88/F88M-09.

[0071] In certain embodiments, the packaged product may comprise a compressible product in a compressed state and a polymeric MDO film, wherein the MDO film encloses at least part of the compressible product in the compressed state and at least two parts of the MDO film are sealed (so as to keep the compressible product in a compressed state), and characterised in that the seal has a seal elongation at failure of about 20% to about 100%, as measured in accordance with ASTM F88/F88M-09.

[0072] In certain embodiments, when the compressible product, such as a mineral wool product, is a roll, one sheet of MDO film as defined herein may enclose at least part of the cylindrical outer surface of the roll.

[0073] In certain embodiments, when the compressible product, such as a mineral wool product, is a slab (or plate) or a pile of slabs (or plates), one sheet of the MDO film as defined herein may enclose at least part of the upper and the lower surface of the slab (or plate) or pile of slabs (or plates). Alternatively, in certain embodiments, when the compressible product, such as a mineral wool product, is a slab (or plate) or a pile of slabs (or plates), one sheet of the MDO film as defined herein (i.e., the upper or first sheet of MDO film) may enclose at least part of the upper surface of the slab (or plate) or pile of slabs (or plates) and another sheet of the MDO film as defined herein (i.e., the lower or second sheet of MDO film) may enclose at least part of the lower surface of the slab (or plate) or pile of slabs (or plates).

[0074] In certain embodiments, at least two packaged products as defined herein may be further packaged in a compressed state in an MDO film as defined herein. For instance, at least three, at least four, at least five, at least six, at least seven at least eight, at least nine, at least ten, at least eleven, or at least twelve packaged products as defined herein may be further packaged in a compressed state in an MDO film as defined herein.

[0075] The term "multipack", as used herein refers, to a package comprising at least two packaged products, such as mineral wool rolls or slabs, packaged in a compressed state in an MDO film as defined herein. For example, a multipack comprises at least three, at least four, at least five, at least six, at least seven at least eight, at least nine, at least ten, at least eleven, or at least twelve packaged products, such as mineral wool rolls or slabs, packaged in a compressed state in an MDO film as defined herein.

[0076] In certain embodiments, at least two multipacks as defined herein may be further packaged in a compressed state in an MDO film as defined herein. For instance, at least three, at least four, at least five, at least six, at least seven at least eight, at least nine, at least ten, at least eleven, or at least twelve multipacks as defined herein may be further packaged in a compressed state in an MDO film as defined herein.

[0077] The term "arrangement", as used herein refers, to a package comprising at least two multipacks packaged in a compressed state in an MDO film as defined herein. For example, an arrangement comprises at least three, at least four, at least five, at least six, at least seven at least eight, at least nine, at least ten, at least eleven, or at least twelve multipacks packaged in a compressed state in an MDO film as defined herein.

[0078] In certain embodiments, when the compressible product is a multipack, one sheet of the MDO film as defined herein may enclose at least part of the upper and the lower surface of the pile of multipacks. Alternatively, in certain embodiments, when the compressible product is a multipack, one sheet of the MDO film as defined herein (i.e., the upper or first sheet of MDO film) may enclose at least part of the upper surface of the pile of multipacks and another sheet of the MDO film as defined herein (i.e., the lower or second sheet of MDO film) may enclose at least part of the lower surface of pile of multipacks.

[0079] In certain embodiments, the packaged products, multipacks, or arrangements, as taught herein, may be stacked next to each other on a base member. Since the packaged products, multipacks, or arrangements as taught herein have reduced dimensions, they advantageously allow optimizing the number of packaged products, multipacks, or arrangements that can be stacked next to each other on a base member, such as a pallet. Such optimization advantageously allows increasing the efficiency of internal and external storage and/or transport of the compressible product, and thereby reducing the cost of storage and/or transport.

[0080] The term "base member", as used herein, refers to a member on which other elements, such as the compressible products packaged in a compressed state rest or are supported. Preferably, the base member is a pallet. Dimensions of pallets are standardized and known in the art. For instance, a "European" pallet, named europallet, has dimensions of 1200mm x 800mm and advantageously fits standard doorways.

[0081] In certain embodiments of the methods, uses, or packaged products, as taught herein, the compressible product may be an insulation product.

[0082] The terms "insulation product" or "insulation material" may be used interchangeably herein and refer to a product or material capable of reducing or preventing the transfer, flow, or conduct of heat, sound, or electricity.

[0083] In certain embodiments of the methods, uses, or packaged products, as taught herein, the insulation product may be building insulation, acoustic insulation, thermal insulation, or electrical insulation.

[0084] In certain embodiments of the methods, uses, or packaged products, as taught herein, the compressible product, in particular the insulation product, may be a mineral wool product, such as a mineral wool slab or a mineral wool roll.

[0085] The term "mineral wool" generally refers to fibres made from natural or synthetic minerals. Non-limiting examples of synthetic minerals are fibreglass or glass wool; ceramic fibres; and stone wool or rock wool. The terms "mineral wool", "mineral fibres", or "man-made mineral fibres" may be used interchangeably.

[0086] In certain embodiments of the methods, uses, or packaged products, as taught herein, the compressible material may be a glass wool product and/or a rock wool product.

[0087] A further aspect relates to a polymeric MDO film as recited in the appended claims for packaging a compressible product in a compressed state, characterised in that the MDO film, when at least two parts of the MDO film are sealed, provides a seal with a seal elongation at failure of about 20% to about 100%, as measured in accordance with ASTM F88/F88M-09. In other words, an aspect relates to a polymeric MDO film as recited in the appended claims for packaging a compressible product in a compressed state, wherein, when at least two parts of the MDO film are sealed, the seal has a seal elongation at failure of about 20% to about 100%, as measured in accordance with ASTM F88/F88M-09.

[0088] The term "film", as used herein, is meant to encompass any film used for packaging applications of compressible products in a compressed state.

[0089] The term "machine direction oriented film" or "MDO film", as used herein, refers to a film which has been oriented in the machine direction.

[0090] In certain embodiments of the MDO films, methods, uses, or packaged products, as taught herein, the MDO film may be oriented only in the machine direction (i.e., longitudinal direction). In certain embodiments, the MDO film may be oriented in the longitudinal or machine direction and in the transverse direction. In certain preferred embodiments, the MDO film may be oriented in the longitudinal or machine direction. Preferably, the MDO film is a mono-oriented film. Such MDO films result in better sealing properties.

[0091] In certain embodiments, the MDO film may be mono-oriented.

[0092] The term "mono-oriented film" generally refers to a film which has been stretched in the machine direction (i.e., longitudinal direction) by means of a Machine Direction Orienter (MDO) unit in or out of line with the extrusion process. Typically orienting is achieved by passing the film between two or more drawing rolls which rotate at different speed, such as a pair of drawing rolls in which one roll rotates at a higher speed than the other. In certain embodiments, the MDO film may be stretched in two or more steps using two or more stretching units. The oriented film may subsequently

be relaxed in a relaxation unit.

[0093] In certain embodiments, the MDO film may be prepared by stretching or orienting a film in the machine direction with a stretching ratio of about 1:1.5 to about 1:4.

[0094] As used herein, the term "stretching ratio" means the ratio of the total film length before stretching to the total film length after stretching. Thus, a stretching ratio of 1:2 means that the film has been stretched by 100% of its length before said stretching. Regarding thickness of the film, this means that a 120 μm film is draw down to 60 μm .

[0095] In certain embodiment, the MDO film may be prepared by stretching or orienting a film in the machine direction with a stretching ratio of about 1:1.5 to about 1:3.5, for instance with a stretching ratio of about 1:2 to about 1:3.5, of about 1:2.5 to about 1:3.5, or of about 1:2.5 to about 1:3.

[0096] The MDO film as taught herein may be prepared by a variety of processes. The MDO film as taught herein film may be prepared by co-extrusion, coating, or other laminating processes. The MDO film as taught herein may be prepared by casting or blown film processes. After the preparation of the film, the resulting film may be stretched to obtain an MDO film as defined herein, such as a mono-oriented MDO film.

[0097] Preferably, the MDO film as taught herein film is prepared by co-extrusion. Preferably, the MDO film as taught herein film is a blown film. Preferably, MDO film as taught herein is produced by means of blown film extrusion. It is also possible to produce MDO film as taught herein by means of cast film extrusion.

[0098] A mono-oriented film is typically prepared as follows. After the preparation of the starting film, the film may be uniaxially stretched or oriented in the machine direction to a thinner mono-oriented film. During this machine direction orientation, the film such as a multilayer film from the blown-film line or other film process may be heated to an orientation temperature. The heating is preferably performed utilizing multiple heated rollers. The heated film may be fed into a slow drawing roll with a nip roller, which has a similar rolling speed as the heated rollers. The film may then enter a fast drawing roll which has a speed that is 1.1 to 10 times faster than the slow draw roll, which effectively orients the film on a continuous basis. The mono-oriented film may be annealed by holding the film at an elevated temperature during a limited period of time to allow stress relaxation. Finally, the mono-oriented film may be cooled down by contacting the film with rollers at ambient temperature and may be wound to a reel.

[0099] In certain embodiments of the methods, uses, packaged products, or MDO films, as taught herein, the MDO film as defined herein may have a tensile creep in the machine direction of about 0.10% to about 0.50% per μm thickness of the film, as measured in accordance with ISO 899-1-2003. In certain embodiments of the methods, uses, packaged products, or MDO films, as taught herein, the MDO film as defined herein may have a tensile creep in the machine direction of about 0.10% to about 0.50% per μm thickness of the film, as measured in accordance with ISO 899-1-2003 with following conditions: sample width of 15 mm, grip distance of 100 mm, a load of 2300 g, for 24 hours, and at 23°C. Such tensile creep allows packaging a compressible product in a highly compressed state and to store and/or transport the packaged product with a limited size, diameter, or volume in an efficient and economical way.

[0100] The tensile creep generally refers to the change in the distance between the grips, relative to the initial distance, produced by the applied load at any given time during a creep test, expressed as a percentage. In order to determine the tensile creep, the increase in the distance between the clamp grips under load is measured.

[0101] The term "tensile creep" as used herein refers to the nominal tensile-creep strain, as measured in accordance with the ISO 899-1:2003 standard. The sample with a width of 15 mm is clamped between two grips with a distance of 100 mm and loaded with a load of 2300 g during 24 hours at 23°C. The tensile creep test consists of measuring the extension of a specimen subject to a constant load of 2.3 kg at 23° for 24 hours.

[0102] In certain embodiments, the MDO film as defined herein may have a tensile creep in the machine direction of about 0.10% to about 0.45% per μm thickness of the film, about 0.10% to about 0.40% per μm thickness of the film, about 0.15% to about 0.40% per μm thickness of the film, or about 0.15% to about 0.35% per μm thickness of the film, as measured in accordance with ISO 899-1-2003, preferably with following conditions: sample width of 15 mm, grip distance of 100 mm, a load of 2300 g, for 24 hours, and at 23°C. Such a tensile creep allows packaging a compressible product in a compressed state to get a packaged product with a limited size, diameter, or volume which can be efficiently stored and transported.

[0103] In certain embodiments of the methods, uses, packaged products, or MDO films, as taught herein, the MDO film as defined herein may have a thickness of about 15 μm to about 100 μm . In certain embodiments, the MDO film as defined herein may have a thickness of about 15 μm to about 95 μm , about 20 μm to about 95 μm , about 25 μm to about 95 μm , about 30 μm to about 95 μm , about 40 μm to about 90 μm , about 45 μm to about 85 μm , about 50 to about 80 μm , or about 60 μm to about 70 μm . Films with such a thickness are advantageous for economical and ecological reasons. Fewer raw materials are required to produce such films. Also, such thinner films advantageously allow complying with certain ecological requirements. Using thinner films may also reduce the costs to cope with the generated waste.

[0104] The term "thickness", as used herein, refers to the thickness of the MDO film after the orientation of the film in the machine direction.

[0105] In certain embodiments of the methods, uses, packaged products, or MDO films, as taught herein, the MDO

film as defined herein may have an elongation at break in the machine direction of about 100% to about 300%, as measured in accordance with ASTM D882. In certain embodiments, the MDO film as defined herein may have an elongation at break in the machine direction of about 100% to about 300%, of about 100% to about 250%, or of about 150% to about 250%, as measured in accordance with ASTM D882. Such an elongation at break provides satisfactory sealing properties to the MDO film. Such an elongation at break also allows that the MDO film can be sealed without the continuous need to adjust and adapt the sealing bars by aligning them.

[0106] The term "elongation at break" or "elongation capability", as used herein, refers to the percentage of elongation until break, measured in accordance with the ASTM D882 standard, in which a strip of film (in the longitudinal direction) with a width of 15 mm is clamped between two clamps situated at a distance of 50 mm from each other, and the film is subsequently stretched at a rate of 500 mm/min until the film breaks or tears. At least five strips of the film must be tested. The mean value of the measurements indicates the elongation capability or elongation at break. Preferably, the elongation at break is measured in accordance with ASTM D882-12.

[0107] In certain embodiments, the MDO film may be produced by stretching or orienting a film in the machine direction with a stretching ratio of about 1:1.5 to about 1:4, so that the MDO film has an elongation at break in the machine direction of about 100% to about 300%, as measured in accordance with ASTM D882. For instance, the MDO film may be produced by stretching or orienting a film in the machine direction with a stretching ratio of about 1:1.5 to about 1:4, of about 1:1.5 to about 1:3.5, of about 1:2 to about 1:3.5, of about 1:2.5 to about 1:3.5, or of about 1:2.5 to about 1:3, so that the MDO film has an elongation at break in the machine direction of about 100% to about 300%, of about 100% to about 250%, or of about 150% to about 250%, as measured in accordance with ASTM D882. Such MDO films provide satisfactory sealing properties when sealing the MDO film. Such MDO films allow improved sealing of at least two parts of the MDO film without the continuous need to adjust the sealing bars by aligning them.

[0108] In certain embodiments of the methods, uses, packaged products, or MDO films, as taught herein, the MDO film may comprise one or more, such as two or more, three or more, four or more, five or more, six or more, seven or more, eight or more, nine or more, ten or more, eleven or more, twelve or more, thirteen or more, or fourteen or more layers. In certain embodiments, the MDO film may be a multilayer film. Such an MDO film advantageously has good sealing properties.

[0109] In certain embodiments, the MDO film may comprise at least two layers. In certain embodiments, the MDO film may comprise at least three, at least four, at least five, at least six, at least seven, at least eight, at least nine, at least ten, at least eleven, at least twelve, at least thirteen, or at least fourteen layers. In certain embodiments, the MDO film may comprise at least two layers joined to one another. In certain embodiments, the MDO film may comprise at least three, at least four, at least five, at least six, at least seven, at least eight, at least nine, at least ten, at least eleven, at least twelve, at least thirteen, or at least fourteen layers joined to one another.

[0110] The term "polymeric" refers to a film comprising at least one polymer such as a polyolefin.

[0111] In certain embodiments, the MDO film as defined herein may be substantially made of polyolefin. The term "polyolefin" generally refers to homopolymers, or copolymers having a methylene linkage between monomer units which may be formed by any method known to those skilled in the art. Examples of polyolefins broadly includes polymers such as polyethylene and ethylene copolymers having a small amount of a copolymer such as ethylene- α olefin copolymers (LLDPE), polypropylene, polybutene, and other polymeric resins falling in the "olefin" family classification, polyethylene (PE), low density polyethylene (LDPE), linear low-density polyethylene (LLDPE), very low-density polyethylene (VLDPE), ultra low-density polyethylene (ULDPE), medium-density polyethylene (MDPE), high-density polyethylene (HDPE), ultra high-density polyethylene (UHDPE), ethylene/propylene copolymers, polypropylene (PP), propylene/ethylene copolymer, polyisoprene, polybutylene, polybutene, poly-3-methylbutene-1, poly-4-methylpentene-1, or copolymers of ethylene with one or more α -olefins such as butene-1, hexene-1 or octene-1.

[0112] In certain embodiments, the MDO film as defined herein may comprise LLDPE and/or mLLDPE and/or plastomers. LLDPE and/or mLLDPE and/or plastomers allow preparing an MDO film with satisfactory sealing properties.

[0113] The term "linear low density polyethylene" or "LLDPE" refers to a substantially linear polymer, with (significant numbers of) short branches, typically made by copolymerization of ethylene with longer-chain olefins such as 1-butene, 1-hexene, and 1-octene. LLDPE generally has a density lower than 942 kg/m³, preferably lower than 930 kg/m³.

[0114] The term "metallocene linear low density polyethylene" or "mLLDPE" refers to LLDPE produced in the presence of a metallocene catalyst.

[0115] The term "plastomer" generally refers to a polymer material which combines qualities of elastomers and plastics. Suitable non-limiting examples of plastomers are ethylene- α olefin copolymers. Commercially available plastomers include Affinity® produced by Dow, Queo® produced by Borealis, Lucene® produced by LG Chem and others.

[0116] In certain embodiments, the MDO film may comprise from about 10% to about 99% by weight of LLDPE and/or mLLDPE and/or plastomers, with % by weight relative to (i.e., compared with) the total weight of the MDO film as taught herein. For instance, the MDO film may comprise from about 15% to about 95%, from about 20% to about 90%, from about 25% to about 85%, from about 30% to about 80%, from about 35% to about 70%, or from about 40% to about 60% by weight of LLDPE and/or mLLDPE and/or plastomers, with % by weight relative to (i.e., compared with) the total

weight of the MDO film as taught herein.

[0117] In certain embodiments of the methods, uses, packaged products, or MDO films, as taught herein, the MDO film as defined herein comprises one or more polymers selected from the group consisting of high density polyethylene (HDPE), medium density polyethylene (MDPE), polypropylene (PP), cyclic olefin copolymer (COC), and styrene butadiene copolymer (SBC). Such polymers advantageously allow increasing the stiffness of the MDO film as taught herein.

[0118] The term "high density polyethylene" or "HDPE", as used herein, refers to polyethylene with a density of about 941 kg/m³ to about 970 kg/m³. Preferably, HDPE has a density of about 945 kg/m³ to about 965 kg/m³. HDPE may be prepared by the polymerization of ethylene monomers and optionally longer-chain olefins such as 1-hexene.

[0119] In certain embodiments, the HDPE may be metallocene high density polyethylene (mHDPE).

[0120] The term "metallocene high density polyethylene" or "mHDPE" refers to HDPE produced in the presence of a metallocene catalyst.

[0121] The term "medium density polyethylene" or "MDPE" refers to polyethylene with a density of about 926 kg/m³ to about 940 kg/m³. MDPE may be prepared by the polymerization of ethylene monomers and optionally longer-chain olefins such as 1-hexene.

[0122] In certain embodiments, the MDPE may be metallocene medium density polyethylene (mMDPE).

[0123] The term "metallocene medium density polyethylene" or "mMDPE" refers to MDPE produced in the presence of a metallocene catalyst.

[0124] The term "polypropylene" or "PP" refers to a polymer of propylene. Suitable polypropylene includes homopolymer polypropylene, random copolymer polypropylene, and heterophasic block copolymer.

[0125] The term "cyclic olefin copolymer" or "COC" refers to a copolymer of ethylene with a cyclic monomer (such as norbornene), or to a polymer of cyclic monomers. Cyclic olefin copolymers using a single type of cyclic monomer are also referred to as cyclic olefin polymers (COP).

[0126] Cyclic olefin copolymers can be 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 ethylene (such as TOPAS® produced by TOPAS Advanced Polymer, or APEL™ produced by Mitsui Chemical), or by ring-opening metathesis polymerization of various cyclic monomers followed by hydrogenation (such as ARTON produced by Japan Synthetic Rubber, or Zeonex® and Zeonor® produced by Zeon Chemical).

[0127] The term "styrene butadiene copolymer" or "SBC" refers to a copolymer of styrene and butadiene. A suitable non-limiting example of a SBC is K-Resin® SBC supplied by Chevron Phillips.

[0128] In certain embodiments of the methods, uses, packaged products, or MDO films, as taught herein, the MDO film as defined herein may comprise from about 1 % to about 90% by weight of one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC, with % by weight compared with the total weight of the MDO film as taught herein. For instance, the MDO film may comprise from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 65%, from about 30% to about 60%, or from about 40% to about 60% by weight of one or more polymers selected from HDPE, MDPE, PP, COC, and SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film as taught herein. For instance, the MDO film may comprise at least about 1%, at least about 2%, at least about 3%, at least about 4%, at least about 5%, at least about 6%, at least about 7%, at least about 8%, at least about 9%, at least about 10%, at least about 15%, at least about 20%, at least about 25%, or at least about 30% by weight of one or more polymers selected from HDPE, MDPE, PP, COC, and SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film as taught herein.

[0129] In certain embodiments, the MDO film as defined herein may comprise from about 1% to about 90% by weight of HDPE and/or mHDPE, with % by weight compared with the total weight of the MDO film. In certain embodiments, the MDO film may comprise from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 60%, or from about 30% to about 50% by weight of HDPE and/or mHDPE, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0130] In certain embodiments, the MDO film as defined herein may comprise from about 1% to about 90% by weight of MDPE and/or mMDPE, with % by weight compared with the total weight of the MDO film. In certain embodiments, the MDO film may comprise from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 65%, from about 30% to about 60%, or from about 40% to about 60% by weight of MDPE and/or mMDPE, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0131] In certain embodiments, the MDO film as defined herein comprises from about 1% to about 90% by weight of PP, with % by weight compared with the total weight of the MDO film. For instance, the MDO film may comprise from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 60%, or from about 30% to about 50% by weight of PP, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0132] In certain embodiments, the MDO film as defined herein comprises from about 1% to about 90% by weight of COC, with % by weight relative to (i.e., compared with) the total weight of the MDO film. For instance, the MDO film may comprise from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 60%, from about 30% to about 50% by weight of COC, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0133] In certain embodiments, the MDO film as defined herein comprises from about 1% to about 90% by weight of SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film. For instance, the MDO film may comprise from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 60%, from about 30% to about 50% by weight of SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film. For instance, the MDO film may comprise from about 1% to about 25%, from about 1% to about 20%, from about 1% to about 15%, from about 1% to about 10%, from about 5% to about 25%, or from about 10% to about 25% by weight of SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0134] In certain embodiments, the MDO film as defined herein may comprise linear low density polyethylene (LLDPE) and/or metallocene linear low density polyethylene (mLLDPE) and/or plastomers, and one or more polymers selected from the group consisting of high density polyethylene (HDPE), medium density polyethylene (MDPE), polypropylene (PP), cyclic olefin copolymer (COC), and styrene butadiene copolymer (SBC).

[0135] In certain embodiments, the MDO film as defined herein may comprise from about 10% to about 99% by weight of LLDPE and/or mLLDPE and/or plastomers, and from about 1% to about 90% by weight of one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film. For instance, the MDO film as defined herein may comprise from about 10% to about 99%, from about 15% to about 95%, from about 20% to about 90%, from about 25% to about 85%, from about 30% to about 80%, from about 35% to about 70%, or from about 40% to about 60% by weight of LLDPE and/or mLLDPE and/or plastomers, and from about 1% to about 90%, from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 65%, from about 30% to about 60%, or from about 40% to about 60% by weight of one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film as taught herein.

[0136] In certain preferred embodiments, the MDO film as defined herein may comprise from about 10% to about 99%, from about 15% to about 95%, from about 20% to about 90%, from about 25% to about 85%, from about 30% to about 80%, from about 35% to about 70%, or from about 40% to about 60% by weight of LLDPE and/or mLLDPE and/or plastomers, and from about 1% to about 90%, from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 60%, or from about 30% to about 50% by weight of HDPE and/or mHDPE, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0137] In certain preferred embodiments, the MDO film as defined herein may comprise from about 10% to about 99%, from about 15% to about 95%, from about 20% to about 90%, from about 25% to about 85%, from about 30% to about 80%, from about 35% to about 70%, or from about 40% to about 60% by weight of LLDPE and/or mLLDPE and/or plastomers, and from about 1% to about 90%, from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 65%, from about 30% to about 60%, or from about 40% to about 60% by weight of MDPE and/or mMDPE, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0138] In certain preferred embodiments, the MDO film as defined herein may comprise from about 10% to about 99%, from about 15% to about 95%, from about 20% to about 90%, from about 25% to about 85%, from about 30% to about 80%, from about 35% to about 70%, or from about 40% to about 60% by weight of LLDPE and/or mLLDPE and/or plastomers, and from about 1% to about 90%, from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 60%, or from about 30% to about 50% by weight of PP, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0139] In certain preferred embodiments, the MDO film as defined herein may comprise from about 10% to about 99%, from about 15% to about 95%, from about 20% to about 90%, from about 25% to about 85%, from about 30% to about 80%, from about 35% to about 70%, or from about 40% to about 60% by weight of LLDPE and/or mLLDPE and/or plastomers, and from about 1% to about 90%, from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 60%, from about 30% to about 50% by weight of COC, with % by weight relative to (i.e., compared with) the total weight of the

MDO film. In certain preferred embodiments, the MDO film as defined herein may comprise from about 10% to about 99%, from about 15% to about 95%, from about 20% to about 90%, from about 25% to about 85%, from about 30% to about 80%, from about 35% to about 70%, or from about 40% to about 60% by weight of LLDPE and/or mLLDPE and/or plastomers, and from about 1% to about 25%, from about 1% to about 20%, from about 1% to about 15%, from about 1% to about 10%, from about 5% to about 25%, or from about 10% to about 25% by weight of COC, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0140] In certain preferred embodiments, the MDO film as defined herein may comprise from about 10% to about 99%, from about 15% to about 95%, from about 20% to about 90%, from about 25% to about 85%, from about 30% to about 80%, from about 35% to about 70%, or from about 40% to about 60% by weight of LLDPE and/or mLLDPE and/or plastomers, and from about 1% to about 90%, from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 60%, from about 30% to about 50% by weight of SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film. In certain preferred embodiments, the MDO film as defined herein may comprise from about 10% to about 99%, from about 15% to about 95%, from about 20% to about 90%, from about 25% to about 85%, from about 30% to about 80%, from about 35% to about 70%, or from about 40% to about 60% by weight of LLDPE and/or mLLDPE and/or plastomers, and from about 1% to about 25%, from about 1% to about 20%, from about 1% to about 15%, from about 1% to about 10%, from about 5% to about 25%, or from about 10% to about 25% by weight of SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0141] In certain embodiments of the methods, uses, packaged products, or MDO films, as taught herein, the MDO film as defined herein may have an elongation at break in the machine direction of about 100% to about 300%, as measured in accordance with ASTM D882, and may comprise one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC. Such an MDO film allows packaging a compressible product in a highly compressed state for storage and/or transportation thereof, and the resulting packaged product is able to withstand expansion forces of the compressed product and to resist movements and shocks associated with transporting the packaged product without popping open.

[0142] In certain embodiments of the methods, uses, packaged products, or MDO films, as taught herein, the MDO film may have an elongation at break in the machine direction of about 100% to about 300%, as measured in accordance with ASTM D882, and the MDO film may comprise from about 1% to about 90% by weight of one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film. For instance, the MDO film may have an elongation at break in the machine direction of about 100 % to about 300 %, of about 100% to about 250%, or of about 150% to about 250%, as measured in accordance with ASTM D882, and the MDO film may comprise from about 1% to about 90%, from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 65%, from about 30% to about 60%, or from about 40% to about 60% by weight of one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0143] In certain embodiments, the MDO film may have an elongation at break in the machine direction of about 100% to about 300%, of about 100% to about 250%, or of about 150% to about 250%, as measured in accordance with ASTM D882, and the MDO film may comprise at least about 1%, at least about 2%, at least about 3%, at least about 4%, at least about 5%, at least about 6%, at least about 7%, at least about 8%, at least about 9%, at least about 10%, at least about 15%, at least about 20%, at least about 25%, or at least about 30% by weight of one or more polymers selected from HDPE, MDPE, PP, COC, and SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film as taught herein.

[0144] In certain embodiments of the methods, uses, packaged products, or MDO films, as taught herein, the MDO film may be produced by stretching or orienting a film in the machine direction with a stretching ratio of about 1:1.5 to about 1:4, so that the MDO film has an elongation at break in the machine direction of about 100% to about 300%, as measured in accordance with ASTM D882, and the MDO film may comprise one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC. Such an MDO film has satisfying heat sealing properties and allows packaging a compressible product in a compressed state by sealing at least two parts of the MDO film without the need to adapt the heat sealing bars on a packaging line. Furthermore, a seal prepared with the present MDO film is able to withstand expansion forces of the compressed product and is able to withstand movements and shocks associated with transporting the packaged product. At the same time, the present MDO film allows to package a compressible product in a highly compressed state and to store and/or transport the packaged product with a limited size, diameter, or volume in an efficient and economical way.

[0145] In certain embodiments of the methods, uses, packaged products, or MDO films, as taught herein, the MDO film may be produced by stretching or orienting a film in the machine direction with a stretching ratio of about 1:1.5 to about 1:4, so that the MDO film has an elongation at break in the machine direction of about 100% to about 300%, as measured in accordance with ASTM D882, and the MDO film may comprise from about 1% to about 90% by weight of

one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film. For instance, the MDO film may be produced by stretching or orienting a film in the machine direction with a stretching ratio of about 1:1.5 to about 1:4, of about 1:1.5 to about 1:3.5, of about 1:2 to about 1:3.5, of about 1:2.5 to about 1:3.5, or of about 1:2.5 to about 1:3, so that the MDO film has an elongation at break in the machine direction of about 100% to about 300%, of about 100% to about 250%, or of about 150% to about 250%, as measured in accordance with ASTM D882, and the MDO film may comprise from about 1% to about 90%, from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 65%, from about 30% to about 60%, or from about 40% to about 60% by weight of one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0146] In certain embodiments, the MDO film may be produced by stretching or orienting a film in the machine direction with a stretching ratio of about 1:1.5 to about 1:4, of about 1:1.5 to about 1:3.5, of about 1:2 to about 1:3.5, of about 1:2.5 to about 1:3.5, or of about 1:2.5 to about 1:3, so that the MDO film has an elongation at break in the machine direction of about 100% to about 300%, of about 100% to about 250%, or of about 150% to about 250%, as measured in accordance with ASTM D882, and the MDO film may comprise at least about 1%, at least about 2%, at least about 3%, at least about 4%, at least about 5%, at least about 6%, at least about 7%, at least about 8%, at least about 9%, at least about 10%, at least about 15%, at least about 20%, at least about 25%, or at least about 30% by weight of one or more polymers selected from HDPE, MDPE, PP, COC, and SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film as taught herein.

[0147] In certain embodiments, the MDO film as defined herein may further comprise ethylene vinyl acetate (EVA), ethylene methyl acetate (EMA), or ethylene butyl acetate (EBA). EVA, EMA, or EBA allow forming a multilayer film.

[0148] In certain embodiments, the MDO film as defined herein may further comprise one or more additives selected from the group consisting of UV-stabilizers (like hindered amine light stabilizers (HALS) and others), pigments (like TiO₂ and other colour pigments), and fillers (like CaCO₃, talc, and others).

[0149] In certain embodiments, the MDO film as defined herein may be prepared from a film with m layers by blocking the film in the nip rollers to a film with 2 times m (i.e., $2xm$) layers, wherein m may be two or more, such as m may be two, three, four, five, six, or seven.

[0150] In certain embodiments, the MDO film as defined herein may be prepared from a film with at least an outer layer and an inner layer, wherein the film is blocked in the nip rollers to form a film with at least an outer layer, an inner layer, an inner layer, and an outer layer.

[0151] In certain embodiments, the MDO film as defined herein may be prepared from a film with at least an outer layer, a core layer, and an inner layer, wherein the film is blocked in the nip rollers to form a film with at least an outer layer, a core layer, an inner layer, an inner layer, a core layer, and an outer layer.

[0152] In certain embodiments, the MDO film as defined herein may be prepared from a film with three layers comprising an outer layer, a core layer, and an inner layer, wherein the film is blocked in the nip rollers to a film with six layers.

[0153] In certain embodiments, the outer layer may comprise LLDPE and/or mLLDPE and/or plastomers. The outer layer allows sealing at least two parts of the MDO film as defined herein.

[0154] In certain embodiments, the core layer may comprise one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC. In certain embodiments, the core layer may comprise LLDPE and/or mLLDPE and/or plastomers and one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC. The core layer advantageously provides stiffness to the MDO film as defined herein.

[0155] In certain embodiments of the methods, uses, packaged products, or MDO films, as taught herein, the core layer of the MDO film as defined herein may comprises from about 1% to about 90% by weight of one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC, with % by weight compared with the total weight of the MDO film as taught herein. For instance, the core layer of the MDO film as defined herein may comprise from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 65%, from about 30% to about 60%, or from about 40% to about 60% by weight of one or more polymers selected from HDPE, MDPE, PP, COC, and SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film as taught herein.

[0156] In certain embodiments, the core layer of the MDO film as defined herein may comprise from about 1 % to about 90% by weight of HDPE and/or mHDPE, with % by weight compared with the total weight of the MDO film. In certain embodiments, the core layer of the MDO film may comprise from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 60%, or from about 30% to about 50% by weight of HDPE and/or mHDPE, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0157] In certain embodiments, the core layer of the MDO film as defined herein may comprise from about 1% to about 90% by weight of MDPE and/or mMDPE, with % by weight compared with the total weight of the MDO film. In certain embodiments, the core layer of the MDO film may comprise from about 5% to about 90%, from about 5% to about 85%,

from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 65%, from about 30% to about 60%, or from about 40% to about 60% by weight of MDPE and/or mMDPE, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0158] In certain embodiments, the core layer of the MDO film as defined herein comprises from about 1 % to about 90% by weight of PP, with % by weight compared with the total weight of the MDO film. For instance, the core layer of the MDO film may comprise from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 60%, or from about 30% to about 50% by weight of PP, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0159] In certain embodiments, the core layer of the MDO film as defined herein comprises from about 1% to about 90% by weight of COC, with % by weight relative to (i.e., compared with) the total weight of the MDO film. For instance, the core layer of the MDO film may comprise from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 60%, from about 30% to about 50% by weight of COC, with % by weight relative to (i.e., compared with) the total weight of the MDO film. For instance, the core layer of the MDO film may comprise from about 1% to about 25%, from about 1% to about 20%, from about 1% to about 15%, from about 1% to about 10%, from about 5% to about 25%, or from about 10% to about 25% by weight of COC, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0160] In certain embodiments, the core layer of the MDO film as defined herein comprises from about 1% to about 90% by weight of SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film. For instance, the core layer of the MDO film may comprise from about 5% to about 90%, from about 5% to about 85%, from about 10% to about 80%, from about 15% to about 75%, from about 20% to about 70%, from about 25% to about 60%, from about 30% to about 50% by weight of SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film. For instance, the core layer of the MDO film may comprise from about 1% to about 25%, from about 1% to about 20%, from about 1% to about 15%, from about 1% to about 10%, from about 5% to about 25%, or from about 10% to about 25% by weight of SBC, with % by weight relative to (i.e., compared with) the total weight of the MDO film.

[0161] In certain embodiments, the inner layer may comprise EVA and/or EBA and/or EMA and/or plastomers. The inner layer allows both inner layers to stick or bind to each other when the extruded blown film is blocked in the nip rollers.

[0162] In certain embodiments, the MDO film as defined herein may comprise additional or further layers between the inner layer and the core layer, and/or between the core layer and the outer layer. In certain embodiments, the additional layer may comprise LLDPE and/or mLLDPE and/or plastomers. In certain embodiments, the additional layer may comprise one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC. In certain embodiments, the additional layer may comprise LLDPE and/or mLLDPE and/or plastomers and one or more polymers selected from the group consisting of HDPE, MDPE, PP, COC, and SBC.

[0163] In certain embodiments, the thickness of the layers (e.g., outer layer, core layer, inner layer, and additional layer(s)) in the MDO film as defined herein may vary. In certain embodiments, the outer and inner layer may be thinner than the core layer. For example, the MDO film as defined herein may have a film structure of 20%/60%/20%/20%/60%/20% for the outer layer/core layer/inner layer/inner layer/core layer/outer layer. The layer configuration may be dependent on the die design and extruder size.

[0164] The ensuing statements provide additional illustration of subject-matter that has been disclosed in the specification:

1. A method for packaging a compressible product in a compressed state, comprising the step of sealing at least two parts of a polymeric machine direction oriented (MDO) film which encloses at least part of the compressible product in the compressed state, characterised in that the seal has a seal elongation at failure of about 20% to about 100%, as measured in accordance with ASTM F88/F88M-09.

2. The method according to statement 1, wherein the seal has a seal elongation at failure of about 25% to about 100%, preferably the seal has a seal elongation at failure of about 30% to about 90%, more preferably the seal has a seal elongation at failure of about 35% to about 80%, even more preferably the seal has a seal elongation at failure of about 35% to about 55%, as measured in accordance with ASTM F88/F88M-09.

3. The method according to statement 1 or 2, wherein the sealing comprises heat sealing, preferably wherein the sealing is heat sealing.

4. The method according to any one of statements 1 to 3, wherein the compressible product is an insulation product.

5. The method according to any one of statements 1 to 4, wherein the compressible product is a mineral wool product, such as a mineral wool slab or a mineral wool roll.

6. The method according to any one of statements 1 to 5, wherein the MDO film has a tensile creep in the machine direction of about 0.10% to about 0.50% per μm thickness of the film, as measured in accordance with ISO 899-1-2003 with following conditions: sample width of 15 mm, grip distance of 100 mm, a load of 2300 g, for 24 hours, and at 23°C.

5 7. The method according to any one of statements 1 to 6, wherein the MDO film has a thickness of about 15 μm to about 100 μm .

8. The method according to any one of statements 1 to 7, wherein the MDO film has an elongation at break in the machine direction of about 100% to about 300%, preferably wherein the MDO film has an elongation at break in the machine direction of about 150% to about 250%, as measured in accordance with ASTM D882.

9. The method according to any one of statements 1 to 8, wherein the MDO film comprises one or more polymers selected from the group consisting of high density polyethylene (HDPE), medium density polyethylene (MDPE), polypropylene (PP), cyclic olefin copolymer (COC), and styrene butadiene copolymer (SBC).

10. The method according to any one of statements 1 to 9, wherein the MDO film comprises from about 1% to about 90% by weight of one or more polymers selected from the group consisting of one or more of HDPE, MDPE, PP, COC, and SBC, with % by weight relative to the total weight of the MDO film.

11. A compressible product in a compressed state packaged in a polymeric machine direction oriented (MDO) film which encloses at least part of the compressible product, wherein at least two parts of the MDO film are sealed and characterised in that the seal has a seal elongation at failure of about 20% to about 100%, as measured in accordance with ASTM F88/F88M-09.

12. The packaged product according to statement 11, wherein the seal has a seal elongation at failure of about 25% to about 100%, preferably the seal has a seal elongation at failure of about 30% to about 90%, more preferably the seal has a seal elongation at failure of about 35% to about 80%, even more preferably the seal has a seal elongation at failure of about 35% to about 55%, as measured in accordance with ASTM F88/F88M-09.

13. The packaged product according to statement 11 or 12, wherein the sealing comprises heat sealing, preferably wherein the sealing is heat sealing.

14. The packaged product according to any one of statements 11 to 13, wherein the compressible product is an insulation product.

15. The packaged product according to any one of statements 11 to 14, wherein the compressible product is a mineral wool product, such as a mineral wool slab or a mineral wool roll.

16. The packaged product according to any one of statements 11 to 15, wherein the MDO film has a tensile creep in the machine direction of about 0.10% to about 0.50% per μm thickness of the film, as measured in accordance with ISO 899-1-2003, with following conditions: sample width of 15 mm, grip distance of 100 mm, a load of 2300 g, for 24 hours, and at 23°C.

17. The packaged product according to any one of statements 11 to 16, wherein the MDO film has a thickness of about 15 μm to about 100 μm .

18. The packaged product according to any one of statements 11 to 17, wherein the MDO film has an elongation at break in the machine direction of about 100% to about 300%, preferably wherein the MDO film has an elongation at break in the machine direction of about 150% to about 250%, as measured in accordance with ASTM D882.

19. The packaged product according to any one of statements 11 to 18, wherein the MDO film comprises one or more polymers selected from the group consisting of high density polyethylene (HDPE), medium density polyethylene (MDPE), polypropylene (PP), cyclic olefin copolymer (COC), and styrene butadiene copolymer (SBC).

20. The packaged product according to any one of statements 11 to 19, wherein the MDO film comprises from about 1 % to about 90% by weight of one or more polymers selected from the group consisting of one or more of HDPE, MDPE, PP, COC, and SBC, with % by weight relative to the total weight of the MDO film.

21. A polymeric machine direction oriented (MDO) film for packaging a compressible product in a compressed state, characterised in that the MDO film, when at least two parts of the MDO film are sealed, provides a seal with a seal elongation at failure of about 20% to about 100%, as measured in accordance with ASTM F88/F88M-09.

22. The MDO film according to statement 21, wherein the seal has a seal elongation at failure of about 25% to about 100%, preferably the seal has a seal elongation at failure of about 30% to about 90%, more preferably the seal has a seal elongation at failure of about 35% to about 80%, even more preferably the seal has a seal elongation at failure of about 35% to about 55%, as measured in accordance with ASTM F88/F88M-09.

23. The MDO film according to statement 21 or 22, wherein the sealing comprises heat sealing, preferably wherein the sealing is heat sealing.

24. The MDO film according to any one of statements 21 to 23, wherein the MDO film has a tensile creep in the machine direction of about 0.10% to about 0.50% per μm thickness of the film, as measured in accordance with ISO 899-1-2003 with following conditions: sample width of 15 mm, grip distance of 100 mm, a load of 2300 g, for 24 hours, and at 23°C.

25. The MDO film according to any one of statements 21 to 24, wherein the MDO film has a thickness of about 15 μm to about 100 μm .

26. The MDO film according to any one of statements 21 to 25, wherein the MDO film has an elongation at break in the machine direction of about 100% to about 300%, preferably wherein the MDO film has an elongation at break in the machine direction of about 150% to about 250%, as measured in accordance with ASTM D882.

27. The MDO film according to any one of statements 21 to 26, wherein the MDO film comprises one or more polymers selected from the group consisting of high density polyethylene (HDPE), medium density polyethylene (MDPE), polypropylene (PP), cyclic olefin copolymer (COC), and styrene butadiene copolymer (SBC).

28. The MDO film according to any one of statements 21 to 27, wherein the MDO film comprises from about 1% to about 90% by weight of one or more polymers selected from the group consisting of one or more of HDPE, MDPE, PP, COC, and SBC, with % by weight relative to the total weight of the MDO film.

[0165] While preferred embodiments of the present invention have been shown and described herein, it will be obvious to those skilled in the art that such embodiments are provided by way of example only.

[0166] The above aspects and embodiments are further supported by the following non-limiting examples.

EXAMPLES

Example 1: Elongation at break of an MDO film according to an embodiment of the invention

[0167] A machine direction oriented (MDO) film according to an embodiment of the present invention (i.e., MDO Film A1) was produced by stretching a film with a thickness of 205 μm in an MDO unit in the machine direction with a stretching ratio of 1:2.9. The MDO Film A1 was prepared from a 5-layer coextruded blown film containing the following polymers: layer A: 75% by weight of LLDPE and 25% by weight of plastomer; layer B: LLDPE; layer C: 75% by weight of LLDPE and 25% by weight of cyclic olefin copolymer (COC); layer D: LLDPE; layer E: ethylene-vinyl acetate (EVA). The % by weight is compared with the total weight of each layer. If no percentages are given, the entire layer is prepared of the indicated polymer. This coextruded blown film was blocked in the nip rolls of the blown film line due to the stickiness of layer E, to form a 10 layer film (2 times 102.5 μm). The resulting film was then brought into the MDO unit where it was oriented in machine direction with a stretching ratio of 1:2.9 to a mono-oriented film with a thickness of 70 μm , i.e., MDO Film A1.

[0168] The MDO Film A1 was subjected to a tensile elongation at break test in the machine direction on a laboratory tensile tester in accordance with ASTM D882. A strip of film having a width of 15 mm was clamped between two clamps which have a distance of 50 mm from each other. Subsequently, the film was stretched at a rate of 500 mm/min until the film broke.

[0169] Table 1 shows the results of the measurements of the elongation at break (in %) and the force at break (in N) of MDO Film A1. MDO Film A1 had an average elongation at break in the machine direction of 210% and an average force at break of 113N.

Table 1: Elongation at break (in %) and force at break (in N) of MDO Film A1 according to an embodiment of the present invention (n=6)

Measurement number	Elongation at break (%)	Force at break (N)
1	195	105
2	218	112
3	201	114
4	209	114
5	220	117
6	216	118
Average $\pm$ SD	210 $\pm$ 10	113 $\pm$ 5
SD: standard deviation		

[0170] The MDO Film A1 had an elongation at break different from the elongation at break of existing mono-oriented films currently on the market used for packing compressible product such as mineral wool products, which typically have an elongation at break in machine direction of about 20% to about 90%. An exemplary film according to the prior art (i.e., comparative Film B 1) was produced by stretching a film with a thickness of 420 μm in an MDO unit in the machine direction with a stretching ratio of 1:6. The comparative Film B1 was prepared from a 5-layer coextruded blown film containing the following polymers: layer A: 75% by weight of LLDPE and 25% by weight of plastomer; layer B: LLDPE; layer C: LLDPE; layer D: LLDPE; layer E: EVA. The % by weight is compared with the total weight of each layer. If no percentage is given, the entire layer is prepared of the indicated polymer. This coextruded blown film was blocked in the nip rolls of the blown film line due to the stickiness of layer E, to a 10 layer film (2 times 210 μm). The resulting film was then brought into the MDO unit where it was oriented in machine direction with a stretching ratio of 1:6 to a mono-oriented film with a thickness of 70 μm , i.e., comparative Film B1.

[0171] The comparative Film B1 was subjected to a tensile elongation at break test in the machine direction on a laboratory tensile tester in accordance with ASTM D882. A strip of film having a width of 15 mm was clamped between two clamps which have a distance of 50 mm from each other. Subsequently, the film was stretched at a rate of 500 mm/min until the film broke.

[0172] Table 2 shows the results of the elongation at break (in %) and the force at break (in N) of the comparative Film B1. The comparative Film B1 had an average elongation at break in the machine direction of 58% and an average force at break of 170N.

Table 2: Elongation at break (in %) and force at break (in N) of a comparative Film B1 (n=5)

Measurement number	Elongation at break (%)	Force at break (N)
1	54	168
2	60	163
3	61	175
4	60	175
5	54	170
Average $\pm$ SD	58 $\pm$ 3	170 $\pm$ 5
SD: standard deviation		

Example 2: Seal elongation at failure of an MDO film according to an embodiment of the invention

[0173] The seal elongation at failure of an MDO film illustrating the principles of invention (i.e., MDO Film A2) and of an mono-oriented film according to the prior art (i.e., comparative Film B2) was determined on samples prepared in accordance with ASTM F2029-08 (Standard practices for making heat seals for determination of heat sealability of flexible webs as measured by seal strength).

[0174] The MDO Film A2 was prepared from a 5-layer coextruded blown film containing the following polymers: layer

A: 75% by weight of LLDPE and 25% by weight of plastomer; layer B: LLDPE; layer C: 75% by weight of LLDPE and 25% by weight of cyclic olefin copolymer (COC); layer D: LLDPE; layer E: ethylene-vinyl acetate (EVA). The % by weight is compared with the total weight of each layer. If no percentage is given, the entire layer is prepared of the indicated polymer. The coextruded blown film was blocked in the nip rolls of the blown film line due to the stickiness of layer E, to a 10 layer film (2 times 87 μm). The resulting film was then brought into the MDO unit where it was oriented in machine direction with a stretching ratio of 1:2.9 to a mono-oriented film with a thickness of 60 μm .

[0175] The comparative MDO film B2 was prepared from a 5-layer coextruded blown film containing the following polymers: layer A: 75% by weight of LLDPE and 25% by weight of plastomer; layer B: LLDPE; layer C: LLDPE; layer D: LLDPE; layer E: EVA. The % by weight is compared with the total weight of each layer. If no percentage is given, the entire layer is prepared of the indicated polymer. The coextruded blown film was blocked in the nip rolls of the blown film line due to the stickiness of layer E, to a 10 layer film (2 times 180 μm). The resulting film was then brought into the MDO unit where it was oriented in machine direction with a stretching ratio of 1:6 to a mono-oriented film with a thickness of 60 μm .

[0176] The samples were sealed perpendicular to the machine direction of the film with heat sealing equipment (Brugger HSG-C) utilizing hot-bar jaws. The following conditions were used: 1 sec. dwell time, 100 N sealing pressure, 5 mm jaw width, and a heat seal temperature of 160°C. The seal elongation at failure of the above prepared film samples was measured in accordance with ASTM F88/F88M-09 (with tail holding technique A) on a tensile testing machine. A sealed sample with a width of 15 mm was clamped between two grips with a distance of 50 mm and tested with a jaw separation speed of 250 mm/min. The tensile testing machine gave the curve of the seal force versus heat seal elongation (grip travel).

[0177] Figure 1 represents a graph illustrating the seal strength (in N) versus the heat seal elongation (in %) of a seal prepared with the MDO film illustrating the principles of the present invention, i.e., MDO Film A2 (Figure 1, full line), and of a seal prepared with a mono-oriented film according to the prior art, i.e., comparative Film B2 (Figure 1, dashed line). MDO Film A2 (Figure 1, full line) had a thickness of 60 μm . Comparative Film B2 (Figure 1, dashed line) also had a thickness of 60 μm .

[0178] MDO Film A2 had a wide window of heat seal elongation and a heat seal elongation at failure of about 75%, while comparative Film B2 had a narrow window of heat seal elongation and a heat seal elongation at failure of about 16% only, as shown in Figure 1. As a consequence, the heat seal of MDO Film A2 had a much higher capacity of absorbing forces of the compressed products, and also of shocks and movements during transport in comparison with the heat seal of the comparative Film B2.

Example 3: MDO films according to embodiments of the present invention

[0179] The advantages of the present invention are further illustrated by a comparison of 5 different films used for packaging compressible products such as mineral wool products in a compressed state.

[0180] The five different films were subjected to a tensile elongation at break test in the machine direction on a laboratory tensile tester in accordance with ASTM D882. A strip of film having a width of 15 mm was clamped between two clamps which have a distance of 50 mm from each other. Subsequently, the film was stretched at a rate of 500 mm/min until the film broke.

[0181] The five different films were subjected to a heat seal test whereby the heat seal elongation at failure was measured. The samples were prepared in accordance with ASTM F2029-08 with following conditions: 1 sec. dwell time, 100 N sealing pressure, 5 mm jaw width and a sealing temperature of 160°C. The heat seal elongation at failure of the film samples prepared as described above were measured in accordance with ASTM F88/F88M-09 (with tail holding technique A) on a tensile testing machine. A sealed sample with a width of 15 mm was clamped between two grips with a distance of 50 mm and tested with a jaw separation speed of 250 mm/min. The tensile testing machine gave a curve of seal force versus heat seal elongation (grip travel).

[0182] The five different films were subjected to a creep test (23°C / 15mm sample width / 2300 g / 100 mm grip distance / 24 hours) in machine direction in accordance with ISO 899-1-2003.

[0183] The five different films were subjected to a practical packaging test at the tertiary packaging stage on machinery (Seelen line from Qubiqua) with adapted heat seal bars (Flexweld sealing bars from Qubiqua). Three multipacks (each containing four mineral wool (glass wool) rolls) were compressed with a force of 2100 N (i.e., high compression).

[0184] Film A: a conventional (non-oriented) blown polyolefin film of manufacturer A with a thickness of 110 μm . The conventional blown polyethylene film was a HDPE blown monolayer film.

[0185] Film B: a mono-oriented film currently on the market of manufacturer B with a thickness of 70 μm .

[0186] Film C: a mono-oriented film currently on the market with a thickness of 70 μm . This comparative mono-oriented film was prepared from a 5-layer coextruded blown film containing the following polymers: layer A: 75% by weight of linear low density polyethylene (LLDPE) and 25% by weight of plastomer; layer B: LLDPE; layer C: LLDPE; layer D: LLDPE; layer E: ethylene-vinyl acetate (EVA). The % by weight is compared with the total weight of each layer. If no percentage is given, the entire layer is prepared of the indicated polymer. The 5-layer coextruded blown film was blocked

in the nip rolls of the blown film line due to the stickiness of layer E, to form a 10 layer film (2 x 210 μm). The resulting film was then brought into the MDO unit, where it was oriented with a stretching ratio of 1:6 to a mono-oriented film with a thickness of 70 μm , i.e., Film C.

[0187] Film D: a machine direction oriented (MDO) film according to an embodiment of the invention with a thickness of 70 μm . This MDO film was prepared from a 5-layer coextruded blown film containing the following polymers: layer A: 75% by weight of LLDPE and 25% by weight of plastomer; layer B: LLDPE; layer C: 65% by weight of LLDPE and 35% by weight of COC; layer D: LLDPE; layer E: EVA. The % by weight is compared with the total weight of each layer. If no percentage is given, the entire layer is prepared of the indicated polymer. The coextruded blown film was blocked in the nip rolls of the blown film line due to the stickiness of layer E, to a 10 layer film (2 x 105 μm). The resulting film was then brought into the MDO unit where it was oriented in machine direction with a stretching ratio of 1:3 to a mono-oriented film with a thickness of 70 μm , i.e., Film D.

[0188] Film E: a machine direction oriented (MDO) film according to an embodiment of the invention with a thickness of 60 μm . This MDO film is a 5-layer coextruded blown film containing the following polymers: layer A: 75% by weight of LLDPE and 25% by weight of plastomer; layer B: LLDPE; layer C: 65% by weight of LLDPE and 35% by weight of COC; layer D: LLDPE; layer E: EVA. The % by weight is compared with the total weight of each layer. If no percentage is given, the entire layer is prepared of the indicated polymer. The coextruded blown film was blocked in the nip rolls of the blown film line due to the stickiness of layer E, to a 10 layer film (2 x 90 μm). The resulting film was then brought into the MDO unit where it was oriented in machine direction with a stretching ratio of 1:3 to a mono-oriented film of 60 μm , i.e., Film E.

[0189] The tensile elongation at break, the heat seal elongation at failure, and the tensile creep in the machine direction (MD) were measured. A practical packaging test was performed with the five different films A, B, C, D and E on machinery (Seelen line from Qubiq) with adapted heat seal bars (Flexweld sealing bars). The results are shown in Table 3.

Table 3: Stretching ratio, thickness, tensile elongation at break, heat seal elongation at failure, tensile creep in the machine direction (MD), and results of packaging test of five films illustrating the present invention

	Stretching ratio	Thickness (μm)	Tensile elongation at break (%)	Heat seal elongation at failure (%)	Tensile creep MD (%)	Packaging test (# open packages)
Film A	None	110	500	230	71	0 out of 10
Film B	$\pm 1:6$	70	60	15	4	9 out of 10
Film C	1:6	70	52	16	4	9 out of 10
Film D	1:3	70	190	45	13	0 out of 10
Film E	1:3	60	180	45	20	0 out of 10

[0190] The conventional non-oriented polyolefin Film A was performing poor regarding creep (i.e., the tendency to elongate) and thickness. Film A had high tensile creep, i.e., high tendency to elongate, resulting in too high growing ratios of the packages. As a consequence, the compression ratios on the mineral wool were limited.

[0191] The comparative mono-oriented Films B and C with a heat seal elongation at failure of 15% and 16% respectively had good creep properties, but were performing poorly in heat sealing when packaging mineral wool in a compressed state. Nearly all packages were popping on the seal.

[0192] The MDO Film D according to an embodiment of the present invention, stretched in machine direction with a stretching ratio of 1:3, and with a tensile elongation at break in machine direction between 150 and 250%, had a heat seal elongation at failure of about 45% (Table 3, Film D). This heat seal elongation at failure was considerably higher in comparison with the heat seal elongation at failure of the comparative mono-oriented films, i.e., heat seal elongation at failure of 15 % and 16%, for Film B and Film C, respectively (Table 3, Film B and C). As a result, the MDO Film D according to an embodiment of the invention gave a very satisfactory seal performance in a practical test without any open packages (Table 3, Film D) in comparison with the poor result of the comparative mono-oriented films (Table 3, Film B and C). Furthermore, although the tensile creep of the MDO Film D was higher than the tensile creep of the comparative mono-oriented Films B and C, the MDO Film D had sufficiently low tensile creep to satisfactorily withstand the expansion forces of the compressed mineral wool packages.

[0193] Even the thinner MDO Film E according to an embodiment of the present invention was performing excellent during practical tests. The MDO Film E also had sufficiently low tensile creep to withstand the expansion forces of the compressed mineral wool packages (Table 3, Film E).

[0194] In conclusion, the MDO films illustrating the principles of the present invention had an enhanced sealing be-

haviour on machinery for packaging compressible products such as mineral wool products. With the MDO films illustrating the principles of the invention, there was no need anymore to regularly align the heat sealing bars on a mineral wool packaging line. Moreover, the present MDO films were perfectly sealed, even on packaging lines which were until now unable to seal mono-oriented films according to prior art. The present MDO films brought an advantageous solution for an economical way of storing and transporting compressible products, such as mineral wool products, in a compressed state. Also regarding cost saving and environmental sustainability, the MDO films illustrating the principles of the present invention were very advantageous because they could be prepared as films with a reduced thickness.

Claims

1. A method for packaging a compressible product in a compressed state, comprising the step of sealing at least two parts of a polymeric machine direction oriented (MDO) film which encloses at least part of the compressible product in the compressed state, wherein the seal has a seal elongation at failure of about 20% to about 100%, as measured in accordance with ASTM F88/F88M-09, wherein the MDO film has an elongation at break in the machine direction of about 100% to about 300%, as measured in accordance with ASTM D882, and the MDO film comprises from about 1% to about 90% by weight of one or more polymers selected from the group consisting of high density polyethylene (HDPE), medium density polyethylene (MDPE), polypropylene (PP), cyclic olefin copolymer (COC), and styrene butadiene copolymer (SBC), with % by weight relative to the total weight of the MDO film.
2. The method according to claim 1, wherein the seal has a seal elongation at failure of about 25% to about 100%, preferably the seal has a seal elongation at failure of about 30% to about 90%, more preferably the seal has a seal elongation at failure of about 35% to about 80%, as measured in accordance with ASTM F88/F88M-09.
3. The method according to claim 1 or 2, wherein the sealing comprises heat sealing, preferably wherein the sealing is heat sealing.
4. The method according to any one of claims 1 to 3, wherein the compressible product is an insulation product.
5. The method according to any one of claims 1 to 4, wherein the compressible product is a mineral wool product, such as a mineral wool slab or a mineral wool roll.
6. The method according to any one of claims 1 to 5, wherein the MDO film has a tensile creep in the machine direction of about 0.10% to about 0.50% per μm thickness of the film, as measured in accordance with ISO 899-1-2003 with following conditions: sample width of 15 mm, grip distance of 100 mm, a load of 2300 g, 24 hours, and at 23°C.
7. The method according to any one of claims 1 to 6, wherein the MDO film has a thickness of about 15 μm to about 100 μm .
8. The method according to any one of claims 1 to 7, wherein the MDO film has an elongation at break in the machine direction of about 150% to about 250%, as measured in accordance with ASTM D882.
9. A compressible product in a compressed state packaged in a polymeric machine direction oriented (MDO) film which encloses at least part of the compressible product, wherein at least two parts of the MDO film are sealed and the seal has a seal elongation at failure of about 20% to about 100%, as measured in accordance with ASTM F88/F88M-09, wherein the MDO film has an elongation at break in the machine direction of about 100% to about 300%, as measured in accordance with ASTM D882, and the MDO film comprises from about 1% to about 90% by weight of one or more polymers selected from the machine consisting of high density polyethylene (HDPE), medium density polyethylene (MDPE), polypropylene (PP), cyclic olefin copolymer (COC), and styrene butadiene copolymer (SBC), with % by weight relative to the total weight of the MDO film.
10. A polymeric machine direction oriented (MDO) film for packaging a compressible product in a compressed state, wherein the MDO film, when at least two parts of the MDO film are sealed, provides a seal with a seal elongation at failure of about 20% to about 100%, as measured in accordance with ASTM F88/F88M-09, wherein the MDO film has an elongation at break in the machine direction of about 100% to about 300%, as measured in accordance with ASTM D882, and the MDO film comprises from about 1% to about 90% by weight of one or more polymers selected from the group consisting of high density polyethylene (HDPE), medium density polyethylene (MDPE), polypropylene (PP), cyclic olefin copolymer (COC), and styrene butadiene copolymer (SBC), with % by weight

relative to the total weight of the MDO film.

11. The packaged product according to claim 9, or the MDO film according to claim 10, wherein the seal has a seal elongation at failure of about 25% to about 100%, preferably the seal has a seal elongation at failure of about 30% to about 90%, more preferably the seal has a seal elongation at failure of about 35% to about 80%, as measured in accordance with ASTM F88/F88M-09.
12. The packaged product according to claim 9 or 11, or the MDO film according to claim 10 or 11, wherein the sealing comprises heat sealing, preferably wherein the sealing is heat sealing.
13. The packaged product according to any one of claims 9, 11, or 12, or the MDO film according to any one of claims 10 to 12, wherein the MDO film has a tensile creep in the machine direction of about 0.10% to about 0.50% per μm thickness of the film, as measured in accordance with ISO 899-1-2003 with following conditions: sample width of 15 mm, grip distance of 100 mm, a load of 2300 g, 24 hours, and at 23°C.
14. The packaged product according to any one of claims 9, or 11 to 13, or the MDO film according to any one of claims 10 to 13, wherein the MDO film has a thickness of about 15 μm to about 100 μm .
15. The packaged product according to any one of claims 9, or 11 to 14, or the MDO film according to any one of claims 10 to 14, wherein the MDO film has an elongation at break in the machine direction of about 150% to about 250%, as measured in accordance with ASTM D882.

Patentansprüche

1. Verfahren zum Verpacken eines komprimierbaren Produkts in einem komprimierten Zustand, umfassend den Schritt des Siegelns von wenigstens zwei Teilen eines in Maschinenrichtung orientierten (MDO-) Polymerfilms, der wenigstens einen Teil des komprimierbaren Produkts in dem komprimierten Zustand umschließt, wobei die Siegelung eine Siegelungsbruchdehnung von etwa 20 % bis etwa 100 %, wie gemessen gemäß ASTM F88/F88M-09, aufweist, wobei der MDO-Film eine Bruchdehnung in der Maschinenrichtung von etwa 100 % bis etwa 300 %, wie gemessen gemäß ASTM D882, aufweist, und der MDO-Film von etwa 1 Gew.-% bis etwa 90 Gew.-% an einem oder mehreren Polymeren ausgewählt aus der Gruppe bestehend aus Polyethylen mit hoher Dichte (HDPE), Polyethylen mit mittlerer Dichte (MDPE), Polypropylen (PP), Cyclisches-Olefin-Copolymer (COC) und Styrol-Butadien-Copolymer (SBC) umfasst, wobei Gew.-% auf das Gesamtgewicht des MDO-Films bezogen sind.
2. Verfahren gemäß Anspruch 1, wobei die Siegelung eine Siegelungsbruchdehnung von etwa 25 % bis etwa 100 % aufweist, vorzugsweise die Siegelung eine Siegelungsbruchdehnung von etwa 30 % bis etwa 90 % aufweist, bevorzugter die Siegelung eine Siegelungsbruchdehnung von etwa 35 % bis etwa 80 % aufweist, wie gemessen gemäß ASTM F88/F88M-09.
3. Verfahren gemäß Anspruch 1 oder 2, wobei das Siegeln Heißsiegeln umfasst, vorzugsweise wobei das Siegeln Heißsiegeln ist.
4. Verfahren gemäß einem der Ansprüche 1 bis 3, wobei das komprimierbare Produkt ein Isolationsprodukt ist.
5. Verfahren gemäß einem der Ansprüche 1 bis 4, wobei das komprimierbare Produkt ein Mineralwollprodukt ist, wie z. B. eine Mineralwollplatte oder eine Mineralwollrolle.
6. Verfahren gemäß einem der Ansprüche 1 bis 5, wobei der MDO-Film Zugkriechen in der Maschinenrichtung von etwa 0,10 % bis etwa 0,50 % pro μm Dicke des Films aufweist, wie gemessen gemäß ISO 899-1-2003 mit folgenden Bedingungen: Probenbreite 15 mm, Greifabstand 100 mm, Last 2300 g, 24 Stunden, und bei 23 °C.
7. Verfahren gemäß einem der Ansprüche 1 bis 6, wobei der MDO-Film eine Dicke von etwa 15 μm bis etwa 100 μm aufweist.
8. Verfahren gemäß einem der Ansprüche 1 bis 7, wobei der MDO-Film eine Bruchdehnung in der Maschinenrichtung von etwa 150 % bis etwa 250 %, wie gemessen gemäß ASTM D882, aufweist.

9. Komprimierbares Produkt in einem komprimierten Zustand verpackt in einem in Maschinenrichtung orientierten (MDO-) Polymerfilm, der wenigstens einen Teil des komprimierbaren Produkts umschließt, wobei wenigstens zwei Teile des MDO-Films gesiegelt sind und die Siegelung eine Siegelungsbruchdehnung von etwa 20 % bis etwa 100 %, wie gemessen gemäß ASTM F88/F88M-09, aufweist, wobei der MDO-Film eine Bruchdehnung in der Maschinenrichtung von etwa 100 % bis etwa 300 %, wie gemessen gemäß ASTM D882, aufweist, und der MDO-Film von etwa 1 Gew.-% bis etwa 90 Gew.-% an einem oder mehreren Polymeren ausgewählt aus der Gruppe bestehend aus Polyethylen mit hoher Dichte (HDPE), Polyethylen mit mittlerer Dichte (MDPE), Polypropylen (PP), Cyclisches-Olefin-Copolymer (COC) und Styrol-Butadien-Copolymer (SBC) umfasst, wobei Gew.-% auf das Gesamtgewicht des MDO-Films bezogen sind.
10. In Maschinenrichtung orientierter (MDO-) Polymerfilm zum Verpacken eines komprimierbaren Produkts in einem komprimierten Zustand, wobei der MDO-Film, wenn wenigstens zwei Teile des MDO-Films gesiegelt werden, eine Siegelung mit einer Siegelungsbruchdehnung von etwa 20 % bis etwa 100 %, wie gemessen gemäß ASTM F88/F88M-09, bereitstellt, wobei der MDO-Film eine Bruchdehnung in der Maschinenrichtung von etwa 100 % bis etwa 300 %, wie gemessen gemäß ASTM D882, aufweist, und der MDO-Film von etwa 1 Gew.-% bis etwa 90 Gew.-% an einem oder mehreren Polymeren ausgewählt aus der Gruppe bestehend aus Polyethylen mit hoher Dichte (HDPE), Polyethylen mit mittlerer Dichte (MDPE), Polypropylen (PP), Cyclisches-Olefin-Copolymer (COC) und Styrol-Butadien-Copolymer (SBC) umfasst, wobei Gew.-% auf das Gesamtgewicht des MDO-Films bezogen sind.
11. Verpacktes Produkt gemäß Anspruch 9 oder MDO-Film gemäß Anspruch 10, wobei die Siegelung eine Siegelungsbruchdehnung von etwa 25 % bis etwa 100 % aufweist, vorzugsweise die Siegelung eine Siegelungsbruchdehnung von etwa 30 % bis etwa 90 % aufweist, bevorzugter die Siegelung eine Siegelungsbruchdehnung von etwa 35 % bis etwa 80 % aufweist, wie gemessen gemäß ASTM F88/F88M-09.
12. Verpacktes Produkt gemäß Anspruch 9 oder 11 oder MDO-Film gemäß Anspruch 10 oder 11, wobei das Siegeln Heißsiegeln umfasst, vorzugsweise wobei das Siegeln Heißsiegeln ist.
13. Verpacktes Produkt gemäß einem der Ansprüche 9, 11 oder 12 oder MDO-Film gemäß einem der Ansprüche 10 bis 12, wobei der MDO-Film Zugkriechen in der Maschinenrichtung von etwa 0,10 % bis etwa 0,50 % pro μm Dicke des Films aufweist, wie gemessen gemäß ISO 899-1-2003 mit folgenden Bedingungen: Probenbreite 15 mm, Greifabstand 100 mm, Last 2300 g, 24 Stunden, und bei 23 °C.
14. Verpacktes Produkt gemäß einem der Ansprüche 9 oder 11 bis 13 oder MDO-Film gemäß einem der Ansprüche 10 bis 13, wobei der MDO-Film eine Dicke von etwa 15 μm bis etwa 100 μm aufweist.
15. Verpacktes Produkt gemäß einem der Ansprüche 9 oder 11 bis 14 oder MDO-Film gemäß einem der Ansprüche 10 bis 14, wobei der MDO-Film eine Bruchdehnung in der Maschinenrichtung von etwa 150 % bis etwa 250 %, wie gemessen gemäß ASTM D882, aufweist.

Revendications

1. Procédé d'emballage d'un produit compressible dans un état comprimé, comprenant l'étape qui consiste à souder au moins deux parties d'un film polymère orienté dans le sens machine (OSM) qui renferme au moins une partie du produit compressible dans l'état comprimé, dans lequel la soudure a un allongement à la rupture d'environ 20 % à environ 100 %, tel que mesuré selon la méthode ASTM F88/F88M-09, dans lequel le film OSM a un allongement à la rupture dans le sens machine d'environ 100 % à environ 300 %, tel que mesuré selon la méthode ASTM D882, et le film OSM comprend d'environ 1 % à environ 90 % en poids d'un ou plusieurs polymères sélectionnés dans le groupe constitué du polyéthylène de haute densité (HDPE), du polyéthylène de moyenne densité (MDPE), du polypropylène (PP), du copolymère d'oléfine cyclique (COC), et du copolymère de styrène-butadiène (SBC), le pourcentage en poids étant exprimé relativement au poids total du film OSM.
2. Procédé selon la revendication 1, dans lequel la soudure a un allongement à la rupture d'environ 25 % à environ 100 %, la soudure a préféablement un allongement à la rupture d'environ 30 % à environ 90 %, et la soudure a plus préféablement un allongement à la rupture d'environ 35 % à environ 80 %, tel que mesuré selon la méthode ASTM F88/F88M-09.
3. Procédé selon la revendication 1 ou 2, dans lequel le soudage comprend un thermosoudage, préféablement dans

lequel le soudage est le thermosoudage.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le produit compressible est un produit d'isolation.
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le produit compressible est un produit en laine minérale, tel qu'une dalle de laine minérale ou un rouleau de laine minérale.
6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le film OSM a un fluage en traction dans le sens machine d'environ 0,10 % à environ 0,50 % par μm d'épaisseur du film, tel que mesuré selon la méthode ISO 899-1-2003 dans les conditions suivantes : une largeur d'échantillon de 15 mm, un écartement des pinces de 100 mm, une charge de 2 300 g, pendant 24 heures, et à une température de 23 °C.
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel le film OSM a une épaisseur d'environ 15 μm à environ 100 μm .
8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel le film OSM a un allongement à la rupture dans le sens machine d'environ 150 % à environ 250 %, tel que mesuré selon la méthode ASTM D882.
9. Produit compressible dans un état comprimé, emballé dans un film polymère orienté dans le sens machine (OSM) qui renferme au moins une partie du produit compressible, dans lequel au moins deux parties du film OSM sont soudées et la soudure a un allongement à la rupture d'environ 20 % à environ 100 %, tel que mesuré selon la méthode ASTM F88/F88M-09, dans lequel le film OSM a un allongement à la rupture dans le sens machine d'environ 100 % à environ 300 %, tel que mesuré selon la méthode ASTM D882, et le film OSM comprend d'environ 1 % à environ 90 % en poids d'un ou plusieurs polymères sélectionnés dans le groupe constitué du polyéthylène de haute densité (HDPE), du polyéthylène de moyenne densité (MDPE), du polypropylène (PP), du copolymère d'oléfine cyclique (COC), et du copolymère de styrène-butadiène (SBC), le pourcentage en poids étant exprimé relativement au poids total du film OSM.
10. Film polymère orienté dans le sens machine (OSM) pour l'emballage d'un produit compressible dans un état comprimé, le film OSM, quand au moins deux parties du film OSM sont soudées, formant une soudure qui a un allongement à la rupture d'environ 20 % à environ 100 %, tel que mesuré selon la méthode ASTM F88/F88M-09, le film OSM ayant un allongement à la rupture dans le sens machine d'environ 100 % à environ 300 %, tel que mesuré selon la méthode ASTM D882, et le film OSM comprenant d'environ 1 % à environ 90 % en poids d'un ou plusieurs polymères sélectionnés dans le groupe constitué du polyéthylène de haute densité (HDPE), du polyéthylène de moyenne densité (MDPE), du polypropylène (PP), du copolymère d'oléfine cyclique (COC), et du copolymère de styrène-butadiène (SBC), le pourcentage en poids étant exprimé relativement au poids total du film OSM.
11. Produit emballé selon la revendication 9, ou film OSM selon la revendication 10, dans lequel la soudure a un allongement à la rupture d'environ 25 % à environ 100 %, la soudure a préféablement un allongement à la rupture d'environ 30 % à environ 90 %, et la soudure a plus préféablement un allongement à la rupture d'environ 35 % à environ 80 %, tel que mesuré selon la méthode ASTM F88/F88M-09.
12. Produit emballé selon la revendication 9 ou 11, ou film OSM selon la revendication 10 ou 11, dans lequel le soudage comprend un thermosoudage, préféablement dans lequel le soudage est le thermosoudage.
13. Produit emballé selon l'une quelconque des revendications 9, 11, ou 12, ou film OSM selon l'une quelconque des revendications 10 à 12, le film OSM ayant un fluage en traction dans le sens machine d'environ 0,10 % à environ 0,50 % par μm d'épaisseur du film, tel que mesuré selon la méthode ISO 899-1-2003 dans les conditions suivantes : une largeur d'échantillon de 15 mm, un écartement des pinces de 100 mm, une charge de 2 300 g, pendant 24 heures, et à une température de 23 °C.
14. Produit emballé selon l'une quelconque des revendications 9, ou 11 à 13, ou film OSM selon l'une quelconque des revendications 10 à 13, le film OSM ayant une épaisseur d'environ 15 μm à environ 100 μm .
15. Produit emballé selon l'une quelconque des revendications 9, ou 11 à 14, ou film OSM selon l'une quelconque des revendications 10 à 14, le film OSM ayant un allongement à la rupture dans le sens machine d'environ 150 % à environ 250 %, tel que mesuré selon la méthode ASTM D882.

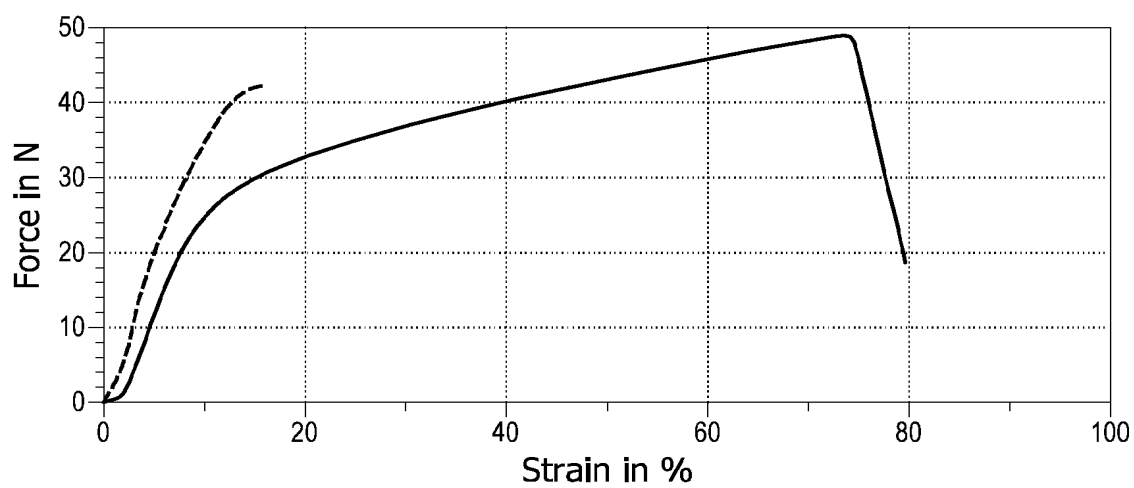


Fig. 1

REFERENCES CITED IN THE DESCRIPTION

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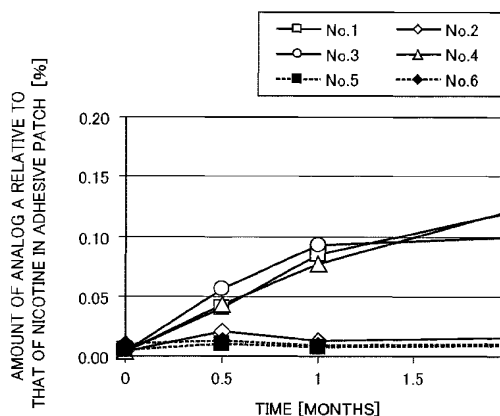
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(54) **PACKAGING**

(57) The objective of the present invention is to provide a method of preventing an oxygen-caused alteration of a drug in an adhesive patch enclosed inside a packaging container. The present invention is a package body comprising a packaging container and a drug-containing adhesive patch enclosed inside the packaging container, wherein the amount of oxygen gas inside the package body is 20 μL or less, and the concentration of oxygen gas is 17.0 to 25.0 vol%. This packaging does not have to contain an oxygen scavenger as a separate member distinct from the drug-containing adhesive patch. Further, the amount of oxygen gas may be 4 $\mu\text{L}/\text{mg}$ or less per amount of a drug in the drug-containing adhesive patch.

FIG. 1A



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a package body.

BACKGROUND ART

10 **[0002]** An adhesive patch is a formulation generally having a drug-containing adhesive layer, and is attached on the skin and the like when used. An adhesive patch is stored in a sealed packaging container in order to prevent an alteration and the like of a drug in the adhesive patch. Various factors may cause an alteration and the like of a drug in an adhesive patch, including, for example, oxygen, light and the like.

15 **[0003]** As a method of preventing an alteration of a drug in an adhesive patch due to oxygen, the followings are used: a method in which an anti-oxidant is blended into an adhesive patch; a method in which an oxygen scavenger and the like is enclosed inside a packaging container along with an adhesive patch; and the like. However, these methods cost time and expense for blending an anti-oxidant or enclosing an oxygen scavenger and the like. Therefore, a more convenient method has been demanded.

20 **[0004]** As another method of preventing an alteration of a drug in an adhesive patch due to oxygen, proposed is a method in which the concentration of oxygen gas inside a packaging container is limited to 3.0 vol% or less (Patent Document 1). Further, among drugs which can be formulated into an adhesive patch, rivastigmine is known as an agent for suppressing symptom progression of Alzheimer type dementia. Rivastigmine-containing formulations are prepared in various dosage forms such as a rivastigmine-containing adhesive patch. For example, a rivastigmine-containing adhesive patch is commercially available under the product name "Exelon®".

25 **[0005]** Rivastigmine contained in a rivastigmine-containing adhesive patch may be altered due to oxygen, light and the like during storage of the adhesive patch. Therefore, methods of storing an adhesive patch have been studied in which an alteration of rivastigmine is prevented. Such storing methods include, for example, a method in which a rivastigmine-containing adhesive patch is enclosed inside a packaging container composed of a multilayered film comprising a polyacrylonitrile layer and an aluminum layer (Patent Document 2).

30 Patent Document 1: Japanese Unexamined Patent Application, Publication No. 2012-51875
 Patent Document 2: Japanese Patent No. 5093545

DISCLOSURE OF THE INVENTION

35 Problems to be Solved by the Invention

40 **[0006]** However, even the method described in Patent Document 1 wherein the concentration of oxygen gas inside a packaging container is limited to 3.0 vol% or less costs time and expense. Therefore a more convenient method has been demanded. Further, Patent Document 1 describes a method of limiting the concentration of oxygen gas inside a packaging container to 3.0 vol% or less, the method comprising mainly enclosing an oxygen scavenger along with an adhesive patch. However, an oxygen scavenger is often bulky, resulting in an increased intercontainer space.

45 **[0007]** Moreover, there may be an occasion where the packaging container described in Patent Document 2 can not sufficiently control an alteration of rivastigmine. Therefore, a method of storing a rivastigmine-containing adhesive patch has been demanded in which an alteration of rivastigmine is more reliably prevented.

50 **[0008]** The present invention is made in order to solve the above problems. An object of the present invention is to provide a method of preventing an oxygen-caused alteration of a drug in an adhesive patch enclosed inside a packaging container.

55 **[0009]** Further, another object of the present invention is to provide a method of preventing an alteration of rivastigmine in a rivastigmine-containing adhesive patch enclosed inside a packaging container.

Means for Solving the Problems

60 **[0010]** The present inventors find that the above problems can be solved by limiting the amount and concentration of oxygen gas inside a packaging container within predetermined ranges. Then the present invention has been completed.

65 **[0011]** Further, the present inventors find that the above problems can be solved by using a packaging container composed of a multilayered film comprising a predetermined layer as a storage container for a rivastigmine-containing adhesive patch. Then the present invention has been completed.

70 **[0012]** Specifically, the present invention provides the followings.

(1) A package body comprising a packaging container and a drug-containing adhesive patch enclosed inside the packaging container, wherein the amount of oxygen gas inside the package body is 20 μL or less, and the concentration of oxygen gas is 17.0 to 25.0 vol%.

(2) The package body according to (1), wherein the package body does not contain an oxygen scavenger as a separate member distinct from the drug-containing adhesive patch.

(3) The package body according to (1) or (2), wherein the amount of oxygen gas is 4 $\mu\text{L}/\text{mg}$ or less per amount of a drug in the drug-containing adhesive patch.

(4) The package body according to any one of (1) to (3), wherein the drug is any of nicotine, rivastigmine or pharmacologically acceptable salts thereof.

(5) The package body according to any one of (1) to (4), wherein the drug-containing adhesive patch comprises a support and an adhesive layer disposed on the support, the adhesive layer comprising an acrylic adhesive substantially free from a carboxyl group.

(6) A package body comprising a packaging container and an adhesive patch enclosed inside the packaging container, wherein the adhesive patch comprises a support and an adhesive layer containing a drug and disposed on the support, the drug comprises at least rivastigmine and/or a pharmaceutically acceptable salt thereof, and the packaging container comprises a multilayered film in which at least a polyacrylonitrile layer, an aluminum layer and a polyethylene terephthalate layer are laminated.

(7) The package body according to (6), wherein the innermost layer of the packaging container is a polyacrylonitrile layer.

(8) The package body according to (7), wherein the multilayered film is a multilayered film in which a polyacrylonitrile layer, an aluminum layer and a polyethylene terephthalate layer are laminated in this order.

(9) The package body according to any one of (6) to (8), wherein the polyacrylonitrile layer has a thickness of 10 to 50 μm , and the aluminum layer has a thickness of 1 to 15 μm , and the polyethylene terephthalate layer has a thickness of 5 to 20 μm .

(10) The package body according to any one of (6) to (9), wherein the package body does not contain any one or more of an oxygen scavenger and an anti-oxidant.

(11) The package body according to any one of (6) to (10), wherein the adhesive layer comprises an acrylic adhesive.

Effects of the Invention

[0013] The present invention provides a method of preventing an oxygen-caused alteration of a drug in an adhesive patch enclosed inside a packaging container.

[0014] Further, the present invention provides a method of preventing an alteration of rivastigmine in a rivastigmine-containing adhesive patch enclosed inside a packaging container.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

Fig. 1A shows the content of a nicotine analog in adhesive patches enclosed in package bodies used in Example.

Fig. 1B shows the content of a nicotine analog in adhesive patches enclosed in package bodies used in Example.

Fig. 2 shows the change in color tone of adhesive patches enclosed in package bodies used in Example.

Fig. 3A shows the content of a rivastigmine analog in adhesive patches enclosed in package bodies used in Example.

Fig. 3B shows the content of a rivastigmine analog in adhesive patches enclosed in package bodies used in Example.

Fig. 4 shows the amounts and concentrations of oxygen gas in the package bodies according to one aspect of the present invention and the conventional package bodies.

Fig. 5 shows the amounts and concentrations of oxygen gas in the package bodies according to one aspect of the present invention and the conventional package bodies.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0016] Below, embodiments of the present invention will be described. Note that the present invention shall not be limited to the following embodiments.

Package body - I

[0017] A first embodiment of the present invention provides a package body (in other words, a packaging product)

comprising a packaging container and a drug-containing adhesive patch enclosed in the above packaging container, wherein the amount of oxygen gas in the above package body is 20 μL or less, and the concentration of oxygen gas is 17.0 to 25.0 vol%. Note that the term "package body" used in the present invention refers to a packaging container in a state where a drug-containing adhesive patch is enclosed inside. Further, a "drug-containing adhesive patch" may simply be referred to as an "adhesive patch." Moreover, a "packaging container" used in the present invention is intended for enclosing an adhesive patch, and may also be called a "packaging bag." Each component of a first package body according to the present invention will be described below.

(The amount and concentration of oxygen gas)

[0018] In the present invention, the amount of oxygen gas inside a package body is adjusted to 20 μL or less, and the concentration of oxygen gas is adjusted to 17.0 to 25.0 vol%. After conducting extensive studies, the present inventors find that the stability of a drug in an adhesive patch enclosed inside a packaging container is less deteriorated when the amount and concentration of oxygen gas fall within such ranges.

[0019] Conventionally, an oxygen scavenger, an anti-oxygen agent and the like are enclosed in order to reduce the amount of oxygen gas inside a package body. However, these agents merely reduce the amount of oxygen gas gradually during storage of an adhesive patch. Therefore, the stability of a drug in an adhesive patch is likely to be deteriorated before the amount of oxygen gas inside a package body is sufficiently reduced.

[0020] Further, for example, Japanese Unexamined Patent Application No. 2012-51875 describes a method in which the concentration of oxygen gas inside a packaging container is reduced to 3.0 vol% or less by means of decompression and the like. However, decompression alone results in a concentration of oxygen gas inside a package body close to the ratio of oxygen in the air (about 20 vol%). Therefore, additional use of an oxygen scavenger and the like is essential in order to reduce the amount of oxygen gas to 3.0 vol% or less in a package body. That is, decompression and the like described in Japanese Unexamined Patent Application No. 2012-51875 is merely an auxiliary means for efficiently reducing the amount of oxygen gas inside a package body to 3.0 vol% or less when a less amount of an oxygen scavenger is used. Therefore, an object thereof can not be considered to sufficiently reduce the total amount of gas inside a package body including oxygen gas as in the present invention.

[0021] Further, as another method for reducing the amount of oxygen gas inside a package body, substitution with inert gas is performed such as nitrogen substitution and argon substitution. However, when a specific element is substituted with oxygen, the total amount of the air inside a packaging container is the same as or higher than that before substitution although the concentration of oxygen gas inside a packaging container becomes low. Therefore, the volume of the resulting package body increases (in this case, the concentration of oxygen gas inside the package body is likely to be about 1.0 to 5.0 vol%). As a result, an adhesive patch may be twisted or bent in a package body, resulting in a poor storability of the adhesive patch. Further, substitution with inert gas costs time and expense in a manufacturing process.

[0022] In contrast, since the amount of oxygen gas is as small as 20 μL or less at a stage where an adhesive patch is enclosed inside the packaging container according to the present invention, the stability of a drug is less deteriorated in the adhesive patch during storage of the adhesive patch. Further, the concentration of oxygen gas inside a packaging container is 17.0 to 25.0 vol%, and the total gas content inside the packaging container is small, preventing an increased volume of a package body.

[0023] The amount of oxygen gas inside a package body is 20 μL or less, preferably 15 μL or less, more preferably 10 μL or less in order to reduce the effects of oxygen on a drug in an adhesive patch. Further, although the amount of oxygen gas inside a package body is preferably zero, an acceptable amount is 0.01 μL or more, preferably 0.1 μL or more since complete removal is difficult. The amount of oxygen gas inside a package body may be 4 $\mu\text{L}/\text{mg}$ or less per amount of a drug in an adhesive patch, preferably 0.002 to 3 $\mu\text{L}/\text{mg}$ in order to reduce the effects of oxygen on the drug in the adhesive patch.

[0024] The concentration of oxygen gas inside a package body may be a concentration close to the ratio of oxygen in the air (about 20 vol%), and is 17.0 to 25.0 vol%, preferably 18.0 to 24.0 vol%.

[0025] As a method of adjusting the amount and concentration of oxygen gas inside a package body to the aforementioned ranges, those in which the amount of gas inside a package body is physically reduced can be used. Such methods include those in which decompression or pressing is used, specifically, those in which a vacuum pump, a compressor and the like are used. According to these methods, the total gas content inside a packaging container can be reduced while the concentration of oxygen gas inside the packaging container is maintained to be close to the ratio of oxygen in the air (about 20 vol%), achieving the aforementioned amount and concentration of oxygen gas.

[0026] In the present invention, methods such as nitrogen substitution and argon substitution are preferably not used in order to set the concentration of oxygen gas inside a package body to the aforementioned range. The reason for this is that the concentration of oxygen gas inside a package body is difficult to be set within the aforementioned range because these methods increase the ratio of a specific element inside a package body.

[0027] The total gas content inside the package body according to the present invention may be 0.5 to 180 μL , preferably 5.0 to 120 μL , more preferably 10 to 100 μL . The package body according to the present invention has a smaller total gas content than the conventional package body.

[0028] The package body according to the present invention can be obtained by placing an adhesive patch inside a packaging container, and adjusting the amount and concentration of oxygen gas inside the packaging container to the aforementioned ranges, and then sealing the packaging container by a method such as heat sealing, sealing with an adhesive and the like. The package body according to the present invention has a sufficiently reduced amount and concentration of oxygen gas inside a package body without an oxygen scavenger enclosed, and therefore, preferably does not contain an oxygen scavenger as a separate member distinct from an adhesive patch. The package body according to the present invention may consist of a packaging container and a drug-containing adhesive patch enclosed in the above packaging container.

[0029] The concentration of oxygen gas inside a packaging container can be determined with an oxygen-gas concentration meter. The amount of oxygen gas inside a packaging container can be determined based on the total gas content and the concentration of oxygen gas inside a package body.

(Packaging container)

[0030] There is no particular limitation for the packaging container as long as it can be hermetically sealed, and those commonly used as packaging containers for adhesive patches such as tapes and cataplasms.

(Drug-containing adhesive patch)

[0031] There is no particular limitation for the form of an adhesive patch enclosed inside the packaging container according to the present invention, and known adhesive patch having a drug-containing layer can be used. For example, it may be an adhesive patch comprising a drug-containing adhesive layer (a sheet-like formulation and the like), or an adhesive patch comprising a support and an adhesive layer (which usually contains a drug) disposed on the above support. Among these, preferred is an adhesive patch comprising a support and an adhesive layer disposed on the above support. Further, the adhesive patch may be those in which a known skin adhesive layer (polyisobutylene and the like), controlled-release membrane and strippable liner (an oxygen impermeable liner and the like) are laminated on an adhesive layer.

[0032] There is no particular limitation for the adhesive included in an adhesive layer of an adhesive patch as long as it is commonly used for adhesive patches to be applied to the skin, and it may be one or more of acrylic adhesives, rubber-based adhesives or a silicon-based adhesives.

[0033] Among the above adhesives, acrylic adhesives are preferred in view of that strength and the like are not lost even under a low-pressure environment where the total gas content inside a package body is small. Among acrylic adhesives, those substantially free from a carboxyl group are preferred in view of that they are less reactive with a drug, and can control the decrease in transdermal absorption of a drug, and are less affected by oxygen. The phrase "substantially free from a carboxyl group" means not only those not containing a carboxyl group at all but also those in which carboxyl groups are all theoretically replaced with substituents such as ester linkages. Those include, for example, a case in which a trace amount of ester linkages and the like are converted into free carboxyl groups due to hydrolysis, and a case in which free carboxyl groups are included as impurities from a raw material.

[0034] There is no particular limitation for the acrylic adhesive substantially free from a carboxyl group, and, for example, adhesives described in Japanese Unexamined Patent Application No. 2005-325101, Japanese Patent No. 3809462 and the like can be used. Among these, in particular, the acrylic adhesive described in Japanese Unexamined Patent Application No. 2005-325101 can be conveniently used.

[0035] An acrylic adhesive substantially free from a carboxyl group and a hydroxy group is particularly preferred as the acrylic adhesive in the present invention in view of that it is less reactive with a drug, and can control the decrease in transdermal absorption of the drug, and is less affected by oxygen.

[0036] There is no particular limitation for the drug contained in an adhesive patch, and even those more susceptible to alteration due to oxygen can be preferably used. Such drugs include any of nicotine (an smoking-cessation aid), rivastigmine (an therapeutic agent for Alzheimer-type dementia) or pharmacologically acceptable salts thereof. The amount of a drug in an adhesive patch may be appropriately adjusted according to the desired pharmacological effect.

[0037] Other components may be contained in an adhesive patch, if desired. Such components include adhesiveness-conferring agents (rosin ester and the like), plasticizing agents, antiseptic agents, pH adjusters, chelating agents, transdermal absorption promoting agents, excipients, flavoring agents, coloring agents, fatty acids, fats and oils and the like. Note that the stability of a drug in an adhesive patch is excellent in the package body according to the present invention even in a case where an anti-oxidant is not blended in the adhesive patch. However, an anti-oxidant such as dibutylhydroxytoluene may be blended into an adhesive patch, if desired.

(Method of manufacturing adhesive patch)

[0038] There is no particular limitation for the method of preparing an adhesive patch, and known preparation methods can be used for preparing an adhesive patch. They include the followings: for example, a method of obtaining an adhesive patch, comprising uniformly dissolving each component into a solution, and coat-drying the resulting solution using a coater; a method of obtaining an adhesive patch, comprising uniformly stirring components of an adhesive layer, and coat-drying the resulting composition onto a surface of a support using a coater.

Package body - II

[0039] In a second embodiment of the present invention, provided is a package body comprising a packaging container and an adhesive patch enclosed in the above packaging container. Note that the term "package body" used in the present invention refers to a packaging container in a state where an adhesive patch is enclosed inside. Further, an "adhesive patch" used in the present invention is also referred to as a "rivastigmine-containing adhesive patch." Moreover, a "packaging container" used in the present invention is intended for enclosing an adhesive patch therein, and may also be called a "packaging bag." Below, each component of the second package body according to the present invention will be described.

(Configuration of packaging container)

[0040] The packaging container according to the present invention comprises a multilayered film in which at least a polyacrylonitrile layer (hereinafter, the polyacrylonitrile layer is also referred to as "PAN"), an aluminum layer (hereinafter, the aluminum layer is also referred to as "AL") and a polyethylene terephthalate layer (hereinafter, the polyethylene terephthalate layer is also referred to as "PET") are laminated. Note that a polyacrylonitrile layer, an aluminum layer and a polyethylene terephthalate layer refer to layers containing polyacrylonitrile, aluminum and polyethylene terephthalate, respectively as a main component. The phrase "containing ... as a main component" used in the present invention means that polyacrylonitrile, aluminum or polyethylene terephthalate is contained in each layer in an amount of 50 mass% or more. Polyacrylonitrile in a polyacrylonitrile layer is preferably 90 mass% or more, and more preferably, a polyacrylonitrile layer consists of polyacrylonitrile. Aluminum in an aluminum layer is preferably 90 mass% or more, and more preferably, an aluminum layer consists of aluminum. Polyethylene terephthalate in a polyethylene terephthalate layer is preferably 90 mass% or more, and more preferably, a polyethylene terephthalate layer consists of polyethylene terephthalate. Other components may be appropriately blended into each layer.

[0041] Traditionally, used are a packaging container composed of a multilayered film comprising PAN and AL (For example, see Japanese Patent No. 5093545) and a packaging container composed of a multilayered film comprising a polyethylene layer (hereinafter, the polyethylene layer is also referred to as "PE") and the like, but not comprising PAN as a storage container of a rivastigmine-containing adhesive patch. However, the present inventors find that an alteration of rivastigmine in an adhesive patch can be better controlled as compared with the conventionally used packaging containers when a packaging container composed of a multilayered film in which at least PAN, AL and PET are laminated.

[0042] There is no particular limitation for the packaging container according to the present invention as long as it comprises a multilayered film in which at least PAN, AL and PET are laminated.

[0043] PAN is preferably used for the innermost layer of a packaging container (i.e., a layer in a multilayered film of a packaging container which directly makes contact with an adhesive patch enclosed inside the packaging container) in view of that it can prevent rivastigmine from being adsorbed by the packaging container while further increasing an alteration controlling effect of rivastigmine. Further, PAN well functions as a sealant layer of a packaging container. AL, which has a function to block the penetration of light and oxygen into a package body, preferably does not make direct contact with an adhesive patch, i.e., preferably is not the innermost layer of a packaging container in view of preventing rivastigmine from being adsorbed by the packaging container. Further, AL is preferably not provided at the outermost layer of a packaging container since it is relatively easily damaged. Further, PET is preferably provided at the outermost layer of a packaging container since it can well function as a surface base material while further increasing an alteration controlling effect of rivastigmine. Therefore, the packaging container according to the present invention preferably comprises a multilayered film in which PAN, AL and PET are laminated in this order from the innermost layer. However, in a multilayered film in which PAN, AL and PET are laminated in this order, other layers may be provided between and/or outside each layer of PAN, AL and PET as long as the object of the present invention is not impaired. For example, the packaging container may comprise a multilayered film in which a known sealant layer/PAN/an anti-oxidant layer/AL/PET/a known surface base material are laminated in this order from the innermost layer.

[0044] Multiple PANs, ALs and PETs may be contained in the multilayered film for each. For example, the multilayered film may have a configuration such as PAN/AL/PAN(PET)/PET (PAN), PAN/PET/AL/PAN (PET) and the like in these orders from the innermost layer. Other layers may be provided between and/or outside each layer as long as the object

of the present invention is not impaired.

[0045] There is no particular limitation for the thicknesses of PAN, AL and PET of a multilayered film, but the thicknesses of PAN, AL and PET may be 10 to 50 μm (preferably 20 to 40 μm), 1 to 15 μm (preferably 5 to 9 μm) and 5 to 20 μm (preferably 10 to 13 μm), respectively. There is no particular limitation for the layer ratio of PAN, AL and PET, but PAN is preferably prepared to be thicker in view of an enhanced alteration controlling effect of rivastigmine. An example of the layer ratio of PAN, AL and PET is the thickness of PAN : the thickness of AL : the thickness of PET = 30:7:12. The layer ratio is 1:0.1-0.3:0.3-0.5 when the thickness of PAN is taken as 1. In a case where multiple PANs, ALs and PETs are contained in a multilayered film for each, the thickness of each layer of PANs, ALs and PETs can be adjusted so that the total value of the thickness of each layer falls within the aforementioned corresponding range. Note that the thickness of each layer of the multilayered film may be determined by the conventionally known method, and the average value of the values obtained may be adjusted within the aforementioned range.

[0046] Layers other than PAN, AL, and PET (for example, a polyethylene layer, a paper layer, a known oxygen-absorbing layer, a known moisture-absorbing layer and the like) may be contained in the multilayered film. The thicknesses of these layers may be appropriately adjusted depending on the desired effect.

[0047] There is no particular limitation for the method of manufacturing a multilayered film, and known laminating methods can be used such as the dry lamination method, the extrusion lamination method and the wet lamination method.

[0048] There is no particular limitation for the method of manufacturing a packaging container from a multilayered film, and known methods can be used such as a seal by heat sealing.

(Configuration of adhesive patch)

[0049] The adhesive patch according to the present invention comprises a support and an adhesive layer containing an adhesive and rivastigmine and disposed on the above support. The adhesive patch may be those in which a known skin adhesive layer (polyisobutylene and the like), controlled-release membrane and strippable liner (an oxygen impermeable liner and the like) are laminated to an adhesive layer.

[Rivastigmine]

[0050] As rivastigmine in the present invention, free rivastigmine which shows an acetylcholinesterase inhibitory action and/or pharmaceutically acceptable salts thereof can be used. Salts of rivastigmine include rivastigmine hydrochloride, rivastigmine tartrate and the like. Among these, free rivastigmine is preferred in view of good skin permeability.

[0051] There is no particular limitation for the content of rivastigmine in an adhesive layer, and it can be appropriately adjusted depending on the desired therapeutic effect. For example, rivastigmine may be contained in an adhesive layer in an amount of 0.1 mass% or more, preferably 1 mass% or more, more preferably 10 mass% or more. Further, rivastigmine may be contained in an adhesive layer in an amount of 40 mass% or less, preferably less than 30 mass%, more preferably 25 mass% or less, most preferably 20 mass% or less.

[Adhesive]

[0052] There is no particular limitation for the adhesive contained in an adhesive layer as long as it is commonly used for an adhesive patch applied to the skin, and it may be one or more of acrylic adhesives, rubber based adhesives or silicon based adhesives.

[0053] Among the above adhesives, acrylic adhesives are preferred in view of that transdermal absorption of rivastigmine is less reduced. Among acrylic adhesives, an acrylic adhesive substantially free from a carboxyl group (a carboxy group) in view of that it is less reactive with rivastigmine, and can control the decrease in transdermal absorption of rivastigmine, and is less affected by oxygen. The phrase "substantially free from a carboxyl group" refers to not only those not containing a carboxyl group at all but also those in which carboxyl groups are all theoretically replaced with substituents such as ester linkages. These include, for example, a case in which a trace amount of ester linkages and the like are converted into free carboxyl groups due to hydrolysis, and a case in which free carboxyl group is included as impurities from a raw material.

[0054] There is no particular limitation for the acrylic adhesive substantially free from a carboxyl group, and, for example, adhesives described in Japanese Unexamined Patent Application No. 2005-325101, Japanese Patent No. 3809462 and the like can be used. Among these, in particular, the acrylic adhesive described in Japanese Unexamined Patent Application No. 2005-325101 can be suitably used.

[0055] As the acrylic adhesive in the present invention, an acrylic adhesive substantially free from a carboxyl group is preferred in view of that it is less reactive with rivastigmine, and can better control the decrease in transdermal absorption of rivastigmine, and is less affected by oxygen. Further, an acrylic adhesive substantially free from a carboxyl group and a hydroxy group is particularly preferred.

[0056] Other components other than those described above may be contained in an adhesive patch, if desired. Such components include adhesiveness-conferring agents, plasticizing agents, antiseptic agents, pH adjusters, chelating agents, transdermal absorption promoting agents, excipients, flavoring agents, coloring agents, fatty acids, fats and oils and the like.

[0057] Inside the package body according to the present invention, the stability of rivastigmine in an adhesive patch is excellent even in a case where an anti-oxidant (agents commonly used for preventing oxidation of a drug in an adhesive patch such as dibutylhydroxytoluene, vitamin E, butylated hydroxyanisole and propyl gallate) is not blended. However, an anti-oxidant may be blended into an adhesive patch, if desired.

(Method of manufacturing adhesive patch)

[0058] There is no particular limitation for the method of preparing an adhesive patch, and known preparing methods can be used for preparing an adhesive patch. They include, for example, a method of obtaining an adhesive patch, comprising uniformly stirring components of an adhesive layer, coat-drying the resulting composition onto a surface of a support using a coater.

(Method of manufacturing package body)

[0059] The package body according to the present invention can be obtained by enclosing an adhesive patch into a packaging container, and sealing the packaging container. When enclosing, an adhesive patch may be placed into a packaging container which is then sealed after adjusting the amount of oxygen gas and the like inside the packaging container. Alternatively, an adhesive patch may be placed into a packaging container which is then sealed as it is. For sealing, known methods can be used such as heat sealing and sealing with adhesives.

[0060] In the case of the package body according to the present invention, an alteration of rivastigmine in an adhesive patch can be controlled without enclosing an anti-oxidant and an oxygen scavenger (agents commonly used for reducing the amount of oxygen inside a package body, such as iron powder, zinc powder, hydrosulfite, ascorbic acid-based agents, polyhydric alcohol-based agents and activated carbon-based agents) into the package body as a separate member distinct from the adhesive patch or a member integrated with the adhesive patch, or without performing inert gas substitution (nitrogen substitution and the like) before enclosing the package body. The package body according to the present invention may consist of a packaging container and an adhesive patch enclosed in the above packaging container. However, enclosing an anti-oxidant and/or an oxygen scavenger and performing inert gas substitution shall not be excluded from the scope of the present invention.

Stability of adhesive patch in package body

[0061] Unlike the conventional package bodies, in the package body according to the present invention, the stability of a drug in an adhesive patch is good without enclosing an anti-oxidant and an oxygen scavenger along with the adhesive patch or without performing inert gas substitution and the like. The stability of a drug in an adhesive patch can be determined by detecting an analog of the drug with HPLC. An analog of a drug is defined as a substance produced when the drug is altered and the like due to oxygen, which shows reduced or no efficacy of the original drug. Therefore, a lower amount of an analog detected indicates that the stability of the drug is high.

[0062] The stability of a drug in an adhesive patch can also be determined by the temporal change of color tone of the adhesive patch. The color tone of an adhesive patch may be determined with a color difference meter.

Stability of rivastigmine in adhesive patch

[0063] In the case of the package body according to the present invention, an alteration of rivastigmine in an adhesive patch can be controlled, and the drug stability is good without enclosing an anti-oxidant and an oxygen scavenger along with the adhesive patch or without performing inert gas substitution and the like. The term "alteration of rivastigmine" used in the present invention means that the amount of rivastigmine is decreased, or a degradation products, an analog of rivastigmine and the like are increased due to decomposition and the like of rivastigmine. Whether an alteration of rivastigmine in an adhesive patch is controlled or not can be determined by determining rivastigmine or an analog thereof and the like in the adhesive patch by HPLC and the like. An analog of rivastigmine is defined as a substance produced when rivastigmine is altered and the like due to oxygen or light which shows reduced or no drug efficacy of the original rivastigmine. Therefore, a lower amount of an analog detected in an adhesive patch indicates that the drug stability of rivastigmine is high.

EXAMPLES

[0064] Below, the present invention will be described in more detail with reference to Examples, but the present invention shall not be limited to these.

Example 1: Evaluation of stability of nicotine in nicotine-containing adhesive patch inside package body

[0065] An acrylic adhesive, nicotine and the like were blended according to a rate shown in "Table 1" to prepare a composition, which was then coat-dried (60°C, 15 minutes) onto a support (a PET film is used) to prepare a drug-containing adhesive layer. A controlled-release membrane and a skin adhesive layer comprising polyisobutylene were laminated on the drug-containing adhesive layer, and a strippable liner was further laminated on the skin adhesive layer to obtain an adhesive patch. Further, an anti-oxidant was blended into some of the formulations in a rate shown in "Table 1."

[0066] Note that the acrylic adhesive used in this Example is described in Japanese Unexamined Patent Application No. 2005-325101 (specifically, an adhesive obtained by mixing a solution obtained in Example 3 of preparing the copolymer (A) and a solution obtained in Example 3 of preparing the copolymer (B) in a mass ratio of 100:5 (the copolymer (A): the copolymer (B)).

[0067] Each adhesive patch obtained was individually placed into a bag in which polyacrylonitrile/aluminum/polyethylene terephthalate are laminated (which corresponds to the packaging container according to the present invention, and hereinafter, referred to as a "PAN/Al/PET bag"). One of the following treatments was performed when the adhesive patch was placed into a PAN/Al/PET bag. In the followings, the package body obtained via the treatment (2) corresponds to the package body according to the present invention.

(1) The adhesive patch is placed into a bag, and the bag is sealed as it is ("Normal" in Table 1).

(2) The adhesive patch is placed into a bag, and the bag is then sealed after the concentration of oxygen gas in the bag is adjusted to 20.6 vol%, and the amount of oxygen gas is adjusted to 7 μ L using a vacuum pump ("Vacuum" in Table 1).

[0068] The sealed adhesive patch was stored at 60°C (a humidity of 75%). The content of a nicotine analog in the adhesive patch was measured by HPLC (UV 254 nm) at each time of: upon the start of storage, 0.5 months after the start of storage, 1 month after the start of storage, 1.5 months after the start of storage, 2 months after the start of storage. The results are shown in Fig. 1. Note that Analog A in Fig. 1A corresponds to a peak detected at 1.95 minutes in HPLC. Further, Analog B in Fig. 1B corresponds to a peak detected at 20.16 minutes in HPLC. Note that nicotine is detected at 15.4 minutes in HPLC.

[Table 1]

No.	Composition of drug-containing adhesive layer (Mass%)				Treatment
	Nicotine	Acrylic adhesive	Lactic acid	Anti-oxidant (Dibutylhydroxytoluene)	
1	42 Mass%	56.8 Mass%	0.2 Mass%	1 Mass%	Normal
2					Vacuum
3					Normal
4					
5		57.8 Mass%	None	None	
6		58 Mass%		None	Vacuum

[0069] As shown in Fig. 1, the generation of analogs of nicotine was controlled in the adhesive patch inside the package bodies where the amount and concentration of oxygen gas were adjusted to the ranges according to the present invention (No. 2, 5 and 6). That is, it is revealed that an alteration of nicotine is controlled in the package body according to the present invention, leading to a good drug stability.

Example 2: Evaluation of color tone of nicotine-containing adhesive patch inside package body

[0070] An adhesive patch was obtained as in Example 1 except that a composition was prepared by blending components according to a rate shown in "Table 2."

[0071] Each adhesive patch obtained was individually placed into a PAN/Al/PET bag. One of the following treatments

was performed when the adhesive patch was placed into a PAN/Al/PET bag.

(1) The adhesive patch is placed into a bag and the bag is sealed as it is ("Normal" in Table 2).

(2) The adhesive patch is placed into a bag, and the bag is sealed after the concentration of oxygen gas in the bag is adjusted to 20.6 vol%, and the amount of oxygen gas is adjusted to 7 μL using a vacuum pump ("Vacuum" in Table 2).

[0072] The sealed adhesive patch was stored at 60°C (a humidity of 75%). The color tone of the adhesive patch was measured in accordance with the following method at each time of: upon the start of storage, 1 month after the start of storage, 2 months after the start of storage, 3 months after the start of storage. The results are shown in Fig. 2.

(Study of tone change of adhesive patch)

[0073] The chromaticity of the adhesive patch (this can be considered to be the same as the chromaticity of a drug-containing adhesive layer) was measured using a color difference meter, and the tone change of the adhesive patch was computed as follows.

[0074] The color tone of the adhesive patch was determined based on the "a-scale" for the degree of red-green, the "b-scale" for the degree of blue-yellow and the "L-scale" for the degree of white-black. Subsequently, the degrees of the tone change before and after the start of storage were expressed in the square root of sum of squares ΔE of the difference in each scale before and after the start of storage (represented by the following formula).

$$\Delta E = ((\Delta a)^2 + (\Delta b)^2 + (\Delta L)^2)^{1/2}$$

[Table 2]

No.	Composition of drug-containing adhesive layer (Mass%)				Treatment
	Nicotine	Acrylic adhesive	Lactic acid	Anti-oxidant (Dibutylhydroxytoluene)	
1	42 Mass%	57.3 Mass%	0.2 Mass%	0.5 Mass%	Normal
2		57.6 Mass%		0.2 Mass%	Normal
3		57.8 Mass%		None	Vacuum

[0075] As shown in Fig. 2, the change over time in the color tone was controlled in the package body where the amount and concentration of oxygen gas were adjusted to the ranges according to the present invention (No. 3). That is, it is revealed that the stability of an adhesive patch is high without using an anti-oxidant in the package body according to the present invention.

Example 3: evaluation of stability of rivastigmine in rivastigmine-containing adhesive patch inside package body

[0076] A composition was prepared by blending 84 parts by mass of an acrylic adhesive and 16 parts by mass of rivastigmine in this rate, and this was coat-dried (60°C, 15 minutes) onto a support (a PET film was used) to obtain an adhesive patch.

[0077] Note that the acrylic adhesive used in this Example is described in Japanese Unexamined Patent Application No. 2005-325101 (specifically, an adhesive obtained by mixing a solution obtained in Example 3 of preparing the copolymer (A) and a solution obtained in Example 3 of preparing the copolymer (B) in a mass ratio of 100:5 (the copolymer (A): the copolymer (B)).

[0078] Each adhesive patch obtained was individually placed into a PAN/Al/PET bag. One of the following treatments was performed when the adhesive patch was placed into a PAN/Al/PET bag.

(1) The adhesive patch is placed into a bag, and the bag is sealed as it is ("Normal" in Table 3).

(2) The adhesive patch is placed into a bag, and the bag is sealed after the concentration of oxygen gas in the bag is adjusted to 18.8 vol%, and the amount of oxygen gas is adjusted to 4 μL using a vacuum pump ("Vacuum" in Table 3).

[0079] The sealed adhesive patch was stored at 60°C (a humidity of 75%). The content of a rivastigmine analog in

the adhesive patch was measured by HPLC (UV 215 nm) at each time of: upon the start of storage, 1 month after the start of storage, 2 months after the start of storage, 3 months after the start of storage, 4 months after the start of storage. The results are shown in Fig. 3. Note that Analog C in Fig. 3A corresponds to a peak detected at 20.4 minutes in HPLC. Further, Analog D in Fig. 3B corresponds to a peak detected at 72.3 minutes in HPLC. Note that rivastigmine is detected at 10.2 minutes in HPLC.

[Table 3]

No.	Anti-oxidant	Treatment
1	None	Normal
2	None	Vacuum
3	None	Vacuum
4	None	Vacuum

[0080] As shown in Fig. 3, the generation of rivastigmine analogs in the adhesive patch was controlled in the package body where the amount and concentration of oxygen gas were adjusted to the ranges according to the present invention (No. 2 to 4). That is, it is revealed that an alteration of rivastigmine is controlled in the package body according to the present invention, leading to a good stability. Example 4: Study about the amount and concentration of oxygen gas inside package body - 1

[0081] The total gas content, the amount of oxygen gas and the concentration of oxygen gas inside a package body were measured for the package bodies No. 1 and No. 2 prepared in Example 1 and the conventional package bodies (in which a nicotine-containing adhesive patch is enclosed). The results are shown in Fig. 4.

[0082] Note that the total gas content inside the package body was determined as follows: an adhesive sheet was attached to the package body in order to prevent gas leakage; piercing each package body (at a place where the adhesive sheet was attached) with a micro syringe under water; then withdrawing air inside the package body by pulling the plunger; and reading a scale on the syringe to determine the total gas content inside the package body when the plunger stopped. The concentration of oxygen gas in the package body was measured with a needle type micro oxygen gas concentration meter (Product name "Microx TX3", Taitec Corporation) pierced into each package body. The amount of oxygen gas inside the package body was computed from the concentration of oxygen gas and the total gas content.

[0083] As shown in Fig. 4, the total gas content inside the package body decreases when a vacuum pump is used. However, the ratio of oxygen inside the package body is about 20 vol%, which is substantially the same as in a case where a vacuum pump is not used (that is, the ratio of oxygen in the normal atmospheric composition) (No. 1 and 2).

Example 5: Study about the amount and concentration of oxygen gas inside package body - 2

[0084] The total gas content, the amount of oxygen gas and the concentration of oxygen gas inside the package body were measured as in Example 4 for the package bodies according to the present invention and the conventional package bodies (those in which a nicotine-containing adhesive patch or a rivastigmine-containing adhesive patch was enclosed). The results are shown in Fig. 5. Note that the "conventional formulation 5-1" and "1" in Fig. 5 are similar to the package bodies of No. 1 and No. 2 prepared in Example 1, respectively. Further, the "conventional formulation 5-4" and "2" are similar to the package bodies of No. 1 and No. 2 prepared in Example 3, respectively. Moreover, an anti-oxidant was blended into the adhesive patches of the conventional formulations 5-2, 5-3, 5-5 and 5-6.

[0085] As shown in Fig. 5, the total gas content inside the package body decreases when a vacuum pump is used. However, the ratio of oxygen inside the package body is about 20 vol%, which is substantially the same as in a case where a vacuum pump is not used (that is, the ratio of oxygen in the normal atmospheric composition). Further, it appeared that the present invention has a lower amount of oxygen gas inside a package body than the conventional formulation, and an alteration of a drug in an adhesive patch due to oxygen can be more efficiently controlled without using an oxygen scavenger, an anti-oxidant or the like.

Example 6: Evaluation of stability of rivastigmine in rivastigmine-containing adhesive patch inside package body - 1

[0086] An acrylic adhesive and rivastigmine were blended according to a rate shown in Table 4 to prepare a composition, which was then coat-dried (60°C, 15 minutes) onto a support to prepare a rivastigmine-containing adhesive patch. Note that a PET film was used as the support.

[0087] Note that the acrylic adhesive used in this Example was prepared as follows. That is, a solution of the copolymer (A) and a solution of the copolymer (B) obtained by the synthesis method shown below were mixed at a mass ratio of

100:5 (the copolymer (A) : the copolymer (B)) to obtain an acrylic adhesive.

[Copolymer (A)]

[0088] Added and mixed were 200 parts by mass of acrylic acid 2-ethylhexyl, 100 parts by mass of butyl acrylate, 50 parts by mass of diacetone acrylamide and 300 parts by mass of ethyl acetate. This mixture was transferred into a separable flask equipped with a stirrer and a reflux condenser, and heated to 75°C with stirring and performing nitrogen substitution. A solution in which 2 parts by mass of benzoyl peroxide was dissolved in 20 parts by mass of ethyl acetate was aliquoted into 5 parts, and one of them was added to the separable flask to start polymerization. The remaining 4 aliquots were added by 1 aliquot at 1 hour intervals starting from 2 hours after the reaction started. The reaction was then allowed for additional 2 hours after the completion of the addition. Note that in order to adjust viscosity, ethyl acetate was added every 2 hours for 4 times each time in an amount of 50 parts by mass after the start of the reaction. This was cooled after the reaction completed, and ethyl acetate was then added to obtain the copolymer (A) with a solid content concentration of 30 mass%.

[Copolymer (B)]

[0089] Added and mixed are 660 parts by mass of ethyl acrylate, 70 parts by mass of diacetone acrylamide, 40 parts by mass of dodecylmercaptan as a molecular weight modifier and 400 parts by mass of ethyl acetate. This mixture was provided in a separable flask equipped with a stirrer and a reflux condenser, and heated to 70°C with stirring and performing nitrogen substitution. A solution in which 5 parts by mass of azobisisobutyronitrile was dissolved in 100 parts by mass of ethyl acetate was aliquoted into 5 parts, and one of them was added to the separable flask to start polymerization. The remaining 4 aliquots were added by 1 aliquot at 1 hour intervals starting from 2 hours after the reaction started. The reaction was then allowed for additional 2 hours after the completion of the addition. Note that ethyl acetate was added every 2 hours for 3 times each time in an amount of 50 parts by mass after the reaction started in order to adjust viscosity. Then, added was a solution in which 40 parts by mass of adipic acid dihydrazide was dissolved in a mixed liquid of 40 parts by mass of purified water, 1600 parts by mass of methanol and 260 parts by mass of ethyl acetate, and 5 parts by mass of concentrated hydrochloric acid was further added, and then heated to 70°C. This was cooled after the reaction completed, and washed 3 times with purified water. Then, the product was dissolved in a mixed solvent of 700 parts by mass of ethyl acetate, 1400 parts by mass of acetone and 400 parts by mass of methanol to obtain the copolymer (B) with a solid content concentration of 30 mass%.

[Table 4]

Composition of rivastigmine-containing adhesive patch (Mass%)		
Adhesive patch number	Acrylic adhesive	Rivastigmine
1~5	84	16
6	Exelon® patch (commercially available product)	

[0090] Each adhesive patch obtained was individually placed into a packaging container comprising a corresponding multilayered film having a configuration shown in Table 5, which was then directly sealed to obtain a package body. Note that the term "multilayered film configuration" shown in Table 5 refers to a lamination order of layers, and the layer shown in the left most side corresponds to the innermost layer of a packaging container (that is, a layer which makes contact with an adhesive patch enclosed inside a packaging container). For example, for the package body No. "1" in Table 5, a multilayered film was used in which the innermost layer was PAN, and AL and PET were then laminated in this order, and the outermost layer was PET.

[Table 5]

Package body number	Adhesive patch number	Multilayered film configuration
1	1	PAN(30μm)/AL(7μm)/PET(12μm)
2	2	PE(30μm)/AL(7μm)/PE(15μm)/PET(12μm)
3	3	PE/oxygen absorbing layer/AL/PET, Product name Oxyguard (Toyo Seikan Co., Ltd.)

(continued)

Package body number	Adhesive patch number	Multilayered film configuration
4	4	PE/moisture absorbing layer/AL/PET, Product name Moisture Guard (Toyo Seikan Co., Ltd.)
5	5	Moisture-absorbing sealant layer (25 μm)/AL (7 μm)/PE (15 μm)/PET (12 μm), moisture-absorbing packaging pouch from Dai Nippon Printing Co., Ltd.
6	6	Exelon® patch (commercially available product)

[0091] Each package body was stored at 60°C (a humidity of 75%). The content of rivastigmine in the adhesive patch was measured by HPLC at each time of: upon the start of storage (Initial), 2 weeks after the start of storage (2w), 1 month after the start of storage (1M), 2 months after the start of storage (2M). The results are shown in Table 6. Note that the measurement results in Table 6 show a relative value when Initial is taken as "100."

[Table 6]

Stability evaluation of rivastigmine				
Package body number	Initial	60°C		
		2w	1M	2M
1	100.00	96.14	97.41	100.27
2	100.00	94.92	93.86	93.39
3	100.00	93.95	92.66	86.71
4	100.00	95.20	91.54	91.42
5	100.00	97.11	95.56	95.52
6	100.00	98.60	97.10	94.30

[0092] As shown in Table 6, the package body according to the present invention (package body No. 1) showed less variation from the start of storage in the content of rivastigmine in the adhesive patch even after long storage, showing that an alteration of rivastigmine was controlled. In contrast, for the package bodies No. 2 to No. 5 which do not contain PAN, AL and PET in their multilayered film configurations, the content of rivastigmine in the adhesive patch was decreased, and an alteration of rivastigmine was observed after long storage. Example 7: Evaluation of stability of rivastigmine in rivastigmine-containing adhesive patch inside package body - II

[0093] Two rivastigmine-containing adhesive patches were prepared as in Example 6. Each adhesive patch obtained was individually placed into a packaging container comprising a corresponding multilayered film having a configuration shown in Table 7, which was then directly sealed to obtain a package body. Note that the term "multilayered film configuration" shown in Table 7 refers to, similar to Table 5, the lamination order of layers, and the layer shown in the left most side corresponds to the innermost layer of a packaging container.

[Table 7]

Package body number	Adhesive patch number	Multilayered film configuration
1	1	PAN(30 μm)/AL(7 μm)/PET(12 μm)
2	2	PE(30 μm)/AL(7 μm)/PE(15 μm)/PET(12 μm)

[0094] Each package body was stored at 60°C or 40°C (a humidity of 75%). The content of rivastigmine analogs in the adhesive patch was measured by HPLC (UV 254 nm) at each time of: upon the start of storage (Initial), 2 weeks after the start of storage, 1 month after the start of storage, 2 months after the start of storage or 3 months after the start of storage. The results are shown in Tables 8 to 10. Note that a lower amount of the detected rivastigmine analogs indicates that drug stability of rivastigmine in the adhesive patch is high. Note that rivastigmine is detected at a retention time of 10.2 minutes by HPLC (UV 254 nm).

[Table 8]

Analog 1 (Retention time RT: 5.5 minutes)						
Adhesive patch number	Initial	60°C			40°C	
		2 w	1 M	2M	1 M	3M
1	0.02	0.05	0.06	0.09	0.03	0.07
2	0.02	0.05	0.08	0.13	0.03	0.07

[Table 9]

Analog 2 (Retention time RT: 20.4 minutes)						
Adhesive patch number	Initial	60°C			40°C	
		2 w	1 M	2 M	1 M	3 M
1	0.07	0.14	0.24	0.58	0.11	0.16
2	0.07	0.21	0.41	1.13	0.11	0.20

[Table 10]

Analog 3 (Retention time RT: 72.3 minutes)						
Adhesive patch number	Initial	60°C			40°C	
		2 w	1 M	2 M	1 M	3 M
1	0.07	0.14	0.27	0.70	0.13	0.21
2	0.07	1.20	2.01	3.76	0.74	1.58

[0095] As shown in Tables 8 to 10, for the package body according to the present invention (package body No. 1), the generation of rivastigmine analogs in the adhesive patch was controlled, and an alteration of rivastigmine was controlled after long storage. In contrast, for the package body No. 2 which does not contain PAN, AL and PET in the multilayered film configuration, the amount of generated analogs of rivastigmine in the adhesive patch was increased, and an alteration of rivastigmine was observed after long storage. Such alteration was significantly observed in particular when stored at high temperature (60°C).

Claims

1. A package body comprising a packaging container and a drug-containing adhesive patch enclosed inside the packaging container,
wherein the amount of oxygen gas inside the package body is 20 μL or less, and the concentration of oxygen gas is 17.0 to 25.0 vol%.
2. The package body according to claim 1, wherein the package body does not contain an oxygen scavenger as a separate member distinct from the drug-containing adhesive patch.
3. The package body according to claim 1 or 2, wherein the amount of oxygen gas is 4 $\mu\text{L}/\text{mg}$ or less per amount of a drug in the drug-containing adhesive patch.
4. The package body according to any one of claims 1 to 3, wherein the drug is any of nicotine, rivastigmine or pharmacologically acceptable salts thereof.
5. The package body according to any one of claims 1 to 4, wherein the drug-containing adhesive patch comprises a support and an adhesive layer disposed on the support, the adhesive layer comprising an acrylic adhesive substan-

tially free from a carboxyl group.

- 5 6. A package body comprising a packaging container and an adhesive patch enclosed inside the packaging container, wherein the adhesive patch comprises a support and an adhesive layer containing a drug and disposed on the support, the drug comprises at least rivastigmine and/or a pharmaceutically acceptable salt thereof, the packaging container comprises a multilayered film in which at least a polyacrylonitrile layer, an aluminum layer and a polyethylene terephthalate layer are laminated.
- 10 7. The package body according to claim 6, wherein the innermost layer of the packaging container is a polyacrylonitrile layer.
8. The package body according to claim 7, wherein the multilayered film is a multilayered film in which a polyacrylonitrile layer, an aluminum layer and a polyethylene terephthalate layer are laminated in this order.
- 15 9. The package body according to any one of claims 6 to 8, wherein the polyacrylonitrile layer has a thickness of 10 to 50 μm , and the aluminum layer has a thickness of 1 to 15 μm , and the polyethylene terephthalate layer has a thickness of 5 to 20 μm .
- 20 10. The package body according to any one of claims 6 to 9, wherein the package body does not contain any one or more of an oxygen scavenger and an anti-oxidant.
11. The package body according to any one of claims 6 to 10, wherein the adhesive layer comprises an acrylic adhesive.

FIG. 1A

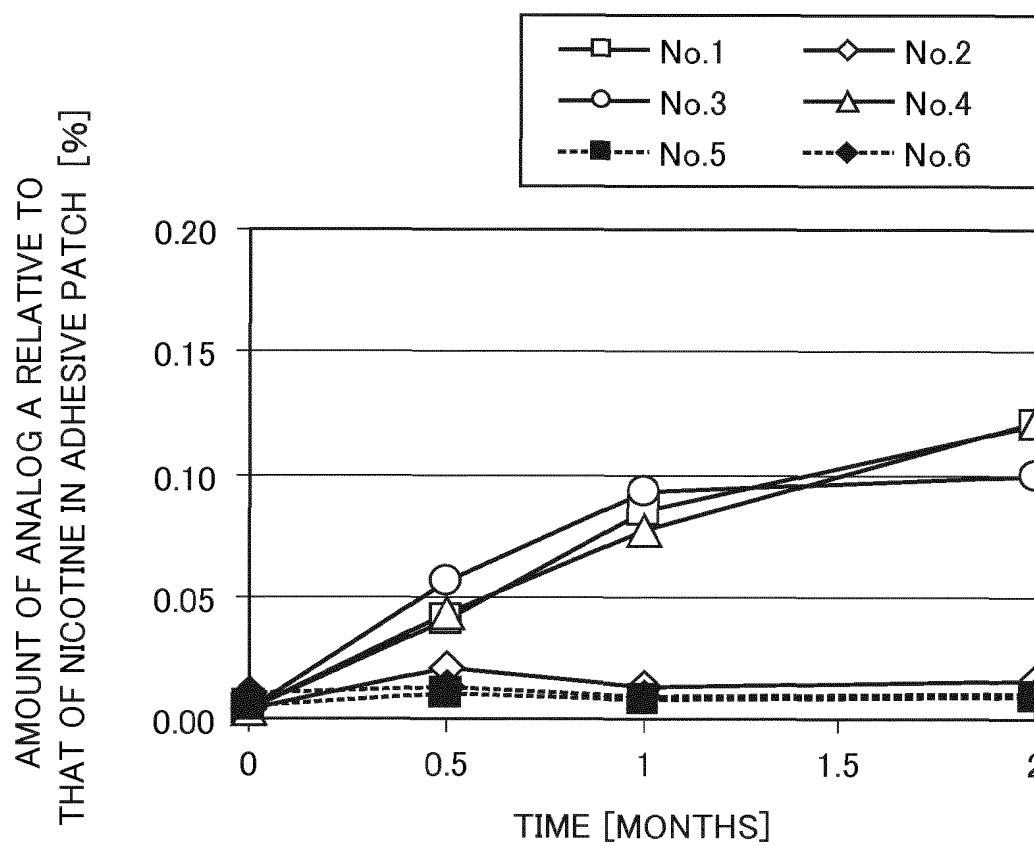


FIG. 1B

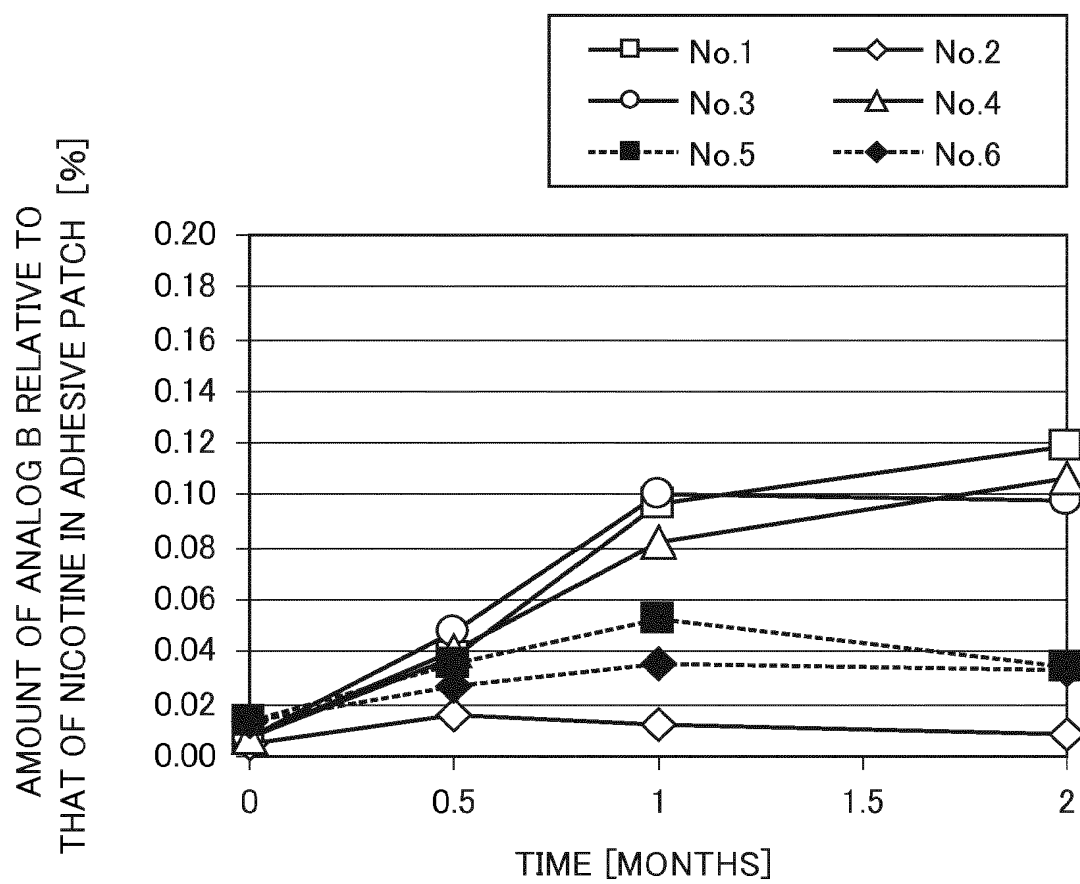


FIG. 2

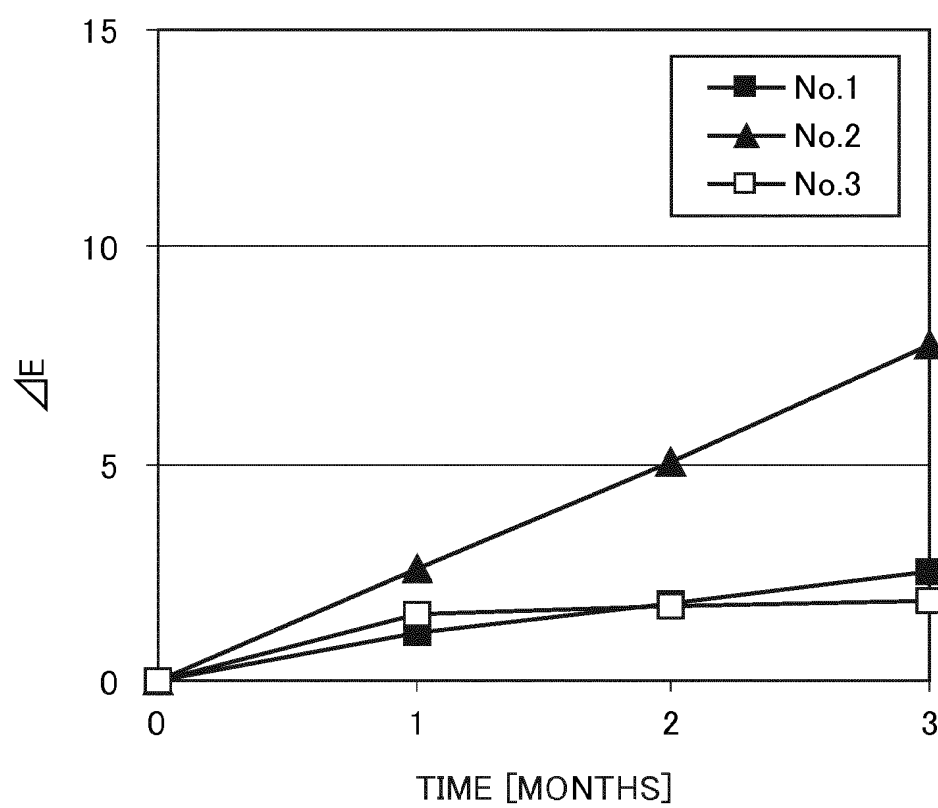


FIG. 3A

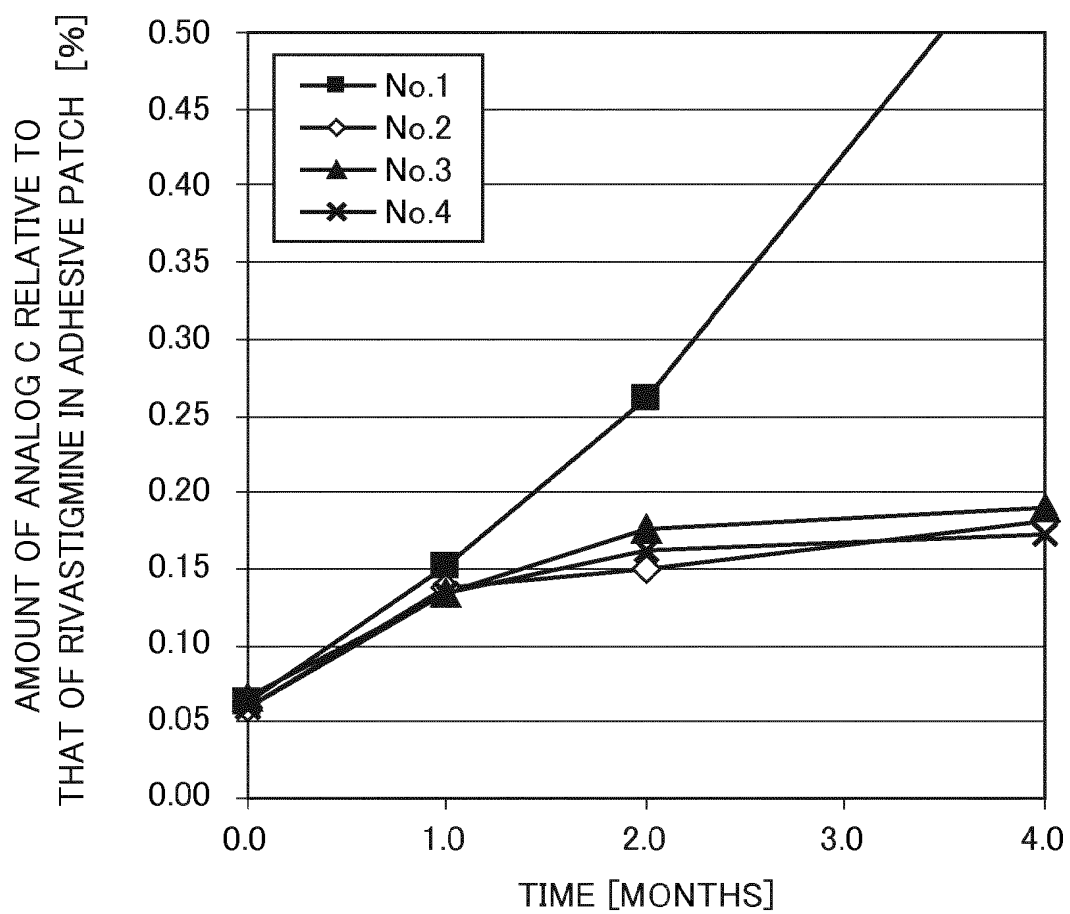


FIG. 3B

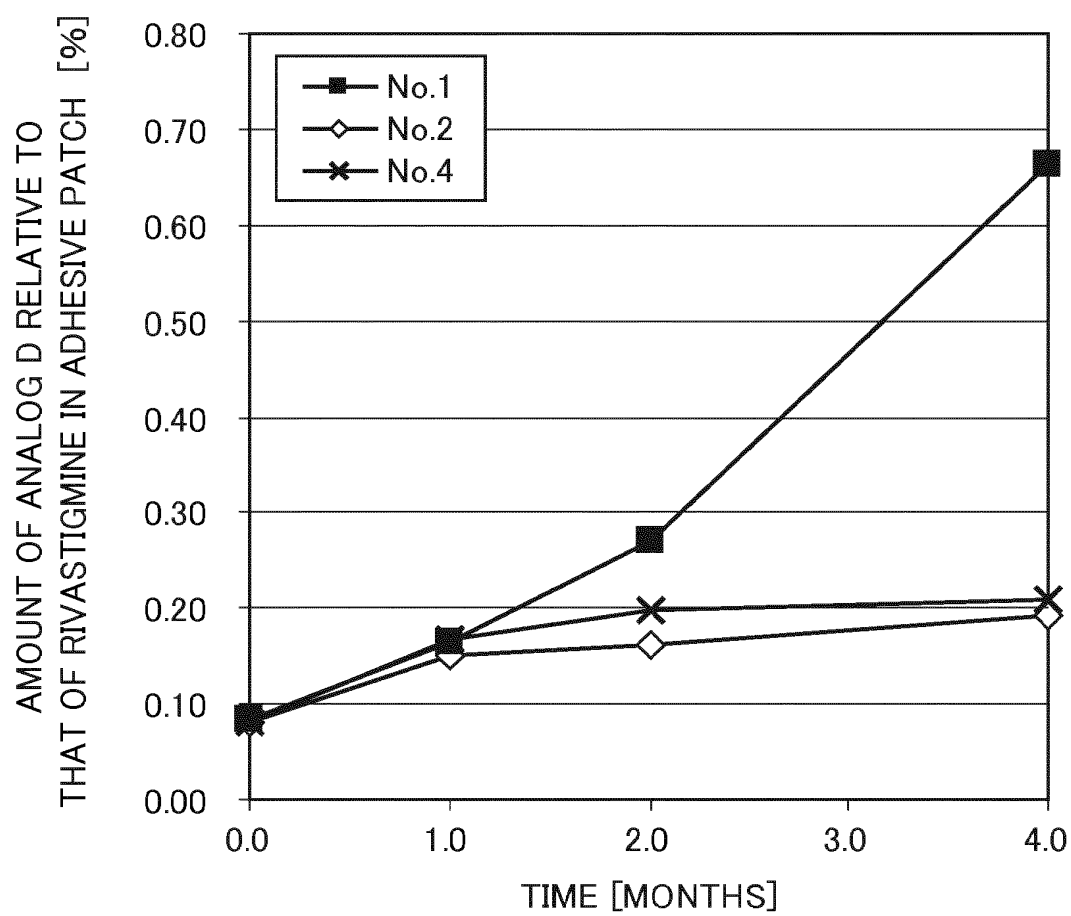


FIG. 4

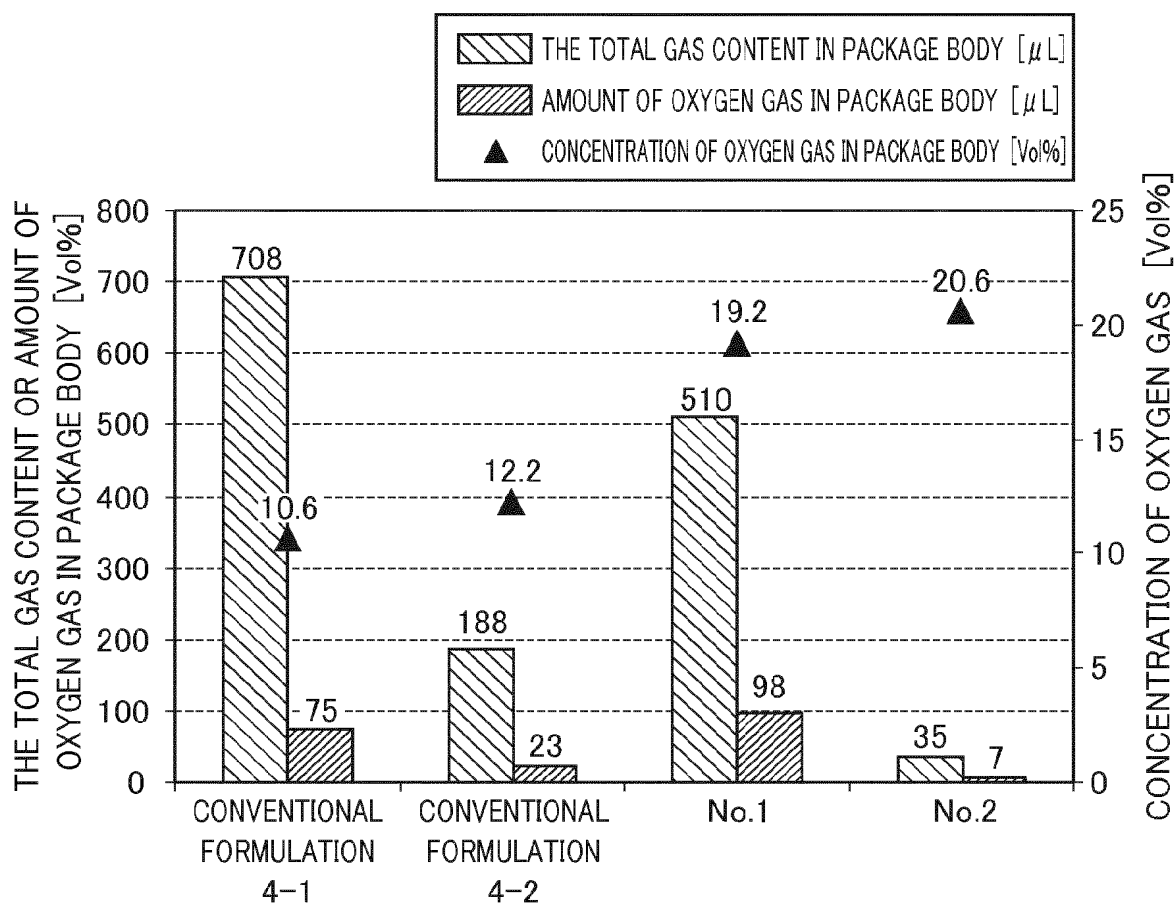
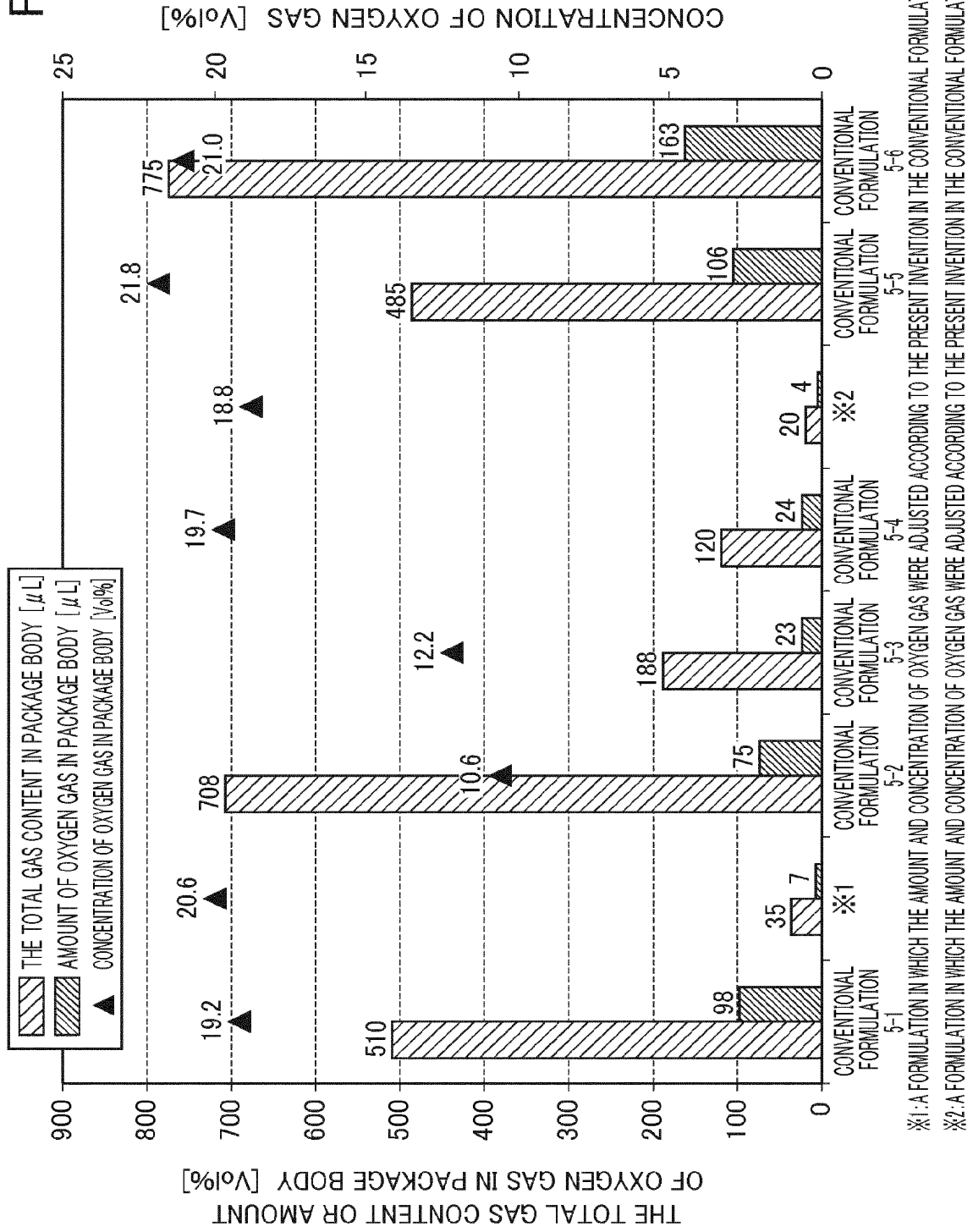


FIG. 5



INTERNATIONAL SEARCH REPORT

International application No.

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5	A. CLASSIFICATION OF SUBJECT MATTER A61K9/70(2006.01)i, A61J1/00(2006.01)i, A61K31/27(2006.01)i, A61K31/465 (2006.01)i, A61K47/32(2006.01)i, A61M37/00(2006.01)i, A61P25/28(2006.01)i, A61P25/34(2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC		
10	B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) A61K9/70, A61J1/00, A61K31/27, A61K31/465, A61K47/32, A61M37/00, A61P25/28, A61P25/34 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)		
20	C. DOCUMENTS CONSIDERED TO BE RELEVANT		
	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
25	Y	JP 2012-51875 A (Hisamitsu Pharmaceutical Co., Inc.), 15 March 2012 (15.03.2012), claims 1 to 2; paragraphs [0001], [0006] to [0009], [0031] to [0046] & US 2012/0031047 A1	1-11
30	Y	JP 2009-39210 A (Hosokawa Yoko Co., Ltd.), 26 February 2009 (26.02.2009), claim 1; paragraphs [0001], [0004] to [0007], [0013] to [0041] (Family: none)	1-5
35	Y	JP 2006-346888 A (Kyodo Printing Co., Ltd.), 28 December 2006 (28.12.2006), paragraphs [0001], [0009] to [0034]; fig. 4 (Family: none)	6-11
40	☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
45	* 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		
50	Date of the actual completion of the international search 17 January, 2014 (17.01.14)		Date of mailing of the international search report 28 January, 2014 (28.01.14)
55	Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
	Facsimile No.		Telephone No.

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2012051875 A [0005] [0020]
- JP 5093545 B [0005] [0041]
- JP 2005325101 A [0034] [0054] [0066] [0077]
- JP 3809462 B [0034] [0054]

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(54) **MULTILAYER ASSEMBLY**

MEHRLAGIGE ANORDNUNG

ENSEMBLE MULTICOUCHE

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Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to a multilayer assembly, suitable for packaging, comprising an antioxidant substance, to a container comprising said assembly, to its use and a method for its production.

BACKGROUND OF THE INVENTION

10 **[0002]** Packaging and storage of air-sensitive materials require special measures to avoid oxidation-related degradation and loss of the initial properties. In particular, upon exposure to oxygen, foodstuffs containing unsaturated fatty acids tend to grow rancid over time and valuable nutriment such as coffee and spices may lose their aromas and flavours on storage.

15 **[0003]** Thus, in addition to being an efficient barrier against light and moisture, the packaging materials must also be able to avoid the intake of external oxygen. However, the packaging materials known in the art are not effectively protective against the residual air, which may become trapped within the package at the moment of sealing.

[0004] Removal of the residual air is advantageous to avoid oxidation of the package content over prolonged time.

[0005] Mainly, removal of atmospheric oxygen from the container prior to sealing is effected either by application of vacuum or by flushing the package and its content with an inert gas, such as nitrogen or carbon dioxide.

20 **[0006]** Each of these two methods has the disadvantage that fragrances, aromas and other volatile compounds are removed from the goods in the container, to the detriment of their organoleptic properties. Moreover, application of vacuum or flushing with an inert gas require additional steps and equipment, with an overall increase in cost and duration of the packaging process. In addition, neither of these methods is capable of removing completely the residual oxygen, which may be trapped within fissures and pores of the contained materials.

25 **[0007]** Packaging materials have been developed as alternative solutions to the above described methods. A packaging material is known from document JP 2002292803 A. This document describes a multilayer assembly comprising a paper layer containing an oxygen absorbent adhesive layer, and polymer layers having barrier properties. The polymer layers are provided on both sides of the adhesive layer containing the oxygen absorbent, wherein catechin is used as the oxygen absorbent. Another packaging material is known from document JP 2003192847 A. This document describes
30 an oxygen-capturing packaging material comprising blending an ethylene-vinyl alcohol copolymer or polyethylene terephthalate barrier resin as a carrier with an oxygen-capturing agent to form an oxygen-capturing dispersion resin, dispersing the formed oxygen-capturing dispersion resin in a polyolefin or polyamide matrix resin to form an oxygen-capturing composite material. Catechin is used as the oxygen-capturing agent.

35 **[0008]** Document JP 2003170526 A describes a packaging material formed of a laminate constituted of a packaging film made of a thermoplastic resin with an electrical insulating tin vapor-deposited layer formed on the surface, a paper layer and a thermoplastic resin layer formed on both sides of the paper layer. The oxygen-barrier resin comprises ethylene/vinyl alcohol copolymer or polyamide as the thermoplastic resin for the packaging film, or an oxygen-barrier resin layer as the laminate. Moreover, document JP 2007246120 A describes a laminated material comprising a thermoplastic resin layer, a paper layer, a gas barrier layer, an adhesive resin layer containing an oxygen absorber, and a
40 thermoplastic resin layer.

SUMMARY OF THE INVENTION

45 **[0009]** The object of the present invention is to provide a packaging material, which can reduce significantly or eliminate degradation of stored materials due to air trapped within the container.

[0010] Another object of the present invention is to provide a safe, simple and cost-effective method to improve shelf-life of stored materials, such as foodstuff, medicines and other perishable substances, while maintaining their organoleptic properties and their content of volatile compounds.

50 **[0011]** To solve these problems, the present invention provides a multilayer assembly comprising at least:

- a) a layer of paper or of a polymeric material selected from polypropylene, polyester, polyamide, polyethylene and their mixtures and copolymers;
- b) at least one adhesive layer; and
- c) a metallic and/or polymeric layer,

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wherein the adhesive layer b) binds layer a) to layer c) and comprises a mixture of at least a catechin and a polymeric adhesive composition, and the polymeric adhesive composition of layer b) comprises a polyurethane adhesive composition,

wherein the mixture of at least a catechin and a polymeric adhesive composition has antiradical/antioxidant properties.

[0012] To solve the problems described above, the present invention also provides a container comprising a plurality of walls defining a inner space, wherein the multilayer assembly as described above forms, at least partially, at least one of said walls, and the layer a), comprising a polymeric material, is facing towards the inner space of the container.

[0013] Another aspect of the invention pertains to a process for the production of the multilayer assembly as described above, said method comprising the steps of laminating the layer a) of paper or polymeric material and at least another layer c), wherein a) is made to adhere to layer c) by means of the adhesive b).

[0014] In another aspect, the present invention comprises the use of the multilayer assembly as described above for packaging of oxidation-sensitive goods.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

Fig. 1 is a graph depicting viscosity (mPas) vs. time (hours) of a NCO-terminated polyurethane adhesive comprising, as an additive, 0% (standard), 0.7% w/w (test A), 1.5% w/w (test B), 3.0% w/w (test C) or 6.0% w/w (Test D) of antioxidant green tea extract as measured according to the Viscosity Brookfield method (ASTM- D2196-10).

Fig. 2 is a graph depicting NCO content (% on wet adhesive according to the %NCO evaluation of ASTM-D2572-97) vs. time (hours) of a NCO-terminated polyurethane adhesive comprising, as an additive, 0% (standard), 0.7% w/w (test A), 1.5% w/w (test B), 3.0% w/w (test C) or 6.0% w/w (Test D) of antioxidant green tea extract.

Fig. 3 is a graph depicting the bond strength of Aluminium-Polyethylene (N/15 mm)-speed 50 mm/min vs. time (hours) according to ASTM-F904-98 of a NCO-terminated polyurethane adhesive comprising, as an additive, 0% (standard), 0.7% w/w (test A), 1.5% w/w (test B), 3.0% w/w (test C) or 6.0% w/w (Test D) of antioxidant green tea extract.

Fig. 4 is a graph depicting viscosity (mPas) vs. time (hours) of an OH-terminated polyurethane adhesive comprising, as an additive, 0% (standard), 3.0% w/w (test E) or 6.0% w/w (Test F) of antioxidant green tea extract as measured according to the Viscosity Brookfield method (ASTM- D2196-10).

Fig. 5 is a graph depicting NCO content (% on wet adhesive according to the %NCO evaluation of ASTM-D2572-97) vs. time (hours) of an OH-terminated polyurethane adhesive comprising, as an additive, 0% (standard), 3.0% w/w (test E) or 6.0% w/w (Test F) of antioxidant green tea extract.

Fig. 6 is a graph depicting the bond strength of Aluminium-Polyethylene (N/15 mm)-speed 50 mm/min vs. time (hours) according to ASTM-F904-98 of a OH-terminated polyurethane adhesive comprising, as an additive, 0% (standard), 3.0% w/w (test E) or 6.0% w/w (Test F) of antioxidant green tea extract.

Fig. 7 is a schematic representation of the multilayer of the invention, showing the catechin-comprising layer b) adjoining layer a) (facing towards oxygen-sensitive materials) and layer c).

Figure 8a displays the results of the analyses of hexanal in the cereal samples of Example 3.

Figure 8b displays the results of the analyses of hexanal in the cereal samples of Example 3.

DETAILED DESCRIPTION OF THE INVENTION

[0016] As used in the present invention, the term "comprises" may refer to a substance, which can be present in a mixture in any percentage, i.e. up to and including 100%. As used herein, unless otherwise specified, all percentages of a component in a mixture are referred to weight of the component with respect to the total weight of the mixture (w/w).

[0017] "Multilayer assembly" as used herein means a material comprising a plurality of layers (e.g. sheets or films), made of the same or of different materials, adjoined (i.e. irreversibly bound) on their largest surface portions (Fig. 7). The multilayer of the invention may comprise other layers, made of the same or of different materials, in addition to layers a) and c) bound by adhesive layer b). The additional layers may be bound by the same mixture of layer b) or by other means.

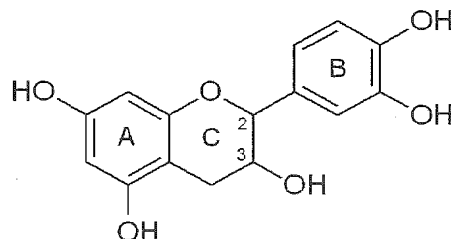
[0018] In one embodiment, the present invention relates to a multilayer assembly comprising at least:

- a) one layer of paper or of a polymeric material selected from polypropylene, polyester, polyamide, polyethylene and their mixtures and copolymers;
- b) at least one adhesive layer; and
- c) a metallic and/or polymeric layer,

wherein the adhesive layer b) binds layer a) to layer c) and comprises a mixture of at least a catechin and a polymeric adhesive composition, and the polymeric adhesive composition of layer b) comprises a polyurethane adhesive composition,

wherein the mixture of at least a catechin and a polymeric adhesive composition has antiradical/antioxidant properties.

[0019] As used in relation to the present invention, "catechin" relates to any member of the catechins family, including isomers and stereoisomers, hydroxylated derivatives, including gallo catechins, salts, naturally occurring glycosides, esters, including gallates, conjugates, including cyclodextrin complexes, and mixtures thereof. Catechins are naturally occurring phenols belonging to the group of flavan-3-ols (also referred to as flavanols), which are part of the flavonoids family.



[0020] Catechins (general formula $C_{15}H_{14}O_6$) possess two benzene rings (called the A- and B- ring) and a dihydropyran heterocycle (the C-ring) with a hydroxyl group on carbon 3. The A ring is similar to a resorcinol moiety, while the B ring is similar to a catechol moiety. There are two chiral centers on the molecule on carbons 2 and 3. Therefore, catechin has four diastereoisomers. The two isomers in trans configuration are called catechin and the other two in cis configuration are called epicatechin.

[0021] The most common catechin isomer is the (+)-catechin. The other stereoisomer is (-)-catechin or ent-catechin. The most common epicatechin isomer is (-)-epicatechin (also known under the names L-epicatechin, epicatechol, (-)-epicatechol, 1-acacatechin, 1-epicatechol, epi-catechin, 2,3-cis-epicatechin or (2R,3R)-(-)-epicatechin).

[0022] Common derivatives and conjugates are (-)-Gallocatechin (GC), (-)-Epigallocatechin (EGC), (-)-Epigallocatechin gallate (EGCG), (-)-Gallocatechin gallate (GCG), (-)-Epicatechin gallate (ECG) and (-)-Catechin gallate (CG).

[0023] Catechins, particularly (+)-catechin and (-)-epicatechin, are found in land plants such as açai palm (*Euterpe oleracea*), peach (*Prunus persica*), argan (*Argania spinosa* L.), cocoa and *Camellia sinensis* (tea).

[0024] Tea extracts are a particularly convenient source of naturally occurring catechins.

[0025] It was surprisingly found that the presence of an antioxidant substance, such as a catechin, effectively reduces the degradation caused by residual air of the materials inside the container, even if catechin is only comprised in an inner layer of the package. In other words, it was found that incorporation of catechins in a layer, which is not in direct contact with the inner portion of the container, surprisingly reduces or eliminates the oxidative degradation of the content of the package. Thus, in the assembly of the invention, the inner layer may consist of a material commonly used in foodstuff or drug packaging, such as polypropylene, polyester, polyamide, polyethylene and their mixtures and copolymers.

The multilayer assembly according to the invention can be flexible, semi-flexible or rigid. Preferably, the multilayer assembly according to the invention is flexible.

For the purpose of example only, and not by way of limitation, the multilayer assembly according to the invention may comprise HDPE, LLDPE, MDPE, LDPE, co-polymer polypropylene with polybutene, EVA, coextruded polymeric materials with nylon, EVOH, etc. Preferably, in the multilayer assembly according to the present invention, the polymeric material of layer a) comprises polyethylene. Preferably, in the multilayer assembly according to the present invention, layer a) has a thickness of 20 to 400 micron, more preferably from 30 to 100 micron. Even more preferably, said layer a) has a thickness from 35 to 85 micron, or of 50 micron.

[0026] It was surprisingly found that catechins are practically not released from the inner (adhesive) layer of the multilayer material of the invention, so that no contamination of the contents of the package with catechins was observed. This is particularly advantageous, because the use of the multilayer assembly according to the present invention minimizes the risk of cross-contamination of sensitive goods. In addition, the use of well-known and widely accepted materials for the layer in direct contact with the package content reduces the need for additional compatibility and stability tests.

[0027] Polyurethane adhesives are commonly used in multilayer packaging materials. However, no antioxidant-containing polyurethane adhesive is known. This is probably linked to the fact that incorporating an active antioxidant substance into a polyurethane may lead to changes in the adhesive and mechanical properties of the adhesive, and the antioxidant itself may be inactivated. It was also found that the catechins in the multilayer assembly of the invention exert their antiradical/antioxidant properties without changing the chemical and mechanical properties of the adhesive. Inventors have surprisingly found that the curing time and the final bond strength of the catechins-containing adhesive are not changed, which eventually results in overall maintenance of the original adhesive performance (Figures 1-6) without delamination of the multilayer product.

It is particularly advantageous that the catechin-containing polyurethanes maintain the chemical and mechanical properties of the commonly used polyurethane adhesives. By virtue of this feature, the assembly of the invention can be manufactured using the machinery and techniques normally used for the preparation of standard multilayer assemblies.

[0028] Several sources of catechins can be used for the preparation of the adhesive composition of layer b) according to the invention. Non-limitative examples of said sources are purified catechins, mixtures of naturally-occurring or synthetic catechins, plant extracts, such as green tea and black tea extracts, standardized or raw, and mixtures thereof.

The polymeric adhesive layer b) of the multilayer composition according to the invention can comprise a polyurethane adhesive, a mono-, bi- or multiple component adhesive, an adhesive comprising blocked isocyanates (i.e. capped isocyanate groups which can be uncapped at high cure temperatures) or a pressure sensitive adhesive (PSA). Non-limiting examples of PSA adhesives are acrylics, bio-based acrylate, butyl rubber, ethylene-vinyl acetate (EVA) with high vinyl acetate content, natural rubber, nitriles, silicone rubbers, requiring special tackifiers based on "MQ" silicate resins, composed of a monofunctional trimethyl silane ("M") reacted with quadrifunctional silicon tetrachloride ("Q"), styrene block copolymers (SBC), also called styrene copolymer adhesives and rubber-based adhesives, styrene-butadienestyrene (SBS), styrene-ethylene/butylene-styrene (SEBS), Styrene-ethylene/ propylene (SEP), styrene-isoprene-styrene (SIS), vinyl ethers or mixtures thereof. Preferably, the polymeric adhesive layer b) of the multilayer composition according to the invention comprises a polyurethane composition.

For purposes of illustration, but not by way of limitation, the isocyanate component of the polyurethane adhesive composition may be aromatic, aliphatic or cycloaliphatic and may have an average functionality equal to or more than 2.

For purposes of illustration but not by way of limitation, said isocyanate may comprise at least one of toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI), phenylene diisocyanate, xylylene diisocyanate, diphenylmethane diisocyanate, polyphenylmethane polyisocyanate (Polymeric MDI), naphthalene diisocyanate, triphenylmethane triisocyanate, diphenyl sulfone diisocyanate, cyclohexane diisocyanates, ethylene diisocyanate, propylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate (IPDI), dimers and trimers of these diisocyanates or mixtures thereof.

For purposes of illustration but not by way of limitation, in certain embodiments, the isocyanate may comprise at least one of toluene 2,4-diisocyanate, toluene 2,6-diisocyanate, naphthylene 1,5-diisocyanate, 4,4'-methylene diphenyl diisocyanate, 2,4'-methylene diphenyl diisocyanate, 1-methyl-2,4-diisocyanatocyclohexane, 1-methyl-2,6-diisocyanatocyclohexane, 4,4'-dicyclohexyl-methane diisocyanate, urethodione diisocyanate, isocyanurate trisocyanate, hexamethylene-1,6-diisocyanate, tetramethylene-1,4-diisocyanate, cyclohexane-1,4-diisocyanate, hexahydrotolylene diisocyanate (and isomers), 1-methoxyphenyl-2,4-diisocyanate, diphenyl methane-4,4'-diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl diisocyanate, 3,3'-dimethyl-4,4'-biphenyldiisocyanate; 3,3'-dimethyl diphenylmethane-4,4'-diisocyanate, 1-isocyanatomethyl-3-isocyanato-1,5,5-trimethyl diisocyanate, dimers or trimers of these isocyanates, or mixtures thereof.

For purposes of illustration but not by way of limitation, in some embodiments the isocyanate may comprise at least one of 1-isocyanatomethyl-3-isocyanato-1,5,5-trimethyl diisocyanate (isophorone diisocyanate, IPDI), toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI), or mixtures thereof.

The isocyanate or polyol component may comprise a prepolymer reaction product comprising the residues of a polyol, and a polymeric isocyanate or a polymeric isocyanate and an aromatic or aliphatic diisocyanate.

For the purpose of illustration only and not by way of limitation, the polyurethane adhesive may be a NCO-terminated polyurethane adhesive obtained via polymerization of a NCO-functionalized polyurethane pre-polymer based on MDI (MW = 15 kDalton) and a polyester polyol obtained from isophthalic acid and trimethylolpropane (MW = 13 kDalton).

For the purpose of illustration only and not by way of limitation, the polyurethane adhesive may be an OH-terminated polyurethane adhesive obtained via polymerization of a polyester based on isophthalic acid and adipic acid (2:1 ratio) and DEG (diethylene glycol) urethanized with IPDI (MW = 25 kDalton) with a HDI-based cross-linker (MW around 500 Dalton).

In certain embodiments, the polyurethane adhesive composition additionally comprises a plasticizer.

The polyurethane adhesive for the purpose of the present invention may be solvent-free, solvent-based or water-based.

In certain embodiments, the polyurethane adhesive composition may additionally comprise at least one of any of a conventional, commercially available catalyst, inorganic filler, colorant, antioxidant, UV light absorber, adhesion promoter, calcium oxide, expandable microspheres including Expancel® products available from AkzoNobel, drying agents, or mixtures thereof. In certain embodiments, the polyurethane adhesive composition may additionally comprise at least one of any of conventional, commercially available organic fillers, chain extenders, UV stabilizers, light stabilizers, fungicides, mildewcides, biocides, fire retardants, surface additives, solvents, mineral oils, dispersing agents, defoaming agents, storage stabilizers, latent hardeners, cure retarders, antifoaming agents, solvents, or mixtures thereof.

[0029] The polyurethane adhesive compositions, comprising at least a catechin, in layer b) of the assembly of the invention can be prepared according to the standard method for preparation of urethane adhesives, commonly known to the person skilled in the art.

The catechin source may be added to one of the components of the polyurethane adhesive prior to the polymerization

reaction or after mixing the two components of the adhesive composition.

Preferably, the catechin source is added to one of the components of the polyurethane adhesive prior to the polymerization reaction. Thus, a mixture of catechins and of the isocyanate and/or of the polyol component can be produced and stored and conveniently used according to the production needs. Preferably, the adhesive layer b) according to the invention comprises from 0.1 to 15.0% w/w of at least a catechin, preferably from 0.5 to 10%, from 1 to 7%, or from 2 to 6.5% and more preferably from 3 to 5%.

[0030] Preferably, in the multilayer assembly according to the invention the adhesive layer b) comprises green tea extract (comprising at least 50% w/w of catechins). It was found that an adhesive composition with antiradical/antioxidant properties is advantageously and easily prepared by addition of green tea extract to the isocyanate and/or to the polyol component of the polyurethane adhesive before or during polymerization.

[0031] A green tea extract can be used for the composition of the present invention, which comprises at least 50% w/w of catechins, preferably at least 70%, more preferably at least 75% w/w of catechins. Non-limiting examples of catechins comprised in the green tea extract in the composition of the present invention are (-)-Gallocatechin (GC), (-)-Epigallocatechin (EGC), (-)-Catechin (C), (-)-Epigallocatechin gallate (EGCG), (-)-Epicatechin (EC), (-)-Gallocatechin gallate (GCG), (-)-Epicatechin gallate (ECG) and (-)-Catechin gallate (CG) and mixtures thereof.

[0032] Preferably, the green tea extract in the adhesive layer b) of the assembly of the invention comprises at least 40% w/w Epigallocatechin gallate (EGCG).

[0033] In addition, said green tea extract may comprise caffeine and gallic acid.

[0034] Preferably, the content of the green tea extract in the adhesive layer of the material of the invention is from 0.5 to 7%, more preferably from 0.7 to 6%, even more preferably from 3 to 5% in weight/overall weight of the adhesive layer.

[0035] Preferably, the adhesive layer comprises, or consists of, a polyurethane adhesive.

[0036] Preferably, in the multilayer assembly according to the invention, the polyurethane adhesive comprised in layer b) is selected from a solvent free, solvent-based or water-based polyurethane, wherein each type can be based on a polyol component selected from the group consisting of polyester polyol, polyether polyol, polyacrylate polyol and polycarbonate polyol, and a mixture thereof, and an isocyanate component selected from an aliphatic isocyanate, an alicyclic isocyanate or aromatic isocyanate. Preferably, in the multilayer assembly according to the invention, the polyurethane adhesive may be a NCO-terminated polyurethane adhesive obtained via polymerization of a NCO-functionalized polyurethane pre-polymer based on MDI (MW = 15 kDalton) and a polyester polyol obtained from isophthalic acid and trimethylolpropane (MW = 13 kDalton), a OH-terminated polyurethane adhesive obtained via polymerization of a polyester obtained from isophthalic/terephthalic acid and ethylenglycol (MW around 60 kDalton) with a IPDI-based crosslinker (MW around 600 Dalton), a OH-terminated polyurethane adhesive obtained via polymerization of a polyester based on isophthalic acid and adipic acid (2:1 ratio) and DEG (diethylene glycol) urethanized with IPDI (MW = 25 kDalton) with a HDI-based cross-linker (MW around 500 Dalton) or a NCO-terminated polyurethane adhesive obtained via polymerization of a NCO-functionalized polyurethane pre-polymer based on isophthalic/oxalic acid and DEG, urethanized with MDI and a PPG as crosslinker.

[0037] The multilayer assembly of the present invention, in addition to the layer a) and to the adhesive layer b), may comprise additional sheets consisting of, or comprising, the following materials (in any sequence): aluminium, polyethylene, aluminized polyethylene, rubber, paper, metalized polyester, polyamide, cellophane, polyvinyl alcohol, polyester, polypropylene, polystyrene, PLA, biopolymers, gas-barrier PET (Alox, Siox), metalized cellophane, co-extruded polymeric materials comprising polyethylene, polypropylene and/or PVC and co-extruded barrier films.

[0038] In an aspect, the present invention relates to a container comprising a plurality of walls defining an inner space, wherein the multilayer assembly as described above forms, at least partially, at least one of said walls, and the layer a), comprising a polymeric material, is facing towards the inner space of the container.

[0039] The container according to the invention may be a flexible, semi-flexible or rigid container, optionally in the form of a pouch, a bag, a single dose pod, a can, a bottle or a four-seal pack, all of which optionally provided with an pressure degassing valve and/or with an opening and reclosing device and/or with a label.

[0040] Said degassing valve may comprise a valve body and a filter, engaging the valve body and positioned in front of the contained product. The filter comprises a catechin-comprising composition, optionally in the form of a green tea extract, a solid or semisolid matrix, a thin layer or a porous bag. In said degassing valve, the filter may comprise the multilayer assembly as described above, i.e. comprising layer a) and the adhesive polyurethane layer b). Optionally, the degassing valve comprises a mobile valve element of the one-way type that is positioned on the valve body, which may allow the passage of gas from the inside of the container towards the external environment when a predefined internal pressure threshold is reached.

[0041] The container according to the invention may be used for storage of a wide variety of goods including fresh, processed or semi-processed foodstuff, in particular ground coffee, dried or fresh coffee beans or pods, tea or tea leaves, fruit juice, chocolate, tomato juice or sauces, rice, cereals, ready meals, fresh dough, yeast, pharmaceutical and nutraceutical products, cosmetics and air-sensitive products in general. Preferably, the container according to the present invention is suitable for packaging of foodstuff, cosmetics and/or pharmaceutical/nutraceutical products.

[0042] In another aspect, the present invention relates to a process for the production of the multilayer assembly as described above, said method comprising the steps of laminating the layer a) of paper or polymeric material and at least another layer c), wherein a) is made to adhere to layer c) by means of the adhesive b). Advantageously, the catechin-containing polyurethane adhesive of layer b) can be used in the lamination process similarly to the commercially available polyurethane adhesives, i.e. employing procedures and machinery that are known to the person skilled in the art. Thus, the process of the invention can be implemented on the commonly available plants with no need for modification of the packaging lines or for any experimentation, in addition to the basic routine activity.

[0043] In another aspect, the present invention relates to a use of the multilayer assembly as described above for packaging of oxidation-sensitive goods.

Preferably, said oxidation-sensitive goods are foodstuff, cosmetics and/or pharmaceutical/nutraceutical products.

More preferably, said oxidation-sensitive goods are ground coffee, dried or fresh coffee beans or pods, tea or tea leaves, fruit juice, chocolate, tomato juice or sauces, rice, cereals, ready meals, fresh dough, yeast.

[0044] Hereinafter, the present invention is described in more detail, and specifically with reference to the Examples, which, however, are not intended to limit the present invention.

EXAMPLES

[0045] In all examples, a green tea extract is added to polyurethane as a source of catechins. The Green Tea extract is obtained from a commercial source.

The specific content of catechins is > 75% w/w, in particular Epigallocatechin gallate (EGCG) > 40% w/w. The content of caffeine is < 10% w/w.

[0046] From a chromatographic analysis, the following catechins are identified: (-)-Gallocatechin (GC), (-)-Epigallocatechin (EGC), (-)-Catechin (C), (-)-Epigallocatechin gallate (EGCG), (-)-Epicatechin (EC), (-)-Gallocatechin gallate (GCG), (-)-Epicatechin gallate (ECG) and (-)-Catechin gallate (CG).

The NCO-terminated polyurethane adhesive is obtained via polymerization of a NCO-functionalized polyurethane pre-polymer based on MDI (MW = 15 kDalton) and a polyester polyol obtained from isophthalic acid and trimethylolpropane (MW = 13 kDalton) or via polymerization of a NCO-functionalized polyurethane pre-polymer based on isophthalic/oxalic acid and DEG, urethanized with MDI and a PPG as crosslinker.

The OH-terminated polyurethane adhesive is obtained via polymerization of a polyester based on isophthalic acid and adipic acid (2:1 ratio) and DEG (diethylene glycol) urethanized with IPDI (MW = 25 kDalton) with a HDI-based crosslinker (MW around 500 Dalton) or via polymerization of a polyester obtained from isophthalic/terephthalic acid and ethyleneglycol (MW around 60 kDalton) with a IPDI-based crosslinker (MW around 600 Dalton).

EXAMPLE 1: properties of the adhesive of the invention.

[0047] The chemical and mechanical properties of the adhesives are not substantially changed by the presence of the catechin additive. This means that the curing time and the final bond strength of the catechin-containing adhesive should not be changed so as to reduce its usual performance.

[0048] For these reasons, the curing time of the adhesive in ethyl acetate solution (40% dry content) and the bond strength obtained applying 3 g/m² of dry adhesive between the aluminum foil and the polyethylene layer are investigated. As a comparison, the same adhesive, but without the catechin additive, is also evaluated.

[0049] The curing time of the dry adhesive is analysed via IR spectroscopy, evaluating the signal at 2265 nm, typical of the NCO peak. The aim is to verify that the catechin additive does not change the curing time of the adhesive, prolonging the time necessary for the delivery of the laminated to the customer. For a converter, i.e. a manufacturer of packaging materials, it is important to send the material to its customer only when the adhesive is completely cured.

The curing time of the adhesive in ethyl acetate solution is evaluated through acid-base titration of the NCO percentage and through viscosity analyses with Brookfield viscometer. The aim is to verify that curing of the adhesive does not occur too rapidly. Normally, the time between the preparation of the adhesive and its use in a rotogravure process is from 1 hour to 6 hours. The analysis results hereafter highlight the suitability of the material of the invention for these processes.

Finally, the adhesion between aluminum foil and polyethylene is evaluated after 14 days from the lamination. This is one of the validation processes to understand if the product is in compliance with the standard reference.

The following adhesives are evaluated:

- Standard polyurethane adhesive NCO terminated (no added catechin)
- Standard polyurethane adhesive NCO terminated with 0.7% of green tea extract on dry content (TEST A)
- Standard polyurethane adhesive NCO terminated with 1.5% of green tea extract on dry content (TEST B)
- Standard polyurethane adhesive NCO terminated with 3.0% of green tea extract on dry content (TEST C)
- Standard polyurethane adhesive NCO terminated with 6.0% of green tea extract on dry content (TEST D)

- Standard polyurethane adhesive OH terminated (no added catechin)
- Standard polyurethane adhesive OH terminated with 3.0% of catechins on dry content (TEST E)
- Standard polyurethane adhesive OH terminated with 6.0% of catechins on dry content (TEST F)

[0050] The parameters are evaluated according to the following reference methods:

Viscosity Brookfield: ASTM-D2196-10

Adhesion evaluation: ASTM-F904-98

%NCO evaluation: ASTM-D2572-97

[0051] Fig. 1 is a graph depicting viscosity (mPas) vs. time (hours) of a NCO-terminated polyurethane adhesive comprising, as an additive, 0% (standard), 0.7% w/w (test A), 1.5% w/w (test B), 3.0% w/w (test C) or 6.0% w/w (Test D) of antioxidant green tea extract as measured according to the Viscosity Brookfield method (ASTM- D2196-10).

[0052] Fig. 2 is a graph depicting NCO content (% on wet adhesive according to the %NCO evaluation of ASTM-D2572-97) vs. time (hours) of a NCO-terminated polyurethane adhesive comprising, as an additive, 0% (standard), 0.7% w/w (test A), 1.5% w/w (test B), 3.0% w/w (test C) or 6.0% w/w (Test D) of antioxidant green tea extract

[0053] Fig. 3 is a graph depicting the bond strength of Aluminium-Polyethylene (N/15 mm)-speed 50 mm/min vs. time (hours) according to ASTM-F904-98 of a NCO-terminated polyurethane adhesive comprising, as an additive, 0% (standard), 0.7% w/w (test A), 1.5% w/w (test B), 3.0% w/w (test C) or 6.0% w/w (Test D) of antioxidant green tea extract

[0054] Fig. 4 is a graph depicting viscosity (mPas) vs. time (hours) of an OH-terminated polyurethane adhesive comprising, as an additive, 0% (standard), 3.0% w/w (test E) or 6.0% w/w (Test F) of antioxidant green tea extract as measured according to the Viscosity Brookfield method (ASTM- D2196-10).

[0055] Fig. 5 is a graph depicting the NCO content (% on wet adhesive according to the %NCO evaluation of ASTM-D2572-97) vs. time (hours) of an OH-terminated polyurethane adhesive comprising, as an additive, 0% (standard), 3.0% w/w (test E) or 6.0% w/w (Test F) of antioxidant green tea extract.

[0056] Fig. 6 is a graph depicting the bond strength of Aluminium-Polyethylene (N/15 mm)-speed 50 mm/min vs. time (hours) according to ASTM-F904-98 of a OH-terminated polyurethane adhesive comprising, as an additive, 0% (standard), 3.0% w/w (test E) or 6.0% w/w (Test F) of antioxidant green tea extract.

[0057] The graphs show no considerable differences due to the addition of the catechin-containing powder. In fact, the increase of the viscosity in the time is the same for all adhesives. Of course, the higher the amount of catechins the higher the viscosity at time 0, but this aspect does not represent a problem during the industrial process. The important feature is that the viscosity of the adhesive must not increase exceedingly in the first 6 hours after its preparation, so that the percentage of NCO must not decrease steeply in the same period.

Also the adhesion values are very similar if the standard adhesive is compared to all the catechin-containing adhesives.

[0058] Thus, the addition of catechins to the polyurethane adhesive does not change the physical and chemical properties of the latter.

EXAMPLE 2

ANTIOXIDANT BEHAVIOUR

[0059] The new adhesives containing green tea as antiradical/ antioxidant agent are used to prepare several laminates and the antioxidant performance is evaluated. Two different procedures are used to evaluate the antiradical/ antioxidant performance:

1. Dynamic mode, based on the procedure previously developed by Pezo, D; Salafranca, J; Nerín, C. "Determination of the antioxidant capacity of active food packagings by in situ gas-phase hydroxyl radical generation and high performance liquid chromatography-fluorescence detection", J. of Chromatography A 178, Issues 1-2, 18, 126-133, 2008.

2. Static method, based on the DPPH reaction (Blois, M. S. "Antioxidant determinations by the use of a stable free radical Nature", 1958, 181, 1199-1200), this method is the most widely used in the literature. It is based on the capacity of the 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) to react (through an acceptance of an electron) and to transform into a stable molecule. In the radical form, DPPH absorbs at 515 nm, but, upon reduction by an antioxidant or a radical species, said absorption does not occur.

[0060] Samples (3 and 5 replicates) are prepared in glass vials. Each plastic sample is placed inside a 20 ml glass vial, with 5 ml of a solution of DPPH in methanol and the vial is sealed. Absorbance (515 nm) is measured each hour with a spectrophotometer Unicam Helios (Cambridge, UK), using quartz cuvettes 100-QS (1 cm x 1 cm x 4.5 cm) from

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Suprasil (Spain).

The quantitative value of absorbance is measured in the spectrophotometer.

A calibration graph is built before for quantitative purposes.

[0061] In both dynamic mode and static method, the material containing the catechins in the adhesive shows very good performance as antioxidant. Tables 1, 2 and 3 show the results obtained, expressed as percentage of antioxidant capacity varying the test temperature and the thickness of the PE layer a) (expressed in micron).

Table 1.- ADHESIVE 1, 4, 5. Standard polyurethane adhesive NCO terminated.

Adh 1: blank (adhesive without green tea extract).

Adh 4: adhesive containing 3% green tea extract.

Adh 5: adhesive containing 6% green tea extract.

Table 1.1. 20°C - 35µm

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh 1	0	1
Adh 4	17	1
Adh 5	29	4

Table 1.2. 20°C - 85µm

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh 1	0	1
Adh 4	28	3
Adh 5	30	4

Table 1.3. 40°C - 35µm

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh 1	0	2
Adh 4	17	3
Adh 5	30	2

Table 1.4. 40°C - 85µm

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh 1	0	6
Adh 4	16	2
Adh 5	34	7

Table 2. ADHESIVE 8, 9, 10.

Standard polyurethane adhesive OH terminated.

Adh 8: blank (adhesive without green tea extract).

Adh 9: adhesive containing 3% green tea extract.

Adh 10: adhesive containing 6% green tea extract.

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Table 2.1. 20°C - 35μm

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh 8	0	5
Adh 9	33	2
Adh 10	43	2

Table 2.2. 20 °C - 85μm

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh 8	0	4
Adh 9	35	2
Adh 10	45	3

Table 2.3. 40 °C - 35μm

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh 8	0	6
Adh 9	33	6
Adh 10	53	8

Table 2.4. 40 °C - 85μm

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh 8	0	2
Adh 9	34	3
Adh 10	42	4

Table 3. ADHESIVE 11, 12, 13. Monocomponent polyurethane-based adhesive.

Adh 11: blank (adhesive without green tea extract).

Adh 12: adhesive containing 3% green tea extract according to the invention.

Adh 13: adhesive containing 6% green tea extract according to the invention.

Table 3.1. 20 °C - 35μm

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh 11	0	1
Adh 12	17	1
Adh 13	29	4

Table 3.2. 20 °C - 85μm

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh 11	0	1

(continued)

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh 12	28	3
Adh 13	30	4

Table 3.3. 40 °C - 35µm

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh 11	0	2
Adh 12	17	3
Adh 13	30	2

Table 3.4. 40 °C - 85µm

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh 11	0	6
Adh 12	16	2
Adh 13	34	7

[0062] As can be seen from the tables, the PU adhesives containing 6% of green tea has a high antioxidant capacity.

Table 3.5. 20°C - PE 35µm

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh A (adhesive without catechin)	0	2
Adh B (adhesive with catechin)	46	2

Table 3.6. 20 °C - PE 75µm

Adhesive	% Antioxidant capacity	%RSD (n=3)
Adh C (adhesive without catechin)	0	1
Adh D (adhesive with catechin)	43	1

[0063] Adh A and Adh C are blanks. Adh B and Adh D are adhesives containing green tea extract according to the invention.

All samples are analyzed in triplicate.

Both samples demonstrate good antioxidant behaviour.

EXAMPLE 3

[0064] The assembly according to the invention is tested with respect to extension of the shelf-life of "conguitos" and chocolate cereal produced by the firm LACASA (Spain).

Methodology

[0065] The evaluation of this material is based on the long-term monitoring of key components of the samples.

[0066] For "conguitos" (dark chocolate peanuts) a volatile compounds (i.e., hexanal) and another group of non-volatile compounds (i.e., fatty acid profile) are monitored.

[0067] For cereals samples (milk chocolate cereals) only the volatile compound hexanal is monitored.

[0068] These two types of monitored chemicals are key components in the oxidation process of the food.

[0069] To perform this work two set of experiments are run.

[0070] For "conguitos" experiments, 36 commercial bags of 1 kg size are used. Half of the bags (18) have the active component of the invention and the other 18 are made of standards materials.

[0071] For "cereals" 36 plastic commercial trays are used, half (18) with the active material of the invention (in the sealed lid of the tray) and 18 without the active material (comparative samples).

[0072] Analyses are performed monthly for all type of samples (4 analysis for 4 samples, 2 for each type of product and each type of material "active/not active"). Every 3 months, the fatty acid profile is analyzed only for "conguitos" samples (2 samples, one with the active assembly of the invention and the other with the normal material for comparison).

[0073] The results of the hexanal analyses are shown in figure 8a and 8b (line with square markers is relative to samples with the active assembly according to the present invention, line with diamond markers is relative to comparative samples packed with standard material).

Lipid profile (mg/g):

[0074] The lipidic fraction values of the analyzed samples varies from 7 to 12 % per gram of chocolate peanut (i.e. "conguito"). Data that are relative to samples packed with the material of the invention (A) and to comparative samples packed with a standard material (C), sampled every 3 months (T0= initial values) are reported in Table 4.

Table 4

Acid (Mg/g lipids)	T=0	T=3		T=6		T=9		T=12	
		A	C	A	C	A	C	A	C
Palmitic acid	35	25	24	15	13	15	13	14	10
Stearic acid	40	38	37	35	33	34	32	34	30
Oleic acid	150	146	141	145	127	132	125	126	110
Linoleic acid	76	74	74	70	72	74	70	50	45
Arachidic acid	10	4	3	3	7	3	10	9	9
Behenic acid	27	24	26	22	19	20	20	22	20

Organoleptic tests

[0075] Two different panels tested both products after one year of being packaged either with the active or the non-active material. The first panel was formed in the laboratory with the participation of the Responsible for R+D from the Company LACASA. In addition, a panel of experts in the Company tested the same products after one year of being packaged. In all cases, the test was done with blind samples, where four samples had to be tasted. Each panelist had to identify the active and the non-active product.

[0076] All the panelists identified the active and the non-active material (100% of correct answers). According to the testers' opinions, the product is still acceptable after one year, although clear differences are found between the packaging of the invention and the comparative packaging.

[0077] In conclusion, a lower degradation rate can be seen in the lipid acids profile between the dark chocolate peanuts (i.e., "conguitos") packed with the material of the invention and those packed with standard (comparative) materials.

[0078] A clear increase of hexanal was also recorded for the comparative packaging.

[0079] Both results confirm a clear antioxidant protection of the active material. Organoleptic tests also confirm these results.

EXAMPLE 4

[0080] The effect on coffee of packaging in the assembly of the invention compared to standard (comparative) materials is evaluated.

[0081] The following materials are tested:

C1 (multilayer, comparative):

[0082] Material: layers of PET/Aluminium foil/LDPE; thickness: 12/6.35/75 μm ; total thickness 93.35 μm ; Oxygen Transmission rate (OTR) $<0,1 \text{ cm}^3/\text{m}^2$ in 24h at 23°C with 0% residual humidity (RH); water vapour $<0,1 \text{ g}/\text{m}^2$ in 24h at 38°C con 90% RH.

A1 (multilayer assembly of the invention):

[0083] Material: layers of PET/Aluminium foil/LDPE, layers bound with catechin-containing polyurethane-based adhesive; thickness: 12/6.35/75 μm ; total thickness 93.35 μm ; OTR $<0,1 \text{ cm}^3/\text{m}^2$ in 24 h at 23°C with 0% RH; water vapour $<0,1 \text{ g}/\text{m}^2$ in 24h at 38°C con 90% RH.

C2 (multilayer, comparative):

[0084] Material: layers of Cellophane, starch-derived polymer (biopolymer); thickness: 23/76 μm ; total thickness 99 μm ; Oxygen Transmission rate (OTR) $3 \text{ cm}^3/\text{m}^2$ in 24h at 23°C with 0% residual humidity (RH); water vapour $10 \text{ g}/\text{m}^2$ in 24h at 38°C con 90% RH.

A2 (multilayer assembly of the invention):

[0085] Material: 2 layers of Cellophane/ starch-derived polymer (biopolymer); thickness: 23/76 μm ; total thickness 99 μm ; Oxygen Transmission rate (OTR) $3 \text{ cm}^3/\text{m}^2$ in 24h at 23°C with 0% residual humidity (RH); water vapour $10 \text{ g}/\text{m}^2$ in 24h at 38°C con 90% RH.

[0086] The experimental procedure foresees storing the product at $25 \pm 5^\circ\text{C}$ with analysis at the initial packing time (t_0), at 2, 9, 12, 18 and 24 storage months.

For the storage study, the following analyses are carried out on ground coffee and on the oil extracted from the coffee.

On the oil::

[0087]

- Acidity (grams of oleic acid/100 g di oil)
- Number of peroxides (meq O_2/kg of oil)
- iodine number (grams of bound iodine/ 100 g of oil)
- p-Anisidine (AOCS Official Method Cd 18-90)

[0088] On ground coffee :

- Humidity
- A_w (water activity)
- Aromatic profile with headspace/GC-MS technique

[0089] Results are as follows (data are relative to the initial sample $T=0$ and to the sample for each test after 2 months of storage:

OIL

[0090]

Table 5 (acidity):

Sample	T=0	C1 (after 2 months)	A1 (after 2 months)	C2 (after 2 months)	A2 (after 2 months)
grams of oleic acid/100 g of oil	2.41	2.69	2.80	2.78	2.75

[0091] No significant increase of acidity is observed after two months in storage.

Table 6 (number of peroxides):

Sample	T=0	C1 (after 2 months)	A1 (after 2 months)	C2 (after 2 months)	A2 (after 2 months)
meq O ₂ /kg of oil	2.24	2.25	1.91	2.07	2.33

[0092] No significant increase of peroxides is observed after two months in storage, because no fatty acid oxidation occurred.

Table 7 (iodine number):

Sample	T=0	C1 (after 2 months)	A1 (after 2 months)	C2 (after 2 months)	A2 (after 2 months)
grams of bound iodine/ 100 g of oil	95.36	92.72	90.85	91.04	90.53

[0093] No significant variation in the number of unsaturated fatty acid is observed after two months in storage.

Table 8 (p-Anisidine):

Sample	T=0	C1 (after 2 months)	A1 (after 2 months)	C2 (after 2 months)	A2 (after 2 months)
grams of bound iodine/ 100 g of oil	4.88	4.12	4.33	4.01	4.86

[0094] Secondary oxidation of lipids does not increase over two months in storage.

GROUND COFFEE:

[0095]

Table9

Sample	T=0	C1	A1	C2	A2
Aw	0.093	0.069	0.074	0.112	0.120
Humidity (%)	1.12	1.11	1.12	1.38	1.42

[0096] The variation of 2-methylfurane/2-butanone ratio over time is also determined. It is found that the presence of catechins reduces the 2-methylfurane oxidation and the presence of 2-butanone.

[0097] In general, a higher protection of coffee from oxidation is achieved by using the multilayer assembly of the invention as a packaging material.

Claims

1. A multilayer assembly comprising at least:

- a) a layer of paper or of a polymeric material selected from polypropylene, polyester, polyamide, polyethylene and their mixtures and copolymers;
- b) at least one adhesive layer; and
- c) a metallic and/or polymeric layer,

said adhesive layer b) binds layer a) to layer c), and comprises a mixture of at least a catechin and a polymeric adhesive composition,

characterised in that

the polymeric adhesive composition of layer b) comprises a polyurethane adhesive composition,

said mixture of at least a catechin and a polymeric adhesive composition has antiradical/antioxidant properties.

2. The multilayer assembly according to claim 1 wherein adhesive layer b) comprises green tea extract.

3. The multilayer assembly according to any of the preceding claims, wherein the polymeric material of layer a) comprises polyethylene.

4. The multilayer assembly according to any of the preceding claims, wherein the layer a) has a thickness of 20 to 400 micron.

5. The multilayer assembly according to any of the preceding claims, wherein the polyurethane adhesive comprised in layer b) is selected from a solvent-free, solvent-based or water-based polyurethane, wherein each type can be based on a polyol component selected from the group consisting of polyester polyol, polyether polyol, polyacrylate polyol and polycarbonate polyol, and a mixture thereof, and an isocyanate component selected from an aliphatic isocyanate, an alicyclic isocyanate or an aromatic isocyanate.

6. The multilayer assembly according to any of the preceding claims, wherein the adhesive layer b) comprises from 0.1 to 15.0% weight/total weight of layer b) of at least one catechin.

7. A container comprising a plurality of walls defining an inner space, wherein the multilayer assembly according to any of the preceding claims forms, at least partially, at least one of said walls, and the layer a), comprising a polymeric material, is facing towards the inner space of the container.

8. The container according to claim 7 that is suitable for packaging of foodstuff, cosmetics and/or pharmaceutical products.

9. A process for the production of the multilayer assembly according to any of claims 1-6, comprising the steps of laminating the layer a) of paper or polymeric material and at least another layer c), wherein a) is made to adhere to layer c) by means of the adhesive b).

10. Use of the multilayer assembly according to any of claims 1-6 for packaging of oxidation-sensitive goods.

11. The use of claim 10 wherein said oxidation-sensitive goods are foodstuff, cosmetics and/or pharmaceutical/nutraceutical products.

12. The use of claim 11 wherein said oxidation-sensitive goods are ground coffee, dried or fresh coffee beans or pods, dried tea or tea leaves, fruit juice, chocolate, tomato juice or sauces, rice, cereals, ready meals, fresh dough or yeast.

Patentansprüche

1. Mehrschichtanordnung, umfassend mindestens:

- a) eine Schicht aus Papier oder aus einem Polymermaterial, das aus Polypropylen, Polyester, Polyamid, Polyethylen und deren Mischungen und Copolymeren ausgewählt wird;
- b) mindestens eine Haftschrift; und
- c) eine Metall- und/oder Polymerschicht, wobei die Haftschrift b) die Schicht a) an die Schicht c) bindet und eine Mischung aus mindestens einem Catechin und einer Polymerklebstoffzusammensetzung umfasst,

dadurch gekennzeichnet, dass

die Polymerklebstoffzusammensetzung der Schicht b) eine Polyurethan-Klebstoffzusammensetzung umfasst, wobei das Gemisch aus mindestens einem Catechin und einer Polymerklebstoffzusammensetzung antiradikalische/antioxidative Eigenschaften aufweist.

2. Mehrschichtanordnung nach Anspruch 1, wobei die Klebstoffschicht b) Grüntee-Extrakt umfasst.

3. Mehrschichtanordnung nach einem der vorhergehenden Ansprüche, wobei das Polymermaterial der Schicht a) Polyethylen umfasst.

4. Mehrschichtanordnung nach einem der vorhergehenden Ansprüche, wobei die Schicht a) eine Dicke von 20 bis 400 Mikrometer aufweist.
5. Mehrschichtanordnung nach einem der vorhergehenden Ansprüche, wobei der Polyurethan-Klebstoff, der in der Schicht b) enthalten ist, aus einem lösungsmittelfreien, lösemittelbasierenden oder wasserbasierenden Polyurethan ausgewählt wird, wobei jeder Typ auf einer Polyolkomponente basiert sein kann, die aus der aus Polyesterpolyol, Polyetherpolyol, Polyacrylatpolyol und Polycarbonatpolyol und einer Mischung davon bestehenden Gruppe ausgewählt wird, und auf einer Isocyanatkomponente, die aus einem aliphatischen Isocyanat, einem alicyclischen Isocyanat oder einem aromatischen Isocyanat ausgewählt wird, basiert sein kann.
6. Mehrschichtanordnung nach einem der vorhergehenden Ansprüche, wobei die Haftschrift b) 0,1 bis 15,0 Gew.-%/Gesamtgewicht der Schicht b) von mindestens einem Catechin umfasst.
7. Behälter mit mehreren Wänden, die einen Innenraum begrenzen, wobei die Mehrschichtanordnung nach einem der vorhergehenden Ansprüche mindestens teilweise eine der Wände bildet und die Schicht a), die ein Polymermaterial aufweist, in Richtung des Innenraums des Behälters gerichtet ist.
8. Behälter nach Anspruch 7, der zum Verpacken von Lebensmitteln, Kosmetika und/oder pharmazeutischen Produkten geeignet ist.
9. Verfahren zur Herstellung der Mehrschichtanordnung nach einem der Ansprüche 1 bis 6, umfassend die Schritte des Laminierens der Schicht a) aus Papier oder Polymermaterial und mindestens eine weitere Schicht c), wobei a) an Schicht c) mittels des Klebers b) haftet.
10. Verwendung der Mehrschichtanordnung nach einem der Ansprüche 1 bis 6 zum Verpacken von oxidationsempfindlichen Waren.
11. Verwendung nach Anspruch 10, wobei die oxidationsempfindlichen Waren Nahrungsmittel, Kosmetika und/oder pharmazeutische Produkte /Nutrazeutika sind.
12. Verwendung nach Anspruch 11, wobei die oxidationsempfindlichen Waren gemahlener Kaffee, getrocknete oder frische Kaffeebohnen oder -schoten, getrockneter Tee oder Teeblätter, Fruchtsaft, Schokolade, Tomatensaft oder -saucen, Reis, Cerealien, Fertiggerichte, frischer Teig oder Hefe sind.

Revendications

1. Un assemblage multicouche comprenant au moins:

- a) une couche de papier ou d'un matériau polymère choisi parmi le polypropylène, le polyester, le polyamide, le polyéthylène et leurs mélanges et copolymères ;
- b) au moins une couche adhésive ; et
- c) une couche métallique et/ou polymère, où ladite couche adhésive b) lie la couche a) à la couche c) et comprend un mélange d'au moins une catéchine et d'une composition adhésive polymère,

caractérisé en ce que

la composition adhésive polymère de la couche b) comprend une composition adhésive polyuréthane, ledit mélange d'au moins une catéchine et d'une composition adhésive polymère présente des propriétés antiradi-cataires/antioxydantes.

2. Assemblage multicouche selon la revendication 1, dans lequel la couche adhésive b) comprend un extrait de thé vert.
3. Assemblage multicouche selon l'une quelconque des revendications précédentes, dans lequel le matériau polymère de la couche a) comprend du polyéthylène.
4. Assemblage multicouche selon l'une quelconque des revendications précédentes, dans lequel la couche a) a une épaisseur de 20 à 400 microns.

5. Assemblage multicouche selon l'une quelconque des revendications précédentes, dans lequel l'adhésif de polyuréthane compris dans la couche b) est choisi parmi un polyuréthane sans solvant, à base de solvant ou à base aqueuse, dans lequel chaque type peut être basé sur un composant polyol choisi dans le groupe constitué par le polyester polyol, le polyéther polyol, le polyacrylate polyol et le polycarbonate polyol et leur mélange, et un composant isocyanate choisi parmi un isocyanate aliphatique, un isocyanate alicyclique ou un isocyanate aromatique.
6. Assemblage multicouche selon l'une quelconque des revendications précédentes, dans lequel la couche adhésive b) comprend de 0,1 à 15,0% en poids/poids total de la couche b) d'au moins une catéchine.
7. Un récipient comprenant une pluralité de parois définissant un espace intérieur, où l'ensemble multicouche selon l'une quelconque des revendications précédentes forme au moins partiellement au moins une desdites parois, et la couche a) comprenant un matériau polymère est orientée vers l'espace intérieur du conteneur.
8. Récipient selon la revendication 7 adapté à l'emballage de produits alimentaires, cosmétiques et/ou pharmaceutiques.
9. Procédé de production de l'ensemble multicouche selon l'une quelconque des revendications 1 à 6, comprenant les étapes consistant à stratifier la couche a) de papier ou de matériau polymère et au moins une autre couche c), où l'on fait adhérer a) à la couche c) au moyen de l'adhésif b).
10. Utilisation de l'ensemble multicouche selon l'une quelconque des revendications 1 à 6 pour l'emballage de produits sensibles à l'oxydation.
11. Utilisation selon la revendication 10, où lesdits produits sensibles à l'oxydation sont des produits alimentaires, des cosmétiques et/ou des produits pharmaceutiques/nutraceutiques.
12. Utilisation selon la revendication 11, où lesdits produits sensibles à l'oxydation sont du café moulu, des gousses ou des grains de café séchés ou frais, du thé ou des feuilles de thé séchés, des jus de fruits, du chocolat, du jus ou des sauces de tomates, du riz, des céréales, des plats préparés et de la pâte fraîche ou de la levure.

Fig. 1

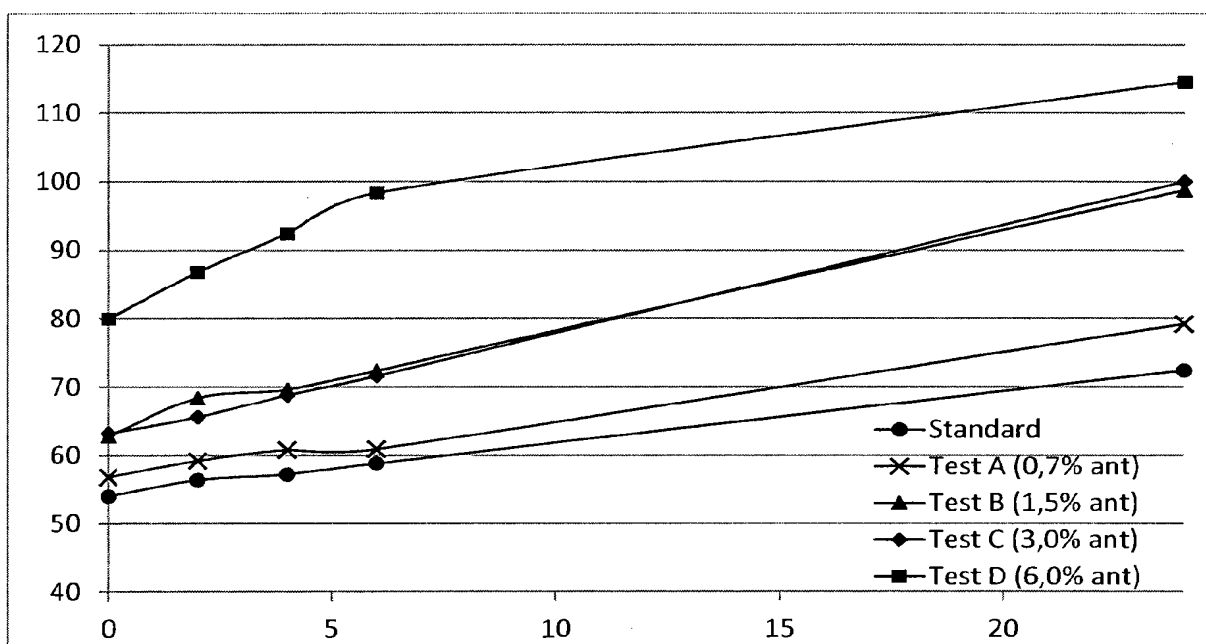


Fig. 2

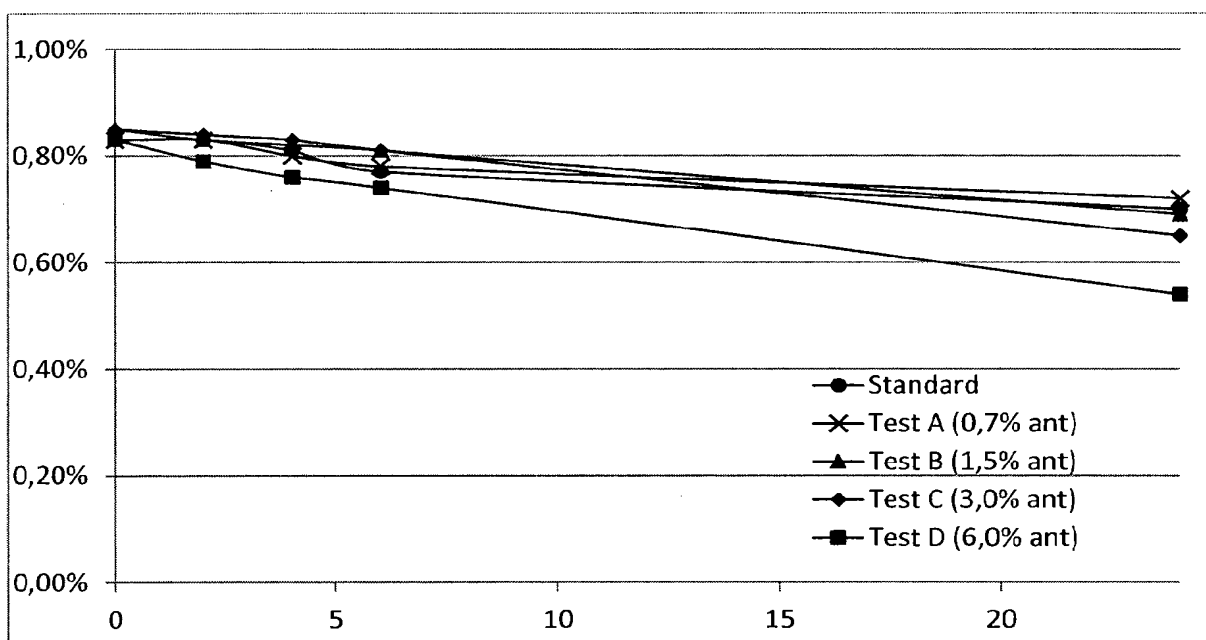


Fig. 3

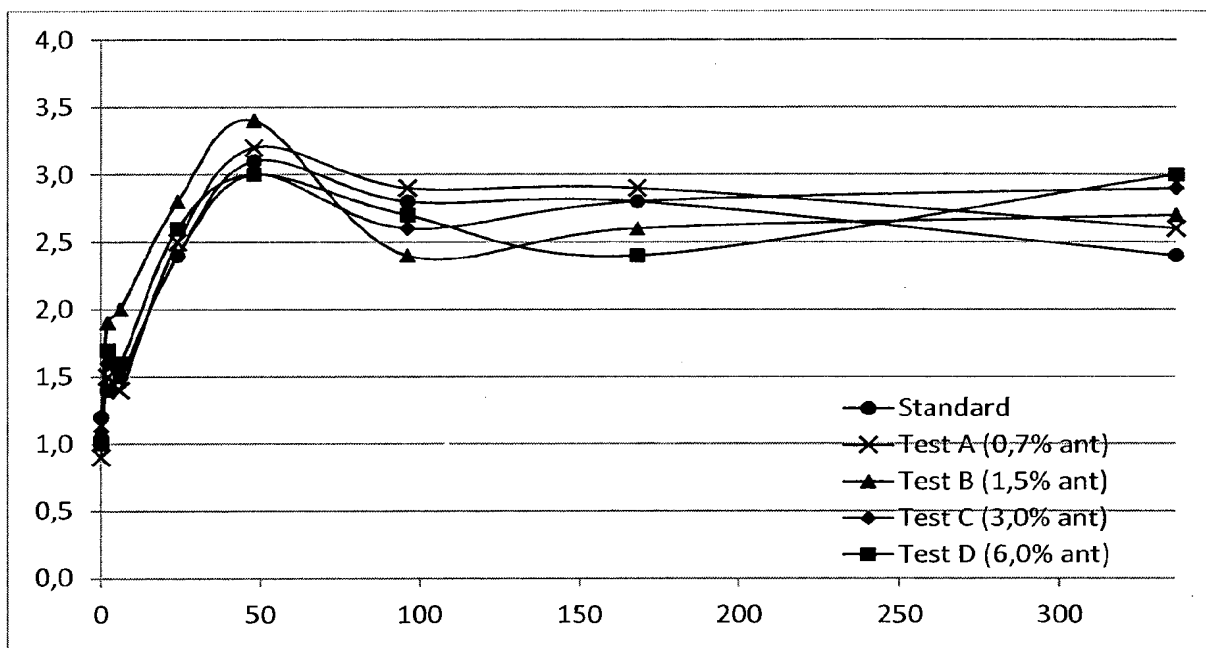


Fig. 4

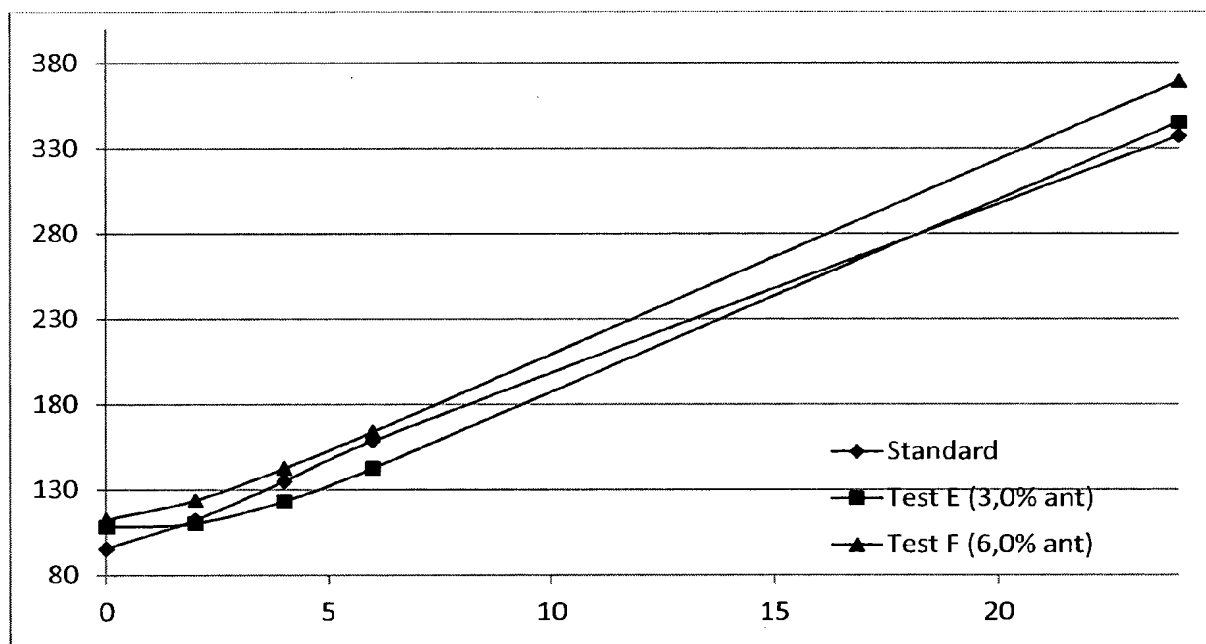


Fig. 5

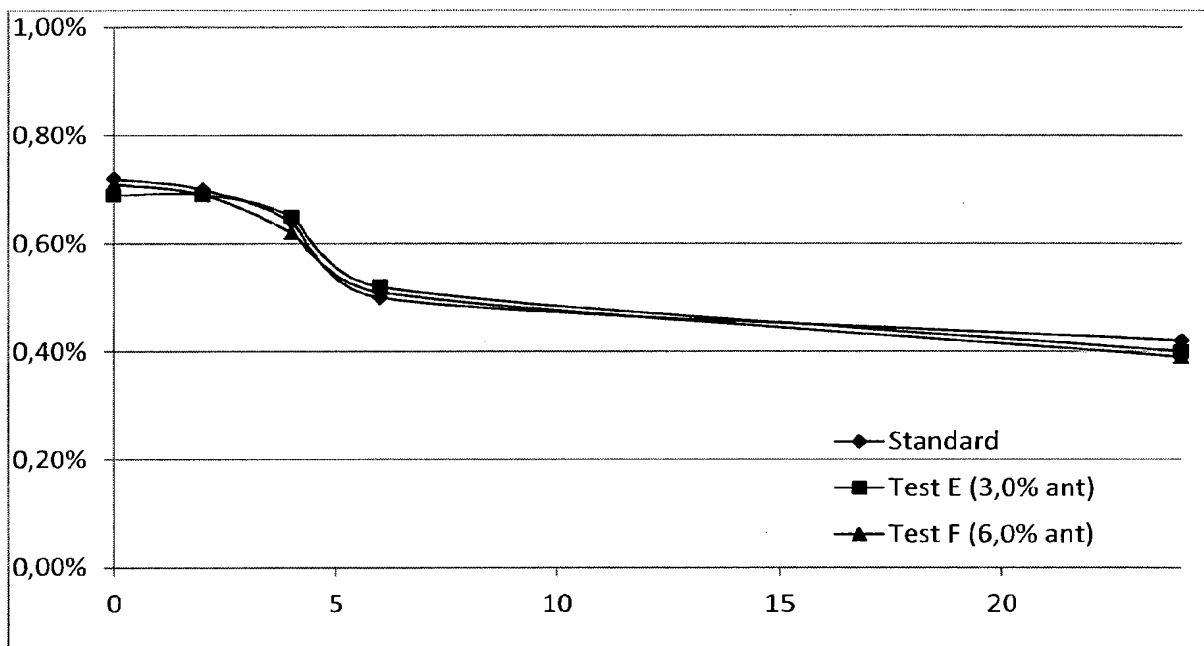


Fig. 6

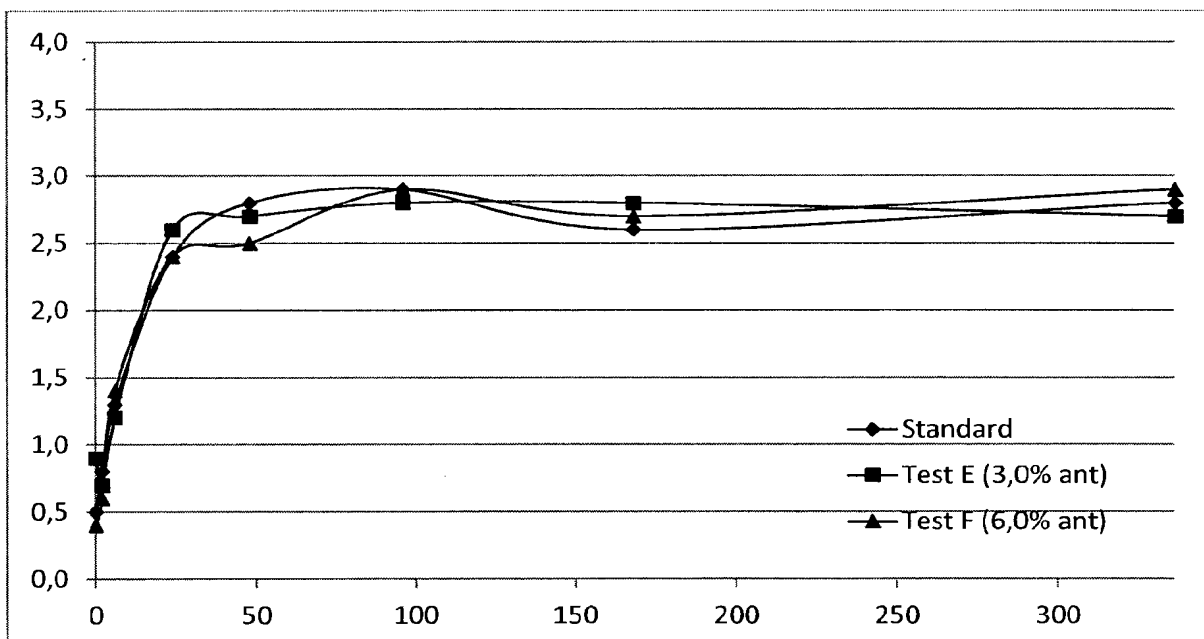


Fig. 7

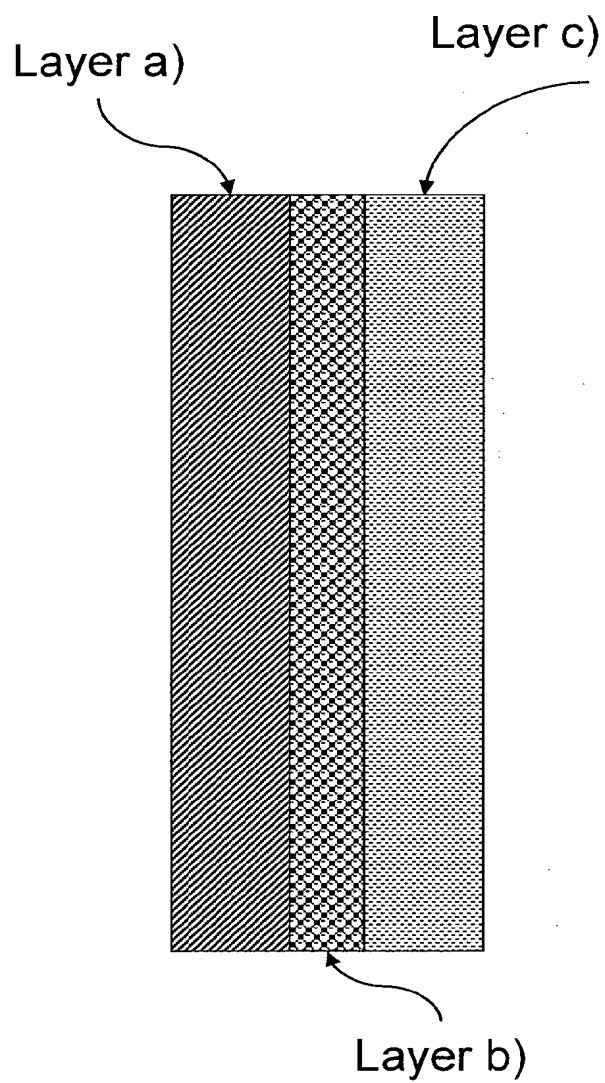


Figure 8a

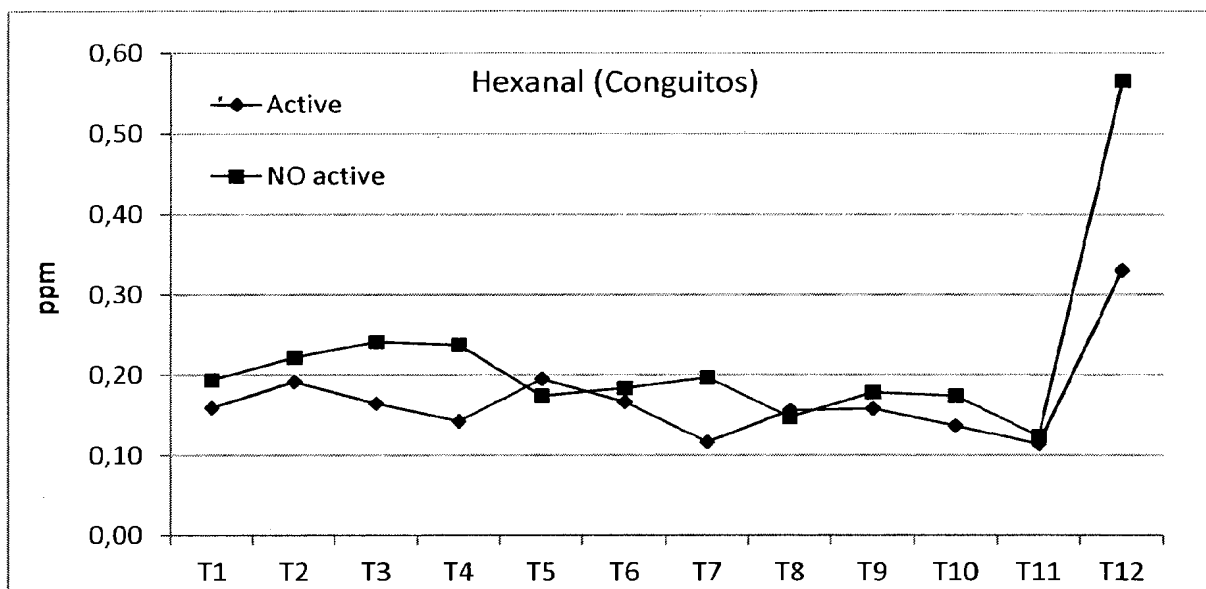
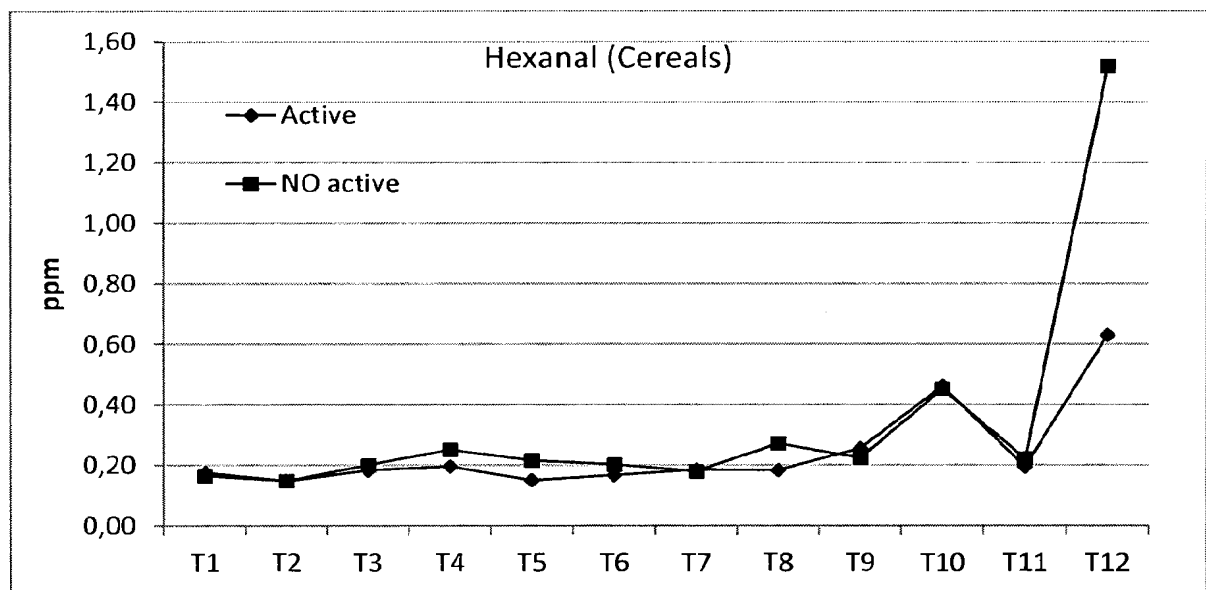


Figure 8b



REFERENCES CITED IN THE DESCRIPTION

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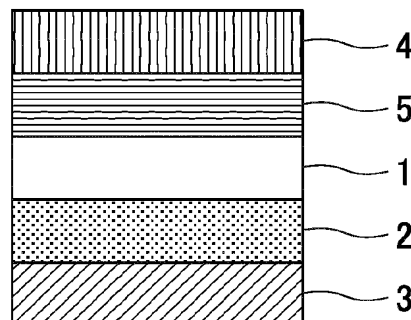
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(54) **LIGHT-SHIELDING SHEET AND CONTAINER**

(57) The present invention provides a light-shielding sheet that has a function of shielding light of a specific wavelength and that is capable of preventing a light-shielding substance from being transferred into the contents and seeping out of a container and a container produced using the light-shielding sheet. This light-shielding sheet of the present invention has a multilayer structure of three or more layers including at least one light-shielding layer (1) that shields a specific wavelength and/or eluate-blocking layer (2) that blocks sub-

stances eluted from the light-shielding layer (1). When producing a container from the light-shielding sheet, an eluate-blocking layer A (2) is provided at least between the light-shielding layer (1) and an innermost layer (3) or on the innermost layer (3), and an eluate-blocking layer B (5) is provided between the light-shielding layer (1) and an outermost layer (4) or on the outermost layer (4). The light-shielding layer (1) may further double as an eluate-blocking layer.

FIG. 1C



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Description

Technical Field

5 **[0001]** The present invention relates to a sheet, a package, and a container for storing pharmaceutical products and medical supplies, such as a blister sheet, an infusion solution and liquid medicine bag, a plastic ampoule and vial, a plastic syringe, and medicines, various cosmetics, foods, and the like as contents. Specifically, the present invention relates to a sheet and a container which make a visual check of contents to be stored possible, have a function of shielding light of a specific wavelength, and are capable of preventing contamination resulting from elution of substances
10 from the sheet or the container into contents or bleeding out of the substances to the outside.

Background Art

15 **[0002]** Conventionally, shielding light of a specific wavelength has often been suggested as a function of enhancing storage stability of contents in sheets, packages, and containers for storing pharmaceutical products, medical supplies, various cosmetics, foods and the like as contents.

20 **[0003]** Sheets and containers that prevent deterioration in quality of contents by the influence of deterioration due to ultraviolet rays and the like are demanded for some of pharmaceutical products and medical supplies such as medicines, various cosmetics, foods, and the like, which are stored in PTP packaging and blister packaging, obtained by thermo-forming a blister sheet, a soft bag such as an infusion solution and liquid medicine bag, a plastic ampoule and vial, and a syringe.

25 **[0004]** Containers for infusion solutions and liquid medicines are used for various infusion solutions and pharmaceutical products. However, when drugs which are easily deteriorated by light, particularly, vitamins and amines are contained in various infusion solutions and pharmaceutical products, it is necessary to protect the contents from light and to shield light not only in an ultraviolet range but also in a visible range from these drugs.

30 **[0005]** These infusion solutions and liquid medicines are prepared in advance or prepared when being used (dripped). Since these infusion solutions and liquid medicines are generally stored in a packing material having light-shielding properties such as cardboard until being used, there is substantially no possibility that these solutions and liquid medicines are exposed to light and a main problem is deterioration due to light while being used. Therefore, when these solutions and medicines are used, a container such as an infusion solution bag is covered with a cover made of a light-shielding film in many cases. However, since the light-shielding film is colored, it is difficult to visually check the state of the infusion solution in the infusion solution container and changes in the liquid level and the dripping progress state cannot be grasped. Thus, there is a possibility that appropriate dripping cannot be achieved.

35 **[0006]** In order to solve such a problem, Patent Document 1 discloses a light-shielding cover for an infusion solution container that is covered an infusion solution bag with a colored film later for realizing light-shielding and provided with a window for checking the amount of contents remaining. However, with this configuration, an infusion solution bag which is an immediate container does not have any light-shielding function and there is a concern of deterioration in quality of contents such as drugs which are sensitive to light due to light such as ultraviolet rays in a step of drug filling or in a step of inspection.

40 **[0007]** Patent Document 2 discloses a laminated body that is used for PTP packaging or blister packing. A laminating material for pharmaceutical products and medical supplies is a laminating material which has a function of shielding light of a specific wavelength (light shielding properties) and oxygen barrier properties and an ultraviolet absorber and a yellow pigment are kneaded in the laminating material. Application of ink imparts a function of shielding light of a specific wavelength and an oxygen barrier function. However, countermeasures for inhibiting substances from being eluted from
45 the ultraviolet absorber, yellow pigment and ink, which are used for imparting a light-shielding function, into the contents are not taken.

50 **[0008]** In addition, the total light transmittance at a wavelength of 500 nm is 5% or lower, and the visibility of the contents is not good. For example, in the testing method for pharmaceutical containers described in the Japanese Pharmacopoeia, regarding the transparency of containers, the total light transmittance at a wavelength of 450 nm is 55% or more. It is relatively easy to shield light with a wavelength of 500 nm or less. However, it is not easy to achieve a total light transmittance at a wavelength of 450 nm of 55% or more while shielding light in an ultraviolet range with a wavelength of 400 nm or less.

55 **[0009]** Patent Document 3 discloses a light-shielding laminated sheet as an outer packaging bag for a prefilled syringe. As described above, there are many examples of outer packaging bags in which a light-shielding function is not imparted to an immediate container that comes into contact with a pharmaceutical product and these outer packaging bags are preferable from the viewpoint of safety of contents. However, with the same configuration as in the Patent Document 1, a prefilled syringe which is an immediate container does not have any light-shielding function and there is a concern of deterioration in quality of contents such as drugs, which are sensitive to light, due to light such as ultraviolet rays in a

step of drug filling or in a step of inspection.

[0010] On the other hand, Patent Document 4 discloses a container obtained using a coloring pigment in an infusion solution bag itself as a container in which a light-shielding function is provided to an immediate container that comes into contact with the contents. Among these, an infusion solution bag is strictly restricted by the testing method for plastic containers for infusion solutions described in the Japanese Pharmacopoeia of Pharmaceutical Affairs Law. For example, a general organic absorbent cannot be used in an eluate test. Further, there are difficulties that the ignition residue is limited to 0.10% or less and an inorganic ultraviolet absorber such as titanium dioxide particulates cannot be used. Therefore, there is disclosed a colored resin composition for an infusion solution bag which did not exist in the past and has excellent physiological safety, a high degree of transparency, heat resistance, and an ultraviolet absorbing effect over almost the entire ultraviolet range in a pigment composition investigation without causing elution. This resin composition can be suitably used for an infusion solution bag and a packaging material thereof.

[0011] However, the composition almost completely shields the light of a wavelength of 450 nm and the content visibility is not good. As described above, in the testing method for pharmaceutical containers described in the Japanese Pharmacopoeia, regarding the transparency of containers, the total light transmittance at a wavelength of 450 nm is 55% or more. It is relatively easy to shield light of 500 nm or less as in Patent Document 4. However, it is not easy to achieve a total light transmittance at a wavelength of 450 nm of 55% or more while shielding light in an ultraviolet range of 400 nm or less.

[0012] As a container in which a light-shielding function is provided to an immediate container for storing a pharmaceutical product, Patent Document 5 discloses a plastic ampoule. From the viewpoint of preventing elution of a pigment and an ultraviolet absorber into a drug, cyclic olefin having a glass transition temperature of 60°C to 80°C is used for an intermediate layer of the container. However, since the pigment and the ultraviolet absorber are added to the outer layer of the cyclic olefin layer and in such a container, the pigment and the ultraviolet absorber are bled out of the container. Thus, there is a possibility of causing contamination of the container or other products. In addition, at a glass transition temperature of 60°C to 80°C, for use in a high temperature region, intermolecular motion is promoted and elution of the components into the liquid contents cannot be inhibited. Therefore, these problems are not completely solved.

Citation List

Patent Document

[0013]

[PATENT DOCUMENT 1] Japanese Unexamined Patent Application, First Publication No. 2003-275280

[PATENT DOCUMENT 2] Japanese Unexamined Patent Application, First Publication No. 2008-230112

[PATENT DOCUMENT 3] Japanese Unexamined Patent Application, First Publication No. 2007-302328

[PATENT DOCUMENT 4] Japanese Unexamined Patent Application, First Publication No. H8-193149

[PATENT DOCUMENT 5] Japanese Unexamined Patent Application, First Publication No. 2008-104868

Summary of Invention

Technical Problem

[0014] The present invention is made in consideration of the disadvantages of the related art and an object thereof is to provide a light-shielding sheet and a light-shielding container for storing pharmaceutical products, medical supplies, various cosmetics, foods, and the like while coming into direct contact with the contents, which makes visual inspection of contents to be stored possible, has a function of shielding light of a specific wavelength for enhancing the storage stability of the contents without contamination resulting from elution of light-shielding substances such as an ultraviolet absorber, an organic or inorganic pigment, an inorganic substance, a colored pigment, a fluorescent brightening agent, and a dye into the contents or bleeding out of the substances to the outside.

Solution to Problem

[0015] As a result of intensive investigation conducted by the present inventors to achieve the object, it has been found that the above problems can be solved by forming a multilayer sheet having a total of three or more layers including at least one light-shielding layer that contains at least one component of an ultraviolet absorber, an organic or inorganic pigment, an inorganic substance, a colored pigment, a fluorescent brightening agent, and a dye, and at least one eluate-blocking layer that blocks substances eluted from the light-shielding layer, or a container produced using the sheet, using a cyclic polyolefin-based resin, a fluorine-based resin, a polyester-based resin, or a polyamide-based resin in the

eluate-blocking layer and/or the light-shielding layer as a main component, and the present invention has been accomplished.

[0016] That is, the present invention provides a light-shielding sheet that have a function of shielding light of a specific wavelength without contamination resulting from elution of light-shielding substances such as an ultraviolet absorber, an organic or inorganic pigment, an inorganic substance, a colored pigment, a fluorescent brightening agent, and a dye, into contents or bleeding out of the substances to the outside, and a container. The present invention is configured as follows.

(1) 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, in which 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 (1), in which a total light transmittance of the sheet having the multilayer structure at a wavelength of 380 nm or less is 1% or less and a total light transmittance at a wavelength of 380 nm or more and 400 nm or less is 30% or lower.

(3) The light-shielding sheet according to (1) or (2), in which the eluate-blocking layer has any one of a cyclic polyolefin-based resin or a fluorine-based resin, a polyester-based resin, and a polyamide-based resin as a main component.

(4) The light-shielding sheet according to any one of (1) to (3), in which the light-shielding layer has at least any one of a cyclic polyolefin-based resin, a fluorine-based resin, and a polyester-based resin as a main component.

(5) The light-shielding sheet according to (1), in which 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 polypropylene-based resin having a density of 0.88 or higher as a main component.

(6) The light-shielding sheet according to any one of (1) to (4), in which 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 (6), in which the glass transition temperature of the cyclic polyolefin-based resin is 110°C or higher.

(8) The light-shielding sheet according to any one of (1) to (4), in which 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.

(9) The light-shielding sheet according to any one of (1) to (8), in which a total light transmittance at a wavelength of 450 nm or longer is 15% or higher.

(10) The light-shielding sheet according to (9), in which the total light transmittance at a wavelength of 450 nm or longer is 55% or higher.

(11) A light-shielding container that is produced using the light-shielding sheet according to any one of (1) to (10).

(12) A container in which a solution for pharmaceutical and medical use is stored in the light-shielding container according to (11) as contents and the container is sterilized with high pressure steam at a temperature of 101 °C or higher.

(13) The container according to (11), in which 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 rays and visible light at a wavelength range of 220 nm to 450 nm.

(14) The container according to (13), in which the drug includes one or more of levofloxacin, a derivative thereof, and a modification thereof.

(15) The container according to (13), in which the drug includes one or more of the group consisting of palonosetron hydrochloride, a derivative thereof, and a modification thereof.

(16) A method of producing a light-shielding container including producing a container using the light-shielding sheet according to (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, and injection drawing blow molding, multilayer blow molding, and multilayer injection blow molding.

Effects of Invention

[0017] When the light-shielding sheet of the present invention is formed into a container, visual inspection of contents to be stored is possible and the container has a function of shielding light of a specific wavelength for enhancing the storage stability of contents. Even 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 or the like by heat of

60°C to 70°C, a sterilization treatment with high pressure steam at a temperature of 101°C or higher, and the like, the container has very high safety and excellent practicality as a container which contains pharmaceutical products, medical supplies, various cosmetics, foods, and the like while coming into direct contact with the pharmaceutical products, medical supplies, various cosmetics, foods, and the like without contamination resulting from elution of 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) into the contents or bleeding out of the substances to the outside.

[0018] The details are as follows.

[0019] In the container of the present invention, since the sheet of the present invention has a multilayer structure of three or more layers including a light-shielding layer and/or an eluate-blocking layer, transmission of a specific wavelength can be inhibited, visibility that makes visual inspection possible can be ensured, and eluates of 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) into the container can be inhibited.

[0020] In the container of the present invention, since most of light in a harmful ultraviolet range having a wavelength of 380 nm or shorter can be shielded and light in a high wavelength band of 380 nm to 400 nm also can be shielded, the stability of contents can be enhanced.

[0021] In the container of the present invention, light-shielding substances such as an ultraviolet absorber, an organic or inorganic pigment, an inorganic substance, a colored pigment, a fluorescent brightening agent, a dye and the like can be inhibited from being eluted to the outside of the container.

[0022] In the container of the present invention, an eluate blocking effect can be enhanced by adjusting the component of the eluate-blocking layer in the sheet of the present invention.

[0023] In the container of the present invention, similarly, light-shielding substances such as an ultraviolet absorber, an organic or inorganic pigment, an inorganic substance, a colored pigment, a fluorescent brightening agent, a dye and the like can be inhibited from being eluted into the container or bleeding out of the container.

[0024] In the sheet of the present invention, the light-shielding layer can double as an eluate-blocking layer by selecting the resin for the light-shielding layer. That is, the present invention provides a light-shielding sheet that has a multilayer structure of three or more layers including at least one light-shielding layer. The light-shielding layer is made of a resin that has at least one of a cyclic polyolefin-based resin, a fluorine-based resin, and a polyester-based resin as a main component and further contains at least one of an ultraviolet absorber, an organic pigment, an inorganic pigment, an inorganic substance, a colored pigment, a fluorescent brightening agent, a dye and the like and is provided in an intermediate layer. In the light-shielding sheet, light-shielding substances can be inhibited from being eluted into the container or bleeding out of the container by only the light-shielding layer.

[0025] In the sheet of the present invention, a soft resin can be used as the resin for the light-shielding layer. The flexibility of the sheet and the container produced using the sheet can be enhanced, and the drop impact strength can be enhanced by improving the discharge efficiency of liquid contents.

[0026] In the sheet of the present invention, in the case in which the sheet is formed into a container, the molecular motion of the resin of the eluate-blocking layer and the light-shielding layer can be inhibited by increasing the glass transition temperature of the resin used for the eluate-blocking layer and the light-shielding layer even when the container is placed under a high temperature environment during filling of liquid contents or in sterilization after filling of liquid contents, storage, use, and the like at a high temperature. Thus, light-shielding substances such as an ultraviolet absorber, an organic or inorganic pigment, an inorganic substance, a colored pigment, a fluorescent brightening agent, a dye and the like can be highly inhibited from being eluted into the container or bleeding to the outside of the container.

[0027] In the sheet of the present invention, since the total light transmittance is adjusted, when the sheet is formed into a container, light of a specific wavelength is shielded to enhance the storage stability of contents and visual inspection in an inspection step after filling of the contents is possible.

[0028] The sheet of the present invention can be used for a container for storing a liquid for medical use, which is subjected to high pressure steam sterilization.

[0029] In the container of the present invention, a liquid drug in which at least one of deterioration, lowering of titer, and impurity formation is caused by ultraviolet rays and/or visible light can be stably stored.

[0030] In the container of the present invention, a liquid drug including levofloxacin, a derivative thereof, or a modification thereof can be stably stored and distributed.

[0031] In the container of the present invention, a liquid drug including palonosetron hydrochloride, a derivative thereof, or a modification thereof can be stably stored and distributed.

Brief Description of Drawings

[0032]

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