

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 January 2005 (27.01.2005)

PCT

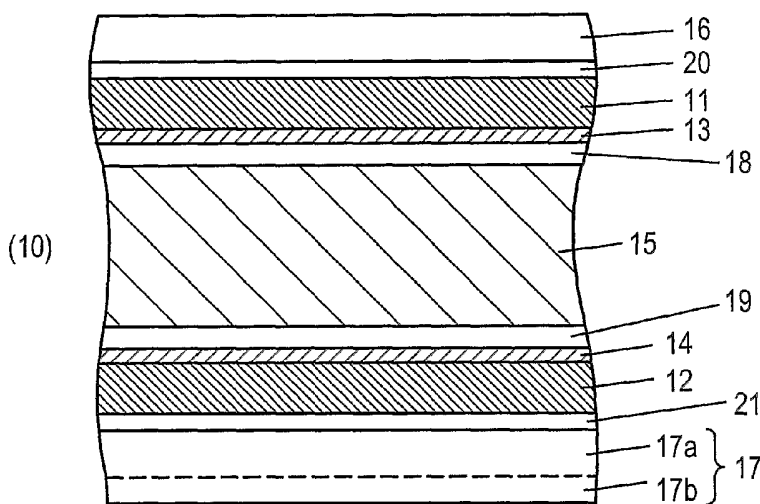
(10) International Publication Number
WO 2005/007518 A2

- (51) International Patent Classification⁷: **B65D** [CH/CH]; Petite Route 2, CH-1061 Villars-Mendraz (CH). **CHIQUET, André** [CH/CH]; Route des Dailles 41, CH-1752 Villars-sur-Glane (CH). **GOLAY, Richard** [CH/CH]; Avenue du Lavaux 10, CH-1009 Pully (CH).
- (21) International Application Number: PCT/US2004/022124
- (22) International Filing Date: 12 July 2004 (12.07.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:

60/487,946	18 July 2003 (18.07.2003)	US
60/530,231	18 December 2003 (18.12.2003)	US
- (71) Applicants (for all designated States except US): **TETRA LAVAL HOLDINGS & FINANCE S.A.** [CH/CH]; Avenue Général-Guisan 70, CH-1009 Pully (CH). **TETRA PAK INC.** [US/US]; 33 West Wacker Drive, 15th Floor, Chicago, Illinois 60606 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **BÜRKI, Monika**
- (74) Agents: **SWECKER, Robert, S.?** et al.; Burns, Doane, Swecker & Mathis, LLP, P. O. Box 1404, Alexandria, Virginia 22313-1404 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

[Continued on next page]

(54) Title: PLASTIC GAS BARRIER PACKAGING LAMINATE



(57) **Abstract:** The invention relates to a gas barrier packaging laminate (10) having durability to stress crack formation and yet a bending stiffness and good integrity between the laminate layers, comprising outer layers of heat-sealable polyolefin (16, 17), two polymer carrier layers (11, 12) each being coated with a SiO_x gas barrier layer (13, 14), wherein the two polymer carrier layers with SiO_x layers are laminated to each other by means of an intermediate polymer layer (15), which includes a thermoplastic polymer having high elastomeric properties. The required stiffness of the packaging laminate is obtained by forming a structural sandwich construction with two stiff carrier layers separated by a relatively thick lower density intermediate layer. Preferably, the thickness of the intermediate polymer layer (15) constitutes from about 30 to about 55% of the total thickness of the packaging laminate (10). The invention also relates to a packaging container such as a pouch or similar manufactured from the packaging laminate and to a method of manufacturing of the packaging laminate.

WO 2005/007518 A2



European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— *without international search report and to be republished upon receipt of that report*

PLASTIC GAS BARRIER PACKAGING LAMINATE

TECHNICAL FIELD OF THE INVENTION

The present invention relates to a gas barrier packaging laminate having
5 durability to stress crack formation and yet a bending stiffness and good integrity
between the laminate layers, comprising outside layers of heat-sealable olefin
polymer, a first gas barrier layer of SiO_x, coated onto a first polymer carrier layer
and a second gas barrier layer of SiO_x, coated onto a second polymer carrier layer,
and an intermediate polymer layer laminated between the first and the second gas
10 barrier coated polymer carrier layers. The invention also relates to a method of
manufacturing the packaging laminate and to packaging containers produced from
the packaging laminate.

BACKGROUND OF THE INVENTION

15 On the market today, there is an increasing demand for packages for
beverage and liquid food of the type that are single-use disposable plastic pouches,
preferably at least partly, at some portion of the package, transparent to display the
contents to the consumer when exposed on the shelf, e.g. in the food store. Most
commonly such packages are provided with a straw for direct drinking or a pull-tab
20 for opening and pouring of the contents. Such packages do not have the advantage
of having the dimension and grip stability of the more common paperboard
packaging laminate drink packages of the Tetra Brik® - type. However, they have
the image of a more positive environmental profile in many countries, with the
argument that the amount of used packaging material as well as the volume of the
25 emptied package is very small and because it may be recyclable with other similar
flexible plastic items. Furthermore, the traditional Tetra Brik-type packages have an
oxygen barrier layer of aluminium foil, which in some countries is less desirable and
which also makes a transparent package impossible.

In the high-speed, continuous packaging processes well known for the
30 paperboard packages of the Tetra Brik® -type, a web of the packaging laminate is
continuously formed into a tube, filled with contents and sealed off to pillow-shaped
packaging containers by a simultaneous heat sealing and cutting operation. The

- 2 -

pillow-shaped packaging container is then normally foldformed into a parallelepipedic packaging container. The main advantage of this continuous tube-forming, filling and sealing packaging process concept is that the web may be sterilized continuously just before tube-forming, thus providing for the possibility of an aseptic packaging process, i.e. a process wherein the liquid content to be filled as well as the packaging material itself are reduced from bacteria and the filled packaging container is produced under clean circumstances such that the filled package may be stored for a long time even at ambient temperature, without the risk of growth of microorganisms in the filled product. An important factor for long-term storage is of course also the gas barrier properties of the filled and sealed packaging container, which in turn is highly dependent on the gas barrier properties of the packaging laminate itself but also on the qualities of the seals and of the opening arrangement of the final package. Another important advantage of the Tetra Brik® -type packaging process is, as stated above, the possibility of continuous high-speed packaging, which has considerable impact on cost efficiency. The pouch-type drink packages available today on the market, are however, typically manufactured by other non-aseptic, more complex and expensive processes of less continuous character.

In the prior art it is also known to apply gas barrier coatings of SiO_x onto a substrate by means of plasma enhanced chemical vapor deposition (PECVD). The advantages with a SiO_x gas barrier layer compared to other gas barrier materials are firstly that it has a positive environmental profile, secondly, that it is not affected, i.e. the barrier properties remain intact, when in contact with surrounding moisture or liquid, it is transparent and since it is applied in very thin layers, also flexible and resistant to cracking when bent or folded.

It is known from EP-A-385054 to laminate two gas barrier layers of a silicon compound, such as silicon dioxide, facing each other, by means of an intermediate adhesive layer. This document, however, is silent on the resistance to stress crack formation and the laminate layer integrity at mechanical stress and the stiffness properties of the laminate and does not describe an intermediate layer providing a shock absorbing but yet stiffening effect to the laminate. Moreover, the silicon

- 3 -

dioxide (SiO₂) layers described are very different from the PECVD-coated layers of SiO_x intended according to this invention.

There is thus a need for a thin, gas-tight, metalfoil-free packaging laminate having suitable properties for an aseptic, continuous high-speed packaging process similar to the Tetra Brik Aseptic® packaging process. Important factors in such a process are the stiffness, elasticity and integrity of the packaging laminate. If the laminate web is too flexible and easy to displace in the high-speed tube-forming operation, the process will not be able to run safely and continuously. On the other hand, if the packaging laminate is too thick in order to obtain the required stiffness and durability, it may be difficult to manage in the fold-forming operation, and if it is not elastic and having shock absorbing properties during transport and handling, it will be prone to cracking and lose its integrity due to mechanical stress. Moreover and naturally, the cost-efficiency of the material itself will be reduced with increasing thickness. The pouch-type drink packages available today on the market often have a laminated structure including a single gas barrier layer of, for example, an ethylene vinyl alcohol polymer (EVOH), and do not have the requirements on stiffness properties according to the present invention.

It is therefore an object of the present invention to provide a packaging laminate that alleviates the above discussed disadvantages and problems.

It is an object of the present invention to provide a non-foil packaging laminate, having gas barrier properties suitable for aseptic packaging and long-term storage, as well as sufficient bending stiffness and integrity and resistance to stress crack formation at mechanical stress to be suitable for continuous, high speed packaging of liquid foods by means of a continuous tube-forming process and to provide packages durable to repetitive stress during transport and handling.

It is a further object of the invention to provide a packaging laminate film having such required stiffness and durability but being sufficiently thin for foldforming of the package at at least one end of the package.

It is a still further object of the invention to provide a packaging laminate film having the above properties but also being transparent for attractive appearance of a package produced from the laminate.

The invention is also directed to a packaging container filled with beverage or liquid food produced from the packaging laminate of the invention as well as to a method of manufacturing of the laminated packaging material of the invention.

5 SUMMARY OF THE INVENTION

The above mentioned object is achieved by means of an intermediate polymer layer laminated between the first and the second gas barrier coated polymer carrier layers. The intermediate polymer layer includes a thermoplastic polymer with high elastomeric properties and having a relatively fair bending stiffness. The
10 whole packaging structure combines both advantages of a structural sandwich construction and of a shock absorber to obtain a film with good bending stiffness and keeping its integrity in aggressive transport conditions.

The facings of a sandwich panel, here represented by the two polymer carrier layer films, act similarly to the flanges of an I-beam, resisting the bending loads and
15 increasing the bending stiffness of the structure, by being distanced from each other by an intermediate layer. However, unlike an I-beam structure, the lower density core in addition gives continuous support to the flanges or facings.

It has been observed, that the elastomeric property of the intermediate layer increases the resistance of the package to crack formation during cyclic loading, i.e.
20 exposure to repeated stresses or vibrations such as might be the case during transport, by absorbing the mechanical stresses with elastical, reversible deformations.

The solution to the above mentioned problem and need, is thus to provide a thin, packaging laminate with good gas barrier properties by means of laminating the
25 two polymer carrier layer films, coated with the SiO_x gas barrier layers, into a construction with an intermediate, distancing layer including a thermoplastic polymer with high elastomeric properties and having a relatively fair bending stiffness, the laminate further having outer heat sealable layers of thermoplastic polymer.

30 Preferably, the polymer carrier layers comprise polyester, polyamide or polypropylene materials and therefore have a certain degree of inherent stiffness, however, other relatively stiff polymers may also be employed for the carrier layers

- 5 -

according to the invention. More preferably, they are oriented films and thus have a higher degree of crystallinity than non-oriented polymer films. The structural sandwich construction of two relatively stiff carrier layers laminated to each side of such an intermediate polymer layer comprising a thermoplastic polymer with high elastomeric properties provides for a laminate having good resistance to cracking during repeated mechanical stress and surprisingly good bending stiffness in relation to its thickness. In addition, the arrangement of the two PECVD-deposited SiO_x-layers has proved to result in a much more than two-fold increased gas barrier, compared to a laminate or film containing merely one SiO_x-layer. Thus, the construction having a distancing intermediate layer also acting as a "buffer" for penetration of gas, in particular oxygen gas, provides for surprisingly improved gas barrier properties, which prove a synergistic effect resulting from this particular construction. Thus, the laminate has excellent gas barrier properties and is both economical and easy to handle in a high speed, continuous packaging process.

Preferably, the thickness of the intermediate layer does not constitute more than from about 30 to about 55 % of the total thickness of the packaging laminate, more preferably from about 35 to about 50 %.

Preferably, the thickness of the carrier layers constitutes from about 5 to about 20, more preferably from about 5 to about 16 % of the total packaging laminate. The carrier layers do not contribute to the total bending stiffness of the packaging laminate only by their mere thickness, but also by their interaction with the relatively thicker distancing intermediate layer.

Preferably, the carrier layer of oriented polymer is a premanufactured film of polyester, polyamide (PA) or polypropylene (PP), such as a cast or co-extrusion cast film or more preferably a mono- or biaxially oriented polyethyleneterephthalate (PET), polyethylenenaphthenate (PEN), polyamide (PA), polypropylene (PP) polymer film or a multilayer film comprising a substrate surface layer of such a polymer or a multilayer film comprising at least one such mono- or biaxially oriented layer. By using premanufactured oriented polymer films as the carrier layers, it is ensured that they have some inherent bending stiffness relative to other layers in the laminate that are extrusion or coextrusion laminated, also at lower thicknesses.

- 6 -

Also preferably, the polymer of the intermediate layer is a very low density polyethylene (VLDPE), ultra low density polyethylene (ULDPE), ethylene-based co-polymer or terpolymer, polyolefin-based elastomer or plastomer. More preferably, the polymer of the intermediate layer is a polyethylene copolymer or is
5 VLDPE or ULDPE either alone or in a blend with another olefin polymer component, such as high density polyethylene (HDPE), medium density polyethylene (MDPE), polypropylene (PP) or copolymers of polypropylene. The other polyolefin component of the blend may be included by up to 35 weight %. A particularly well functioning example of a shock absorbing polymer is "Attane ®"
10 VLDPE from Dow.

Thus, preferably, the polymer of the intermediate layer is a thermoplastic polymer with high elastomeric properties and ability to provide a relatively fair bending stiffness to the laminate, which imparts to the pouch or walls of the packaging laminate flexibility enough to absorb and dampen energy of impacts,
15 without leading to ruptures and leaking along sealing areas, e.g., the transversal top sealing of a wedge-like pouch, and the polymer of the carrier layer is an oriented polypropylene, or preferably, an oriented polyester or polyamide.

Comparative simulation transport tests (more severe, however, than normal reality transport conditions) were carried out on packages made from laminate
20 structures according to the invention having exactly the same outermost sealing layers, two SiOx-coated carrier layers of the same thickness and type and an intermediate layer having the same thickness in all tests. The packages were all produced in the same way. The only difference between the packages tested was that the intermediate layer of the laminate structures was made of VLDPE in some
25 cases, compared to LDPE in some other cases and HDPE in still some other cases. Leakages occurred both among the packages having LDPE and HDPE intermediate layers, while there were practically no leakages from the packages having VLDPE as the intermediate layer. Out of 20 packages tested, i.e., placed on a shaking table and exposed to repetitive vibrations during 30 minutes, having 100 % HDPE in the
30 intermediate layer, there were about 16-19 leaking packages. Out of 20 packages tested having 100% VLDPE in the intermediate layer, there were 0-1 leakages.

- 7 -

Experiments showed also that inclusion of up to 35% HDPE, for example, in a VLDPE intermediate layer, still resulted in significantly improved transport simulation test results.

According to a most preferred embodiment of the invention, the gas barrier
5 layers of SiO_x are positioned in the laminate such that they are facing each other, with the intermediate polymer layer between them. In this way, optimal gas barrier layers may be obtained and the layers of SiO_x will be protected in the best way. However, also embodiments where one or both of the SiO_x layers are facing outwards in the laminate structure are conceivable.

10 The SiO_x layer is preferably deposited by PECVD technique, wherein $x=1.7$ to 2.0, at a thickness of from about 50 to about 500 angstrom (Å), preferably from about 80 to about 300 Å. There exist alternative methods of depositing inorganic layers, such as SiO_x, onto polymer films, which however, generally result in thicker and less flexible layers of the SiO_x. This in turn, due to the formation of cracks in
15 the SiO_x layer, generally results in laminates of lower quality with regard to oxygen barrier properties. It is thus preferred according to the invention that the SiO_x gas barrier layers are applied by means of the continuous method of plasma enhanced chemical vapor deposition, PECVD, of SiO_x from a plasma of an organic silicon compound, such as hexadimethylsiloxane (HDMSO).

20 Preferably, the thickness of the carrier polymer layer is from about 7 to about 30 microns (μm), more preferably from about 8 to about 20, most preferably from about 8 to about 15 μm, and according to a preferred embodiment, the two carrier polymer films have about the same or exactly the same thickness. It is known that the PECVD process works optimally with the above thickness of the carrier layer,
25 which is also preferred from the economical point of view. In order to ensure a symmetrical and reliable behavior in the filling and packaging operation, it is best to employ carrier layers, i.e., the outer layers of the sandwich construction, that have about the same or exactly the same thickness, although it may be possible for certain desired properties to use carrier layers of different thickness or bending stiffness.

30 Preferably, the thickness of the intermediate layer is from about 30 to about 80 μm, more preferably from about 35 to about 65 μm, most preferably from about 40 to about 65 μm and preferably, while the total thickness of the packaging

- 8 -

laminates is from about 100 to about 180 μm , most preferably from about 100 to about 150 μm .

For the optimal shock-absorbing effect, the thickness of the intermediate layer should be from about 40 to about 65 μm , when the intermediate layer
5 comprises a polymer, such as for example VLDPE or VLDPE blended with another polymer, such as HDPE. For other alternative intermediate layer polymers, it may be feasible to use thicker intermediate layers such as up to 80 μm , in particular if the total thickness of the packaging laminate is desired to be from about above 150 to about 180 μm .

10 Thus, preferably, the thickness of the intermediate layer (15) is from 35 to 65 μm , the thickness of the polymer carrier layer (11,12) is from 8 to 15 μm , the thickness of the outside layers of heat-sealable olefin polymer (16,17) is from 10 to 25 μm and from 18 to 30 μm , respectively, and the total thickness of the packaging laminate is from 100-150 μm .

15 More preferably, the thickness of the intermediate layer (15) is from 40 to 65 μm , the thickness of the polymer carrier layer (11,12) is from 12 to 15 μm , the thickness of the outside layers of heat-sealable olefin polymer (16,17) is from 10 to 25 μm and from 18 to 30 μm , respectively, and the total thickness of the packaging laminate is from 100 to 150 μm .

20 According to another preferred embodiment, the thickness of the intermediate layer (15) is from 40 to 65 μm , the thickness of the polymer carrier layer (11,12) is from 8 to 12 μm , the thickness of the outside layers of heat-sealable olefin polymer (16,17) is from 10 to 25 μm and from 18 to 30 μm , respectively, and the total thickness of the packaging laminate is from 100 to 150 μm .

25 Preferably, for an optimal bending stiffness and elastic properties, the ratio between the thickness of the intermediate layer and the carrier layer is from 2 to 8.5 and the ratio of the total thickness of the packaging laminate to the thickness of the intermediate layer is from 1.5 to 5 when the total thickness is from 100 to 150 μm , or, the ratio between the thickness of the intermediate layer and the carrier layer is
30 from 4 to 10 and the ratio of the total thickness of the packaging laminate to the thickness of the intermediate layer is from 1.7 to 3 when the total thickness is from 150 to 180 μm .

- 9 -

A further preferred important advantage is that such a packaging laminate may be transparent to provide packages having at least a portion that is transparent to make the filled contents visible.

According to another aspect of the invention, there is provided a packaging
5 container filled with beverage or liquid food, preferably an aseptic packaging container, produced from the packaging laminate of the invention.

The packaging container according to the invention is a pouch or stand-up pouch or similar and is durable at handling and distribution and resistant to moisture and oxygen gas during long term storage, due to the high quality packaging
10 laminate, which in turn also provides for high seal quality and excellent gas barrier properties. A further important advantage of packaging containers produced from the packaging laminate according to the invention is that they are durable to microwave cooking or thawing, as well as retorting.

According to a further aspect of the invention, there is provided a method of
15 manufacturing of the laminated packaging material of the invention.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

Further advantages and favorable characterizing features of the present invention will be apparent from the following detailed description, with reference to
20 the appended figures, in which:

Figure 1 is a cross-sectional view of a preferred laminated packaging material according to the present invention.

Figure 2 shows a preferred example of a packaging container produced from the packaging laminate according to the invention.

25 Figures 3a, 3b, and 3c show alternative preferred embodiments of methods of manufacturing of the packaging laminate.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Figure 1 thus shows a packaging laminate 10, comprising a first and second
30 carrier layer 11,12 being a film of a preferably oriented polyester, such as for example polyethyleneterephthalate (PET, OPET or BOPET), or a film of a preferably oriented polyamide (PA), onto which are coated thin gas barrier layers of SiOx

- 10 -

13;14 by means of plasma enhanced chemical vapor deposition (PECVD). The two SiOx layers are preferably directed towards the interior of the laminate, thus facing each other. Between the two carrier layers coated with gas barrier layers, is laminated an intermediate layer 15 including a thermoplastic, preferably polyolefin-based, polymer having high elastomeric properties, such as for example very low density polyethylene (VLDPE), ultra low density polyethylene (ULDPE), polyethylene-based copolymers or terpolymers, polyolefin-based elastomers or plastomers. The intermediate layer is thicker than any of the surrounding layers in the packaging laminate, and provides as such a distancing element between the two carrier layer films of oriented polymer.

The preferred oriented polymer films have a certain degree of inherent stiffness in that they are oriented and thus may have a relatively higher degree of crystallinity than non-oriented polymer films. The sandwich construction of two relatively stiff carrier layers laminated on each side of a thicker and relatively soft and/or elastomeric intermediate polymer layer provides for a laminate having surprisingly good bending stiffness in relation to its thickness. For example, two BOPET films of 12 μm thickness were laminated close together by merely a thin lamination layer in between of about 10 g/m^2 of polyolefin-based polymer, e.g., VLDPE. The stiffness value measured on this laminate was 0.6 mNm. Further polyolefin-based outer layers did not alter this result significantly. However, if the same two BOPET films were laminated to each other by means of a thick lamination layer of about 55 g/m^2 of, e.g., VLDPE, the stiffness value measured was 2 mNm, i.e., significantly stiffer. The stiffness contribution of a 55 g/m^2 thick layer of VLDPE on the outside of the laminate (of the two BOPET layers), on the other hand, would not alter the stiffness value much from 0.6 mNm. In addition, the arrangement of the two PECVD-deposited SiOx-layers has proved to result in a much more than two-fold increased gas barrier, compared to a laminate or film containing merely one SiOx-layer. Thus, the arrangement of an intermediate layer also acting as a "buffer" for penetration of gas, in particular oxygen gas, provides for surprisingly improved gas barrier properties, which indicates a synergistic effect resulting from this particular arrangement. As an example, if two films of SiOx-coated BOPET, each having an OTR value of about 4 $\text{cc}/\text{m}^2 \cdot 24\text{h}$ at 23°C and 50%

- 11 -

RH are laminated to each other by a thin polyolefin-based layer, the OTR value of the total construction will be about $2 \text{ cc/m}^2 \cdot 24\text{h}$ at 23°C and 50% RH. When the same films are laminated together with at least one intermediate polyolefin-based polymer layer of a thickness of about 55 g/m^2 , the OTR value is improved to about
5 $0.2 \text{ cc/m}^2 \cdot 24\text{h}$ at 23°C and 50% RH. Similarly, if two films of SiOx-coated BOPET, each having an OTR value of about $1.6 \text{ cc/m}^2 \cdot 24\text{h}$ at 23°C and 50% RH are laminated to each other by a thin polyolefin-based layer, the OTR value of the total construction will be about $0.8 \text{ cc/m}^2 \cdot 24\text{h}$ at 23°C and 50% RH. When the same films are laminated together with at least one intermediate polyolefin-based
10 polymer layer of a thickness of about 55 g/m^2 , the OTR value is improved to about $0.16 \text{ cc/m}^2 \cdot 24\text{h}$ at 23°C and 50% RH. Thus, the improvement of the gas barrier by the "buffer effect" is at least four- to five-fold the improvement from using just double gas barrier films directly laminated to each other.

On the outside of the carrier layer 11, which will constitute the outside wall
15 of a packaging container produced from the packaging laminate, is applied at least one layer 16 of a heat-sealable olefin polymer, preferably a low density polyethylene (LDPE) or a linear low density polyethylene (LLDPE), which include also so-called metallocene-catalysed LLDPE's (m-LLDPE), i.e., LLDPE polymers catalyzed by means of a single site catalyst. Other examples of alternative polymers for the
20 outside packaging wall layer may be medium high density polyethylene (MDPE) or polypropylene (PP).

On the outside of the carrier layer 13, which will constitute the inside wall of a packaging container produced from the packaging laminate, is applied at least one layer 17 of a heat-sealable olefin polymer, preferably a layer of LDPE, more
25 preferably a layer of LLDPE and most preferably a first part-layer 17a of LDPE and a second outermost part-layer 17b of LLDPE.

The outside layers 16, 17 are applied each in a quantity of from about 10 to about $30 \mu\text{m}$, for optimal heat sealability properties in relation to cost efficiency.

For good adhesion between the various layers of the packaging laminate,
30 there are preferably used binder layers of adhesive polymers, tie layers and primers, known in the art. Such binder layers and primers are adapted to the specific choices

- 12 -

of polymer in the various layers and may be selected from polyolefins and modified polyolefins, preferably polyethylene-based polymers, such as for example LDPE and modified LDPE.

Such examples of binder layers are LPDE homo- or copolymers or graft
5 copolymers of polyethylene, grafted with monomers comprising carboxylic or glycidyl functional groups, such as acrylic monomers or maleic anhydride (MAH) monomers, for example ethylene (meth)acrylic acid copolymer (E(M)AA), ethylene-glycidyl(meth)acrylate copolymer (EG(M)A) or MAH-grafted polyethylene (MAH-g-PE).

10 Preferably, for optimal adhesion in the binder layers 18;19 between the layers of SiO_x 13:14 and the intermediate polyolefin layer 15, there is used a polyethylene base polymer graft modified by an unsaturated alkoxy silane compound, such as described in US Patent No. 5,731,092, herein incorporated by reference. See especially column 1, line 39 to column 3, line 21 and Examples 1 and
15 2.

Most preferably, the polyethylene base polymer graft modified by an unsaturated alkoxy silane compound is blended with a non-grafted polyethylene, such as preferably low density polyethylene (LDPE). Surprisingly, it has been found that the number of adhesion points between the grafted sites in the binder and
20 the silicon oxide can be vastly increased if the grafted polyolefin is blended with a non-grafted polyolefin, i.e., the number of adhesion points increases despite less grafted sites in the binder polymer.

This most preferred embodiment is based on the insight that it is not only the number of grafted sites that affects the degree of adhesion, but also their ability to
25 physically come in contact with the silicon oxide. It has been found that the grafting of polyolefin according to US 5,731,092 results in a cross-linking of the polyolefin, which makes the polyolefin less flexible than the non-grafted polyolefin. Due to the impaired flexibility of the grafted polyolefin, the number of contact points between the binding layer composed of the grafted polyolefin and the silicon oxide will be
30 less than for a binding layer solely composed of a non-grafted polyolefin of the same type. However, in a binding layer solely composed of a non-grafted polyolefin, the adhesion in an individual adhesion point of the plurality of adhesion points will not

- 13 -

be as good as in an individual adhesion point of a binding layer composed solely of a grafted polyolefin.

The preferred embodiment in addition solves the problem related to these contradictory aspects of grafted and non-grafted polyolefin binders, by providing a binder that is a blend of a grafted polyolefin and a non-grafted polyolefin. Here, the improved flexibility that is achieved due to the presence of a non-grafted polyolefin provides for an increased number of adhesion points, while the grafted polyolefin provides for improved adhesion in those points, all in all resulting in adhesion properties that are better than the adhesion properties of a grafted polyolefin binder per se and a non-grafted polyolefin binder per se.

Whenever binder layers are used between the intermediate shock absorbing layers and the SiOx layers, the thickness referred to as the thickness of the intermediate layer also includes the thicknesses of such binder layers.

Any of the above discussed polymers may also be used in optional binder layers 20,21 between the outer heat-sealable polyolefin layers 16,17 and the polymer carrier layers 11,12.

Figure 2 shows a preferred example of a packaging container 20 produced from the packaging laminate 10 according to the invention. The packaging container is particularly suitable for small beverage packages for direct use by means of a drinking straw or the like. Typically, such a package has a volume of about 330 ml or less, preferably from about 100 to about 250 ml, for example about 125 ml, 200 ml or about 250 ml. It may be a pouch of any configuration, but is preferably shaped as a wedge 21, such that it is easy to handle and dimensionally stable when put on a shelf in the food store or on a table or the like. In order to obtain such a "wedge-shape", the bottom part 22 of the package is fold formed such that the transversal heat seal 24 of the bottom is hidden under the triangular corner flaps 23, which are folded and sealed against the bottom of the package. The packaging container 20 is preferably transparent.

Figure 3a shows a preferred embodiment 30a of a method of producing the packaging laminate 10 according to the invention.

A first web 331 of a polymer carrier layer 332 coated with a SiOx gas barrier layer 333, and a second web 334 of a polymer carrier layer 335 coated with a SiOx

- 14 -

gas barrier layer 336, are advanced towards an extrusion station 337, the two SiOx layers 333 and 336 preferably facing each other, and laminated to each other by means of extruding an intermediate polymer layer 338 between them and pressing the two webs 331, 334 and the intermediate layer 338 together when passing a roller nip after the extrusion station 337. The intermediate polymer layer 338 may be coextruded together with adjacent layers of binder polymer 339 for improved bonding to the SiOx-layers on the two webs 331 and 334. The resulting laminated web 340 is advanced to an extrusion station 341, where an outside layer of a heat-sealable polyolefin 342 is extruded onto the outside of the polymer carrier layer 335. The thus resulting web 343 is further advanced to an extrusion station 344, where an outside layer of a heat-sealable polyolefin 345 is extruded onto the outside of the polymer carrier layer 332. The resulting packaging laminate 346 will then be wound up and stored onto a reel, not shown.

Figure 3b shows another preferred embodiment 30b of a method of producing the packaging laminate 10 according to the invention.

A first web 331 of a polymer carrier layer 332 coated with a SiOx gas barrier layer 333, and a second web 334 of a polymer carrier layer 335 coated with a SiOx gas barrier layer 336, are advanced towards an extrusion station 337, the two SiOx layers 333 and 336 preferably facing each other, and laminated to each other by means of extruding an intermediate polymer layer 338 between them and pressing the two webs 331, 334 and the intermediate layer 338 together when passing a roller nip after the extrusion station 337. The intermediate polymer layer 338 may be coextruded together with adjacent layers of binder polymer 339 for improved bonding to the SiOx layers on the two webs 331 and 334. The resulting laminated web 340 is advanced to a hot roller nip 341', where an outside layer of a premanufactured film comprising at least one layer of a heat-sealable polyolefin 342' is laminated to the outside of the polymer carrier layer 335, by means of application of heat and pressure in the hot roller nip 341'. The thus resulting web 343' is further advanced to a hot roller nip 344', where an outside layer of a heat-sealable polyolefin 345' is laminated to the outside of the polymer carrier layer 332, by application of heat and pressure in the hot roller nip 344'.

The resulting packaging laminate 346' will then be wound up and stored onto a reel, not shown.

Figure 3c shows a further preferred embodiment 30c of a method of producing the packaging laminate 10 according to the invention.

5 A first web 331 of a polymer carrier layer 332 coated with a SiOx gas barrier layer 333, and a second web 334 of a polymer carrier layer 335 coated with a SiOx gas barrier layer 336, are advanced towards a hot roller nip 337', the two SiOx layers 333 and 336 preferably facing each other, at the same time as a web of a pre-manufactured film of an intermediate polymer layer 338' is advanced between the
10 two webs 331, 334 towards the nip 337'. The three webs are laminated to each other by application of heat and pressure when passing the hot roller nip 337'. The intermediate polymer layer 338' may be a premanufactured film having outer layers of binder polymer 339 for improved bonding to the SiOx-layers on the webs 331,334. The resulting laminated web 340' is advanced to a hot roller nip 341',
15 where an outside layer of a pre-manufactured film comprising at least one layer of a heat-sealable polyolefin 342' is laminated to the outside of the polymer carrier layer 335, by means of application of heat and pressure in the hot roller nip 341'. The thus resulting web 343'' is further advanced to a hot roller nip 344', where an outside layer of a pre-manufactured film comprising at least one layer of a heat-sealable
20 polyolefin 345' is laminated to the outside of the polymer carrier layer 332, by application of heat and pressure in the hot roller nip 344'.

The resulting packaging laminate 346'' will then be wound up and stored onto a reel, not shown.

25 In the method 30a above, the extrusion stations 341 and 344 may be passed in the opposite order according to an alternative preferred embodiment.

In each of the methods 30b and 30c above, the lamination of the outside heat-sealable polyolefin films may be carried out in the opposite order, i.e. by first laminating the premanufactured film 345' to the outer side of the polymer carrier layer 332, in the hot roller nip 344', thus resulting in a web 347. The web 347 is
30 further advanced to a hot roller nip 341', in which the outside heat-sealable pre-manufactured film 342' is then laminated to the outer side of the polymer carrier layer 335, thus resulting in the packaging laminate 346' or 346''.

- 16 -

Other combinations of hot-nip lamination and extrusion lamination are conceivable within the concept of the invention, although not represented by separate drawings. For example, a method wherein the intermediate polymer layer 338' is a pre-manufactured film to be hot-nip laminated as described in Figure 3c, 5 may be combined with extrusion lamination of one or both of the outer heat-sealable layers 342 and 345, such as described in connection with Figure 3a.

According to other preferred embodiments of the methods 30a, 30b and 30c, the surface of the SiO_x gas barrier layer 333, 336 is treated by a surface oxidation treatment such as corona treatment, in order to provide improved adhesion to the 10 intermediate polymer layer 338; 338' or the binder layers 339; 339'.

According to an alternative embodiment of the method of manufacturing the packaging laminate of the invention, the various pre-manufactured webs 331, 334, 338', 342' and 345' are laminated to each other by means of primer lamination, i.e. lamination by means of coating and drying a primer or anchoring agent onto one of 15 the webs and then laminating through a roller nip.

The packaging laminate 10 may be provided with a printed decor layer in order to render the packaging container more attractive and informative to consumers and to protect its contents against light, which printed decor may be applied onto the SiO_x layer 333 or 336, which is directed towards the outside of a 20 package formed from the packaging laminate. Alternatively it may be applied onto the other side of the carrier layer 332 or onto the outside layer of heat-sealable polyolefin 342, 345; 342', 345'. In the latter case, the printed outside should preferably be covered by a thin, transparent protective polymer layer.

By way of conclusion it should be observed that the present invention which 25 has been described above with particular reference to the accompanying figures, is not restricted to these embodiments described and shown exclusively by way of example, and that modifications and alterations obvious to a person skilled in the art are possible without departing from the inventive concept as disclosed in the appended claims.

Claims

1. A gas barrier packaging laminate (10) having durability to stress crack formation and yet a bending stiffness and good integrity between the laminate layers, comprising:
- 5 outside layers of heat-sealable olefin polymer (16, 17);
a first gas barrier layer of SiOx (13) coated onto a first polymer carrier layer (11);
a second gas barrier layer of SiOx (14) coated onto a second polymer carrier layer (12); and
- 10 an intermediate polymer layer (15) laminated between the first and the second gas barrier coated polymer carrier layers,
wherein the intermediate polymer layer includes a thermoplastic polymer with high elastomeric properties and wherein a stiffness of each of the first and second polymer carrier layers interacts with a thickness of the intermediate polymer as a shock absorbing, distancing layer in a structural sandwich construction, to provide the durability to stress-cracking, bending stiffness and good integrity between the layers.
- 15
2. The gas barrier packaging laminate according to claim 1, wherein the durability to stress-cracking, bending stiffness and integrity between the layers renders the packaging laminate suitable for packaging of liquid foods and drinks by a high speed, continuous process.
- 20
3. The gas barrier packaging laminate according to claim 1, wherein the thickness of the intermediate layer (15) is from 30 to 55% of a total thickness of the packaging laminate (10).
- 25
4. The gas barrier packaging laminate according to claim 3, wherein the thickness of the intermediate layer (15) is from 35 to 50% of the total thickness of the packaging laminate (10).
- 30

- 18 -

5. The gas barrier packaging laminate according to claim 1, wherein a thickness of the first polymer carrier layer (11) or a thickness of the second polymer carrier layer (12) is from 5 to 20 % of a total thickness of the packaging laminate (10).

5

6. The gas barrier packaging laminate according to claim 5, wherein the thickness of the first polymer carrier layer (11) or the thickness of the second polymer carrier layer (12) is from 5 to 15 % of the total thickness of the packaging laminate (10).

1.0

7. The gas barrier packaging laminate according to claim 1, wherein the first polymer carrier layer (11) or the second polymer carrier layer (12) is a film of polyester, polyamide or polypropylene or a multilayer film comprising a substrate surface layer of one of said polymers.

1.5

8. The gas barrier packaging laminate according to claim 1, wherein the first polymer carrier layer (11) or the second polymer carrier layer (12) is a film of a polymer selected from the group consisting of mono- or biaxially oriented polyethyleneterephthalate (PET), mono- or biaxially oriented polyethylenenaphthenate (PEN), mono- or biaxially oriented polyamide (PA) and mono- or biaxially oriented polypropylene or a multilayer film comprising at least one oriented layer of one of said polymers.

2.0

9. The gas barrier packaging laminate according to claim 1, wherein the thermoplastic polymer with high elastomeric properties of the intermediate layer (15) is selected from the group consisting of very low density polyethylene, ultra low density polyethylene, polyethylene copolymers, polyethylene terpolymers, polyolefin-based elastomers and plastomers, and a blend of very low density polyethylene or ultra low density polyethylene with another polyolefin.

3.0

10. The gas barrier packaging laminate according to claim 1, wherein the thermoplastic polymer with high elastomeric properties of the intermediate layer

- 19 -

(15) includes very low density polyethylene and a polymer of the first polymer carrier layer (11) and a polymer of the second polymer carrier layer (12) include an oriented polyester or polyamide.

5 11. The gas barrier packaging laminate according to claim 1, wherein the first gas barrier layer of SiO_x (13) and the second gas barrier layer of SiO_x (14) are positioned in the laminate facing towards each other.

10 12. The gas barrier packaging laminate according to claim 1, wherein the first gas barrier layer of SiO_x (13) and the second gas barrier layer of SiO_x (14) are deposited by PECVD technique at a thickness of from 50 to 500 Å, and wherein x=1.7-2.0.

15 13. The gas barrier packaging laminate according to claim 12, wherein the thickness is from 80 to 300 Å.

 14. The gas barrier packaging laminate according to claim 1, wherein a thickness of the first polymer carrier layer (11) or a thickness of the second polymer carrier layer (12) is from 7 to 30 μm.

20

 15. The gas barrier packaging laminate according to claim 14, wherein the thickness of the first polymer carrier layer (11) or the thickness of the second polymer carrier layer (12) is from 8 to 20 μm.

25 16. The gas barrier packaging laminate according to claim 15, wherein the thickness of the first polymer carrier layer (11) or the thickness of the second polymer carrier layer (12) is from 8 to 15 μm.

30 17. The gas barrier packaging laminate according to claim 1, wherein the first polymer carrier layer (11) and the second polymer carrier layer (12) have the same thickness.

- 20 -

18. The gas barrier packaging laminate according claim 1, wherein the thickness of the intermediate layer (15) is from 30 to 80 μm .

19. The gas barrier packaging laminate according claim 18, wherein the
5 thickness of the intermediate layer (15) is from 35 to 65 μm .

20. The gas barrier packaging laminate according claim 19, wherein the thickness of the intermediate layer (15) is from 40 to 65 μm .

10 21. The gas barrier packaging laminate according to claim 1, wherein a total thickness of the packaging laminate is from 100 to 180 μm .

22. The gas barrier packaging laminate according to claim 21, wherein the total thickness of the packaging laminate is from 100 to 150 μm .

15

23. The gas barrier packaging laminate according to claim 1, wherein the thickness of the intermediate layer (15) is from 35 to 65 μm , a thickness of the first polymer carrier layer (11) or a thickness of the second polymer carrier layer (12) is from 8 to 15 μm , a thickness of the outside layers of heat-sealable olefin polymer (16,17) is from 10 to 25 μm and from 18 to 30 μm , respectively, and a total
20 thickness of the packaging laminate is from 100 to 150 μm .

24. The gas barrier packaging laminate according to claim 23, wherein the thickness of the intermediate layer (15) is from 40 to 65 μm and the thickness of
25 the first polymer carrier layer (11) or the thickness of the second polymer carrier layer (12) is from 12 to 15 μm .

25. The gas barrier packaging laminate according to claim 23, wherein the thickness of the intermediate layer (15) is from 40 to 65 μm and the thickness of
30 the first polymer carrier layer (11) or the thickness of the second polymer carrier layer (12) is from 8 to 12 μm .

- 21 -

26. The gas barrier packaging laminate according to claim 1, wherein the intermediate polymer layer (15) is laminated to the adjacent layers of SiO_x (13,14) by means of a binder layer (18,19).

5 27. The gas barrier packaging laminate according to claim 26, wherein the binder layer (18,19) comprises a blend of a graft copolymer of alkoxy silane and polyethylene with a non-grafted polyethylene.

28. The gas barrier packaging laminate according to claim 1, wherein the
10 laminate is transparent.

29. A packaging container manufactured from the packaging laminate according to claim 1.

15 30. A method of manufacturing of a packaging laminate including outside layers of heat-sealable olefin polymer (16, 17), a first gas barrier layer of SiO_x (13) coated onto a first polymer carrier layer (11), a second gas barrier layer of SiO_x (14) coated onto a second polymer carrier layer (12); and an intermediate polymer layer (15) of a thermoplastic polymer having high elastomeric properties
20 laminated between the first and the second gas barrier coated polymer carrier layers, the method comprising the steps of:

advancing a first web (331) and a second web (334) towards each other and towards a first extrusion station (337), the first web (331) comprising a first polymer carrier layer (332) coated with a first SiO_x gas barrier layer (333) and the second
25 web (334) comprising a second polymer carrier layer (335) coated with a second SiO_x gas barrier layer (336);

laminating the first web (331) and the second web (334) to each other by means of extruding an intermediate polymer layer (338), optionally together with a binder layer (339) on each side of the intermediate polymer layer (338), between the
30 first web and the second web and pressing the first web and the second web together at the first extrusion station (337);

- 22 -

extruding a first outside layer (342) onto the outside of the first or second polymer carrier layer (332 or 335) at a second extrusion station 341, the first outside layer (342) comprising a heat-sealable polyolefin; and

extruding a second opposite outside layer (345) onto the outside of the other
5 of the second or first polymer carrier layer (335 or 332) at a third extrusion station 344, the second opposite outside layer (345) comprising a heat-sealable polyolefin.

31. The method according to claim 30, wherein the first web (331) and the second web (334) are advanced towards each other such that the SiOx gas barrier
10 layers (333, 336) are facing each other.

32. The method according to claim 30, wherein the first SiOx gas barrier layer (333) and the second SiOx gas barrier layer (336) are treated by a surface
15 activation treatment before laminating.

33. The method according to claim 32, wherein the a surface activation treatment is corona treatment.

34. A method of manufacturing of a packaging laminate including
20 outside layers of heat-sealable olefin polymer (16, 17), a first gas barrier layer of SiOx (13) coated onto a first polymer carrier layer (11), a second gas barrier layer of SiOx (14) coated onto a second polymer carrier layer (12); and an intermediate polymer layer (15) of a thermoplastic polymer having high elastomeric properties laminated between the first and the second gas barrier coated polymer carrier layers,
25 the method comprising the steps of:

advancing a first web (331) and a second web (334) towards each other and towards a first extrusion station (337), the first web (331) comprising a first polymer carrier layer (332) coated with a first SiOx gas barrier layer (333) and the second web (334) comprising a second polymer carrier layer (335) coated with a second
30 SiOx gas barrier layer (336);

laminating the first web (331) and the second web (334) to each other by means of extruding an intermediate polymer layer (338), optionally together with a

- 23 -

binder layer (339) on each side of the intermediate polymer layer (338), between the first web and the second web and pressing them together at the extrusion station (337);

laminating by application of heat and pressure at a first hot roller nip (341') a first premanufactured film (342') to the outside of the first or second polymer carrier layer (332 or 335), the first premanufactured film (342') comprising at least one layer of a heat-sealable polyolefin; and

laminating by application of heat and pressure at a second hot roller nip (344') a second premanufactured film (345') to the outside of the other of the second or first polymer carrier layer (335 or 332), the second premanufactured film (345') comprising at least one layer of a heat-sealable polyolefin.

35. The method according to claim 34, wherein the first web (331) and the second web (334) are advanced towards each other such that the SiO_x gas barrier layers (333, 336) are facing each other.

36. The method according to claim 34, wherein the first SiO_x gas barrier layer (333) and the second SiO_x gas barrier layer (336) are treated by a surface activation treatment before laminating.

37. The method according to claim 36, wherein the surface activation treatment is corona treatment.

38. A method of manufacturing of a packaging laminate including outside layers of heat-sealable olefin polymer (16, 17), a first gas barrier layer of SiO_x (13) coated onto a first polymer carrier layer (11), a second gas barrier layer of SiO_x (14) coated onto a second polymer carrier layer (12); and an intermediate polymer layer (15) of a soft and/or elastomeric polymer laminated between the first and the second gas barrier coated polymer carrier layers, the method comprising the steps of:

advancing a first web (331) and a second web (334) towards each other and towards a first hot roller nip (337), the first web (331) comprising a first polymer

- 24 -

carrier layer (332) coated with a first SiOx gas barrier layer (333) and the second web (334) comprising a second polymer carrier layer (335) coated with a second SiOx gas barrier layer (336);

laminating the first web (331) and the second web (334) to an intermediate pre-manufactured web (338') by advancing the intermediate pre-manufactured web (338') between the first web (331) and second web (334) and applying heat and pressure in the first hot roller nip (337'), the intermediate pre-manufactured web (338') comprising an intermediate polymer layer (338') and, optionally, a binder layer (339') on each side of the intermediate polymer layer (338');

laminating by application of heat and pressure at a second hot roller nip (341') a first premanufactured film (342') to the outside of the first or second polymer carrier layer (332 or 335), the first premanufactured film (342') comprising at least one layer of a heat-sealable polyolefin; and

laminating by application of heat and pressure at a third hot roller nip (344') a second premanufactured film (345') to the outside of the other of the second or first polymer carrier layer (335 or 332), the second premanufactured film (345') comprising at least one layer of a heat-sealable polyolefin.

39. The method according to claim 38, wherein the first web (331) and the second web (334) are advanced towards each other such that the SiOx gas barrier layers (333, 336) are facing each other.

40. The method according to claim 38, wherein the first SiOx gas barrier layer (333) and the second SiOx gas barrier layer (336) are treated by a surface activation treatment before laminating

41. The method according to claim 40, wherein the surface activation treatment is corona treatment.

1/2

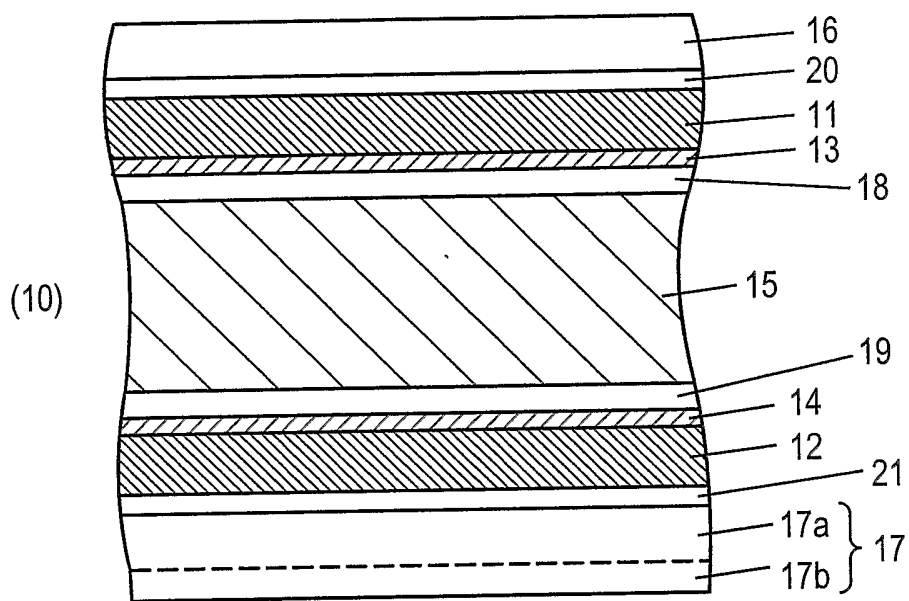


FIG. 1

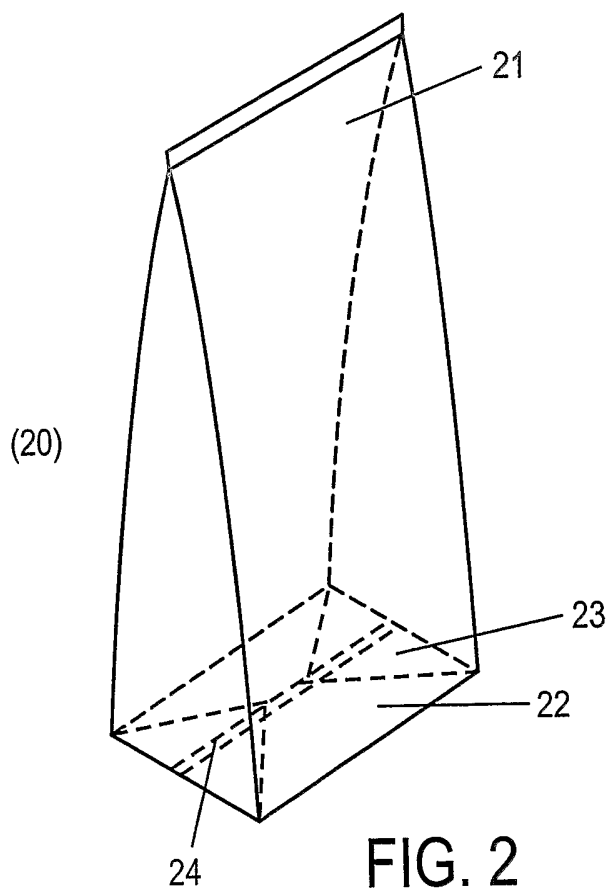


FIG. 2

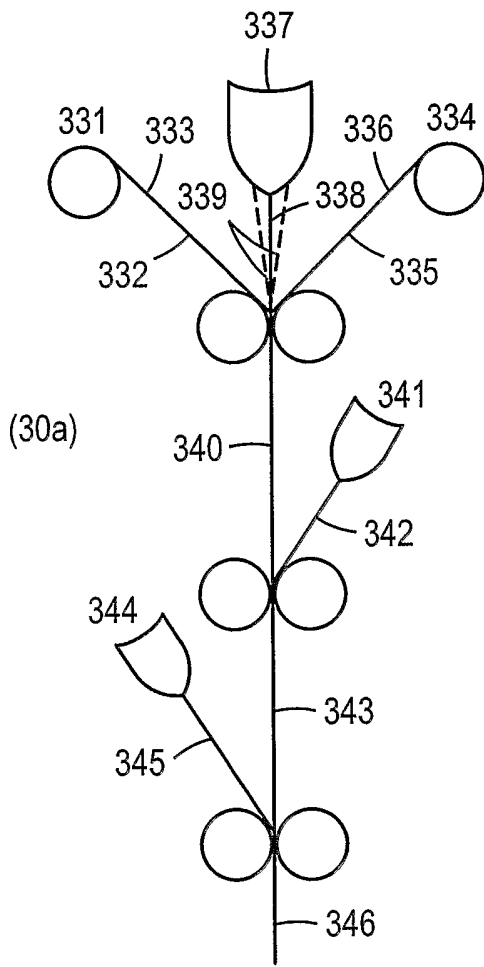


FIG. 3A

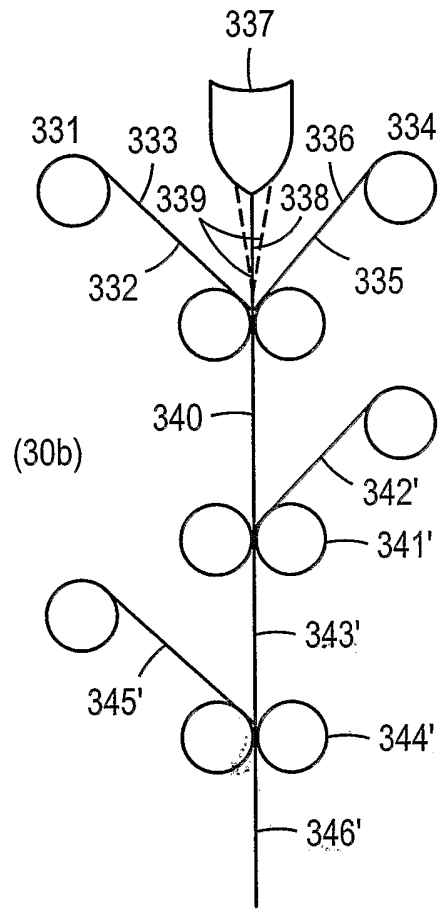


FIG. 3B

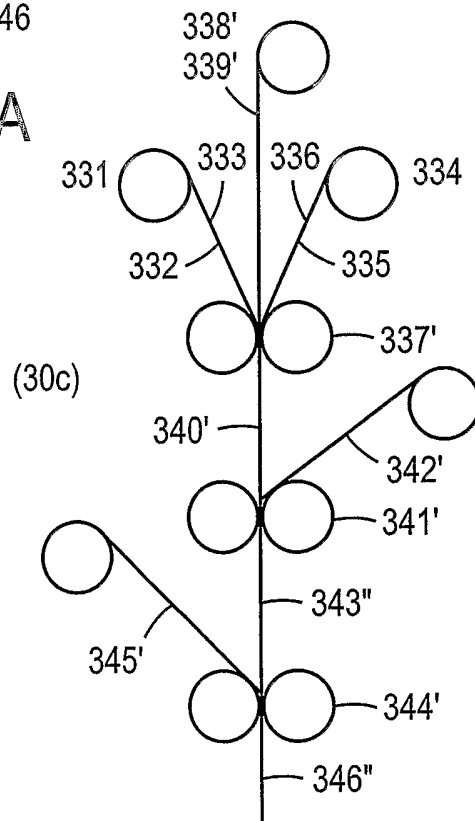


FIG. 3C