

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
21 November 2002 (21.11.2002)

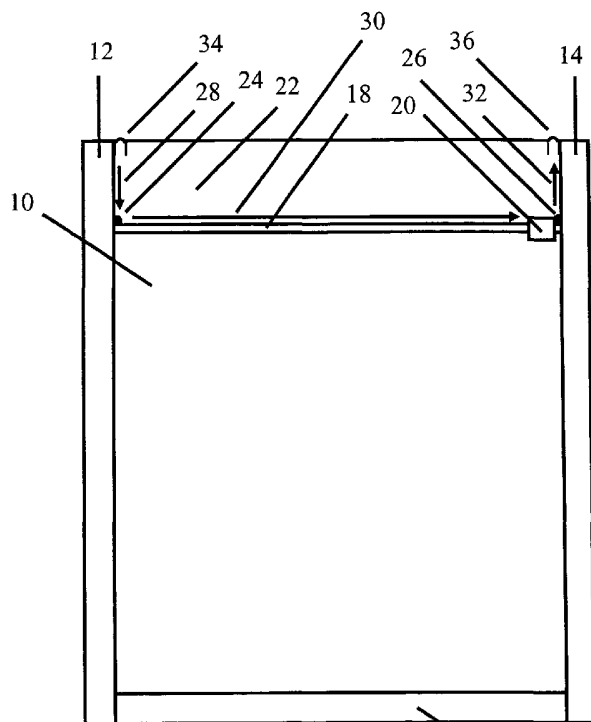
PCT

(10) International Publication Number  
WO 02/092449 A1

- (51) International Patent Classification<sup>7</sup>: B65D 33/25, 75/58, 65/40
- (21) International Application Number: PCT/US02/15442
- (22) International Filing Date: 15 May 2002 (15.05.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 09/855,459 15 May 2001 (15.05.2001) US
- (71) Applicant: HONEYWELL INTERNATIONAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07960 (US).
- (72) Inventors: COLOMBO, Frank, J.; 285 Wyndham Road, Rochester, NY 14609 (US). MOULTON, Jeffrey, D.; 22 Sand Hill Road, Morristown, NJ 07960 (US).
- (74) Agents: CRISS, Roger, H. et al.; Honeywell International Inc., 101 Columbia Avenue, P.O. Box 2245, Morristown, NJ 07960 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, 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, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: RECLOSABLE PACKAGE USING STRAIGHT TEAR FILM AND PROCESS FOR MANUFACTURE



(57) Abstract: A reclosable film package for storage of solid or liquid food products using a straight-tear film package having a zipper. The straight-tear films allow for tearing of the film along straight lines without perforating or laser scoring of the film allowing optimal integrity of the package and product.



WO 02/092449 A1



**Published:**

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

*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.*

RECLOSABLE PACKAGE USING STRAIGHT TEAR FILM AND PROCESS FOR MANUFACTURE

5

## BACKGROUND OF THE INVENTION

### Field of the Invention

10 The invention relates to a reclosable packaging system for enveloping a product. More particularly, the invention pertains to a reclosable plastic film packaging system using a zipper and straight tear films that are capable of tear propagating along substantially straight lines in response to an applied force sufficient to propagate a tear in the films.

15

### Description of the Related Art

Reclosable packages using zipper technology are well known in the art. A conventional reclosable package generally comprises a polymeric envelope comprising overlapping films which are sealed along its outer peripheral edges and having a flexible plastic zipper positioned inward from one of the edges. A plastic zipper generally comprises interlocking zipper tracks positioned below a top edge of the package for opening and closing access to an inner portion of the package. Some prior art packages have also been known to include a moveable slider adjoined to the zipper for assisting with engaging and disengaging the tracks of the zipper. For example, U.S. patent 5,896,627 discloses a high-strength plastic slider for a reclosable bag that is difficult to separate or pry loose from a zipper on which it has been mounted.

20

25

Reclosable bags using zipper technology are known to be useful for storing solid and/or liquid products. They are extremely useful for food storage in a refrigerator or freezer because zipper locking bags typically have very strong seals  
5 that are virtually impermeable to air, providing excellent oxygen and moisture barriers that prevent food from spoiling, while allowing easy access to the stored food product. Reclosable zipper bags have also been known to be used by food manufacturers in storing food products in stores for direct sale to consumers. For example, U.S. patent 6,206,571 teaches a flexible, reclosable bag for storing  
10 cereals. In applications such as these, it is generally necessary that the top edge of the package above the zipper be sealed to prevent tampering with the enclosed food product prior to sale. This feature is illustrated in U.S. patent 6,206,571 wherein a resealable pour spout is located below a sealed top.

15 When a sealed reclosable bag is used to store a product for sale to consumers, it is necessary that the bag be easily openable by the consumer once they purchase the product. A commonly employed technique for providing an easily openable bag having good tamper resistance includes perforating a portion of the bag between a top edge of the bag and the reclosable zipper and between the side edges of the  
20 bag, creating a removable strip above the perforated line. After purchasing the product at a store, the consumer may then tear the removable strip off of the bag revealing the reclosable zipper underneath, and allowing them to access the food product stored therein. Perforation of the film is desirable because it allows the consumer to tear the package along a straight line, allowing for complete removal  
25 of the removable strip so that the packaged food product can be easily poured out of the package if desired.

Various techniques have been known in the art to create such perforations, including microperforating and laser scoring. Microperforating involves the mechanical creation of tiny holes or perforations through a material to facilitate tearing along a straight line. Laser scoring involves the creation of tiny holes or perforations through the material using a laser rather than mechanically.

Although these techniques are particularly useful for easily tearing the plastic in a particular direction, each has the disadvantage of compromising the integrity of the package by allowing microbes and other potentially dangerous organisms to penetrate the package. This is particularly undesirable when the packaged good is a food product for consumption by humans. Further, laser scoring techniques are also undesirable because they are very expensive to conduct. Therefore it would be desirable to provide a plastic bag that is capable of straight tearing without the need for microperforating or laser scoring a portion of the plastic.

#### SUMMARY OF THE INVENTION

The invention provides a reclosable film package comprising:

a) first and second overlapping straight-tear films capable of propagating a tear along a locus of points in one of two substantially straight perpendicular lines in response to an applied force sufficient to propagate a tear in the films, the films being sealed together at top, bottom, left and right edges defining an enclosure, the enclosure having sealed bottom, left and right margins extending for a distance away from the bottom, left and right edges toward a center of the films; each film comprising in order from an outside portion of the enclosure to an inside portion of the enclosure:

- i. a nylon or polyester layer;
- ii. optionally, an adhesive layer; and

- iii. a sealant layer;
- b) a reclosable zipper substantially parallel with and positioned below the top edge of the films and extending between left and right end points located at the left and right margins; said zipper comprising a first track on the first straight-tear  
5 film and a second track on the second straight-tear film, which first and second tracks are adapted to releasably engage each other;
- c) a slider moveably attached to said tracks for engaging and disengaging the tracks between the end points;
- d) left and right nodules positioned at the left and right end points; and  
10 e) a tear propagation line extending from the left nodule to the right nodule substantially parallel along the zipper, and a tear propagation line extending from each of the left and right nodules substantially parallel along the left and right margins to the top edge of the films, defining a removable tear strip between the left and right margins and above the zipper.

15

This invention also provides a reclosable film package comprising:

- a) first and second overlapping straight-tear films capable of propagating a tear along a locus of points in one of two substantially straight perpendicular lines in response to an applied force sufficient to propagate a tear in the films, the films  
20 being sealed together at top, bottom, left and right edges defining an enclosure, the enclosure having sealed bottom, left and right margins extending for a distance away from the bottom, left and right edges toward a center of the films; each film comprising in order from an outside portion of the enclosure to an inside portion of the enclosure:
  - 25 i. a nylon layer;
  - ii. an adhesive layer; and
  - iii. a polyethylene layer;

- b) a reclosable zipper substantially parallel with and positioned below the top edge of the films and extending between left and right end points located at the left and right margins; said zipper comprising a first track on the first straight-tear film and a second track on the second straight-tear film, which first and second
- 5 tracks are adapted to releasably engage each other;
- c) a slider moveably attached to said tracks for engaging and disengaging the tracks between the end points;
- d) left and right nodules positioned at the left and right end points; and
- e) a tear propagation line extending from the left nodule to the right nodule
- 10 substantially parallel along the zipper, and a tear propagation line extending from each of the left and right nodules substantially parallel along the left and right margins to the top edge of the films, defining a removable tear strip between the left and right margins and above the zipper.

- 15 The invention further provides a process for forming a reclosable film package comprising:
- a) forming first and second straight-tear films by attaching a nylon layer to a sealant layer optionally via an intermediate adhesive layer, said films having top, bottom, left and right edges;
- 20 b) forming first and second zipper tracks below and substantially parallel to the top edge of the films, said tracks having left and right end points and said tracks releasably engaging each other;
- c) attaching a moveable slider to the tracks such that the slider is capable of engaging and disengaging the tracks between left and right end points;
- 25 d) adjoining the first and second straight-tear films by sealing the respective left, right and bottom edge of each film together such that the sealant layers are

attached together, and forming left, right and bottom margins, thereby forming an enclosure; and

e) forming a left nodule at an intersection of a left zipper end point and the left margin, and forming a right nodule at an intersection of a right zipper end point  
5 with the right margin.

The present invention provides a solution to the problems of the prior art. The invention provides a package utilizing a straight tearing film that is easily tearable in a particular direction in response to a stress applied in that direction. The  
10 invention also allows for the direction of tearing to be easily changed in a direction perpendicular to the initial tearing direction to facilitate the full removal of a tear strip above a reclosable zipper. The straight tearing films have good toughness, eliminates the need for perforating and provides an excellent barrier to oxygen and moisture while preventing contamination of the food product by  
15 microbes or other organisms.

#### BRIEF DESCRIPTION OF THE DRAWINGS

20 Figure 1 is a schematic representation of a reclosable bag.

Figure 2 is a schematic representation of a reclosable bag after removal of the tear strip.

25

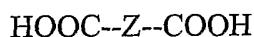


DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention provides a reclosable film package for storage of solid or liquid products, such as foods. The package is formed by joining together a pair of overlapping, multi-layered straight-tear films that are capable of propagating a tear along a locus of points in one of two substantially straight perpendicular lines in response to an applied force sufficient to propagate a tear in the films.

Referring to Figure 1, a reclosable film package 10 is shown. The package comprises first and second overlapping straight-tear films, each straight-tear film being comprised of an oriented nylon or polyester layer attached to a sealant layer, optionally via an intermediate adhesive layer.

The nylon layer preferably comprises polyamide homopolymers or copolymers selected from aliphatic polyamides and aliphatic/aromatic polyamides having a molecular weight of from about 10,000 to about 100,000. General procedures useful for the preparation of polyamides and polyesters are well known to the art. In the case of polyamides, such may include the reaction of a diamine with a diacid. Useful diacids for making polyamides include dicarboxylic acids which are represented by the general formula:



wherein Z is representative of a divalent aliphatic radical containing at least 2 carbon atoms, such as adipic acid, sebacic acid, octadecanedioic acid, pimelic acid, suberic acid, azelaic acid, dodecanedioic acid, and glutaric acid. The dicarboxylic acids may be aliphatic acids, or aromatic acids such as isophthalic

acid and terephthalic acid. Suitable diamines for making polyamides include those having the formula:



5

wherein n has an integer value of 1-16, and includes such compounds as trimethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, octamethylenediamine, decamethylenediamine, dodecamethylenediamine, hexadecamethylenediamine, aromatic diamines such as p-phenylenediamine, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl sulphone, 4,4'-diaminodiphenylmethane, alkylated diamines such as 2,2-dimethylpentamethylenediamine, 2,2,4-trimethylhexamethylenediamine, and 2,4,4 trimethylpentamethylenediamine, as well as cycloaliphatic diamines, such as diaminodicyclohexylmethane, and other compounds. Other useful diamines include heptamethylenediamine, nonamethylenediamine, and the like.

10  
15

Useful aliphatic polyamide homopolymers include poly(4-aminobutyric acid) (nylon 4), poly(6-aminohexanoic acid) (nylon 6, also known as poly(caprolactam)), poly(7-aminoheptanoic acid) (nylon 7), poly(8-aminooctanoic acid)(nylon 8), poly(9-aminononanoic acid) (nylon 9), poly(10-aminodecanoic acid) (nylon 10), poly(11-aminoundecanoic acid) (nylon 11) and poly(12-aminododecanoic acid) (nylon 12), poly(hexamethylene adipamide) (nylon 6,6), poly(hexamethylene sebacamide) (nylon 6,10), poly(tetramethylenediamine-co-oxalic acid) (nylon 4,2), the polyamide of n-dodecanedioic acid and hexamethylenediamine (nylon 6,12), the polyamide of dodecamethylenediamine and n-dodecanedioic acid (nylon 12,12), poly(heptamethylene pimelamide) (nylon 7,7), poly(octamethylene suberamide) (nylon 8,8), poly(hexamethylene

20  
25

azelamide) (nylon 6,9), poly(nonamethylene azelamide) (nylon 9,9),  
poly(decamethylene azelamide) (nylon 10,9), and poly(tetramethylene adipamide  
(nylon 4,6), and the like. Useful nylon copolymers non-exclusively include  
5 caprolactam/hexamethylene adipamide copolymer (nylon 6,6/6), hexamethylene  
adipamide/caprolactam copolymer (nylon 6/6,6), trimethylene  
adipamide/hexamethylene azelaamide copolymer (nylon trimethyl 6,2/6,2), and  
hexamethylene adipamide-hexamethylene-azelaamide caprolactam copolymer  
(nylon 6,6/6,9/6), and the like. Also included are other polyamides which are not  
particularly delineated here. Of these, preferred polyamides include nylon 6;  
10 nylon 6,6; and nylon MXD6 which is a polymer of 1,3-benzenedimethanamine  
(metaxylenediamine, MXDA) with adipic acid. The most preferred polyamide  
comprises a blend of nylon 6 and nylon MXD6, such as described in U.S. patent  
5,541,011.

15 Examples of aliphatic/aromatic polyamides include poly (2,2,2-trimethyl  
hexamethylene terephthalamide), poly(p-xylylene adipamide),  
poly(hexamethylene terephthalamide) (nylon 6,T), poly(hexamethylene  
isophthalamide) (nylon 6, I), poly(dodecamethylene terephthalamide), polyamide  
6T/6I, poly(tetramethylenediamine-co-isophthalic acid) (nylon 4,I), polyamide  
20 6/MXDT/I, polyamide MXDI, hexamethylene adipamide/hexamethylene-  
isophthalamide (nylon 6,6/6I), hexamethylene  
adipamide/hexamethyleneterephthalamide (nylon 6,6/6T) and as well as others  
which are not particularly delineated here. Blends of two or more  
aliphatic/aromatic polyamides and/or aliphatic polyamides can also be used.  
25 Aliphatic/aromatic polyamides can be prepared by known preparative techniques  
or can be obtained from commercial sources. Other suitable polyamides are  
described in U.S. patents 4,826,955 and 5,541,267.

Polyamides used in the practice of this invention may be obtained from commercial sources or prepared in accordance with known preparatory techniques. For example, nylon 6 can be obtained from Honeywell International  
5 Inc., Morristown, New Jersey under the trademark CAPRON®. Suitable variants of CAPRON® for use in the present invention include CAPRON® 8200 nylon, a balanced nylon 6 having a formic acid viscosity (FAV) of 75, CAPRON® 1767 nylon, a balanced nylon 6 having an FAV of 35, and CAPRON® 8224HSL nylon, a heat stabilized, lubricated nylon 6 having an FAV of 60, and CAPRON® 1250  
10 nylon, an amine-terminated nylon 6 with a FAV of 60 and having terminal amino groups of 70 to 78 milliequivalents per gram.

The process of producing polyesters involves the known initial steps of esterification of at least one dibasic acid with at least one polyol, followed by  
15 polycondensation which is conducted until the polyester is formed which has the desired viscosity and/or melting point. Suitable polyesters may be produced by condensing an aromatic dibasic acid (including anhydrides and acid esters), such as a dicarboxylic acid or a lower alkyl ester thereof with a polyol such as a glycol. The diacid should be an aromatic, low molecular weight mono- or di-cyclic  
20 dibasic acid. Among the dicarboxylic acids and their lower alkyl diesters which may be employed are terephthalic; isophthalic; phthalic; naphthalene dicarboxylic; biphenylene dicarboxylic acid, tetrahydroterephthalic acid, tetrahydroisophthalic acid, tetrahydrophthalic acid, hydronaphthalene dicarboxylic acid, cyclohexanedicarboxylic acid, cyclopentyl dicarboxylic acid,  
25 cyclooctyl dicarboxylic acid, succinic; glutaric acid; sebacic; adipic; azelaic; bibenzoic; pimelic acid, malonic acid, fumaric acid, itaconic acid, their monoesters, their diesters, and mixtures thereof, and bis-p-carboxy-

phenoxyethane. Useful naphthalene dicarboxylic acids include the 2,6-, 1,4-, 1,5-, or 2,7- isomers but the 1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 2,3-, 2,4-, 2,5-, and/or 2,8- isomers may also be used; 4,4'-biphenyldicarboxylic acid, 1,4-naphthalene dicarboxylate, 1,3-phenylenediacetic acid, 1,2-phenylenediacetic acid, 1,4-phenylenedipropionic acid, 4-carboxyphenoxy acetic acid, 2,3-naphthalenedicarboxylate, 1,3,5-benzenetricarboxylic acid, , tetrafluoroisophthalic acid, tetrafluoroterephthalic acid, tetrafluorophthalic acid, 2-methoxyisophthalic acid, benzylmalonic acid, 4-bromoisophthalic acid, 3-nitrophthalic acid, 4-nitrophthalic acid, 2,6-naphthalene dicarboxylate, 4,4'-oxy-bisbenzoic acid, 1,4-phenylenediacetic acid, diphenic acid, homophthalic acid, 1,2-phenylenedioxodicarboxylic acid, 1,2,4-benzenetricarboxylic acid, 4,4'-hexafluoro(isopropylidene), 3-fluorophthalic acid, 4-methylphthalic acid, 5-*tert*-butylisophthalic acid, pamoic acid, 4-bromoterephthalic acid, 4,5-dichlorophthalic acid, and 5-octadecyloxyisophthalic acid. Preferred dibasic acids include terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid and mixtures thereof. The dibasic acids may be used in acid form, acid anhydride form or as their esters such as the dimethyl esters.

One or more of these acids and/or their lower alkyl esters is reacted with at least one di- or tri-functional aliphatic organic polyol compound having at least 2 carbon atoms wherein each functionality is selected from the group consisting of alcohols and amines. Preferred are polyols, which include glycols having from about 2 to about 50 carbon atoms, preferably from about 3 to about 10 carbon atoms and include ethylene glycol, propylene glycol, butylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, dipropylene glycol, 1,5-pentanediol, 1,6-hexanediol, diethylene glycol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, neopentyl glycol; 1,8-octanediol, 1,10-decanediol, 1,12-

dodecanediol, diethylene glycol, triethylene glycol, tetraethylene glycol, dihydroxy-terminated higher oligomers of ethylene glycol, dimer of trimethylene glycol, trimer of trimethylene glycol, dimer of tetramethylene glycol, trimer of tetramethylene glycol, dihydroxy-terminated higher oligomers of tetramethylene glycol, polyethylene glycol, pentaerythritol, glycerol, 1,6-hexamethylene diol, 1,8-octamethylene diol, 1,4-cyclohexanedimethanol and mixtures thereof. Preferred glycols include ethylene glycol, 1,4-cyclohexane dimethanol diethylene glycol and mixtures thereof. The 1,4-cyclohexanedimethanol may be in the cis or the trans form or as cis/trans mixtures. Since one or more esters may be reacted with one or more glycols, the polyesters are not limited to homopolyesters but also include mixed polyesters such as copolyesters as well as copolymers with other monomers. Preferred difunctional or trifunctional aliphatic compounds are glycols having at least four carbon atoms and preferably having from about 6 to about 12 carbon atoms. Such may have additional functionalities such as acids and compounds having a mixture of at least two of these functionalities.

The polyol component adds flexibility to the reaction product with the aromatic diacid component. In the preferred embodiment, the mole ratio of the aromatic diacid to flexible polyol ranges from about 1:1 to about 1:4, preferably from about 1:1 to about 1:3. Optionally, the polyester may be a terpolymer or tetramer containing an additional modifying component such as a di-, tri- or tetra-functional aromatic or aliphatic moiety wherein each functionality is selected from the group consisting of an acid, alcohol, amine, anhydride, ester, acid halide and compatible mixed functionalities thereof.

Polyethylene terephthalate may be formed from a polymer produced by the polymerization of bis-(2-hydroxyethyl) terephthalate which is itself formed as an intermediate by one of two different methods. One method for producing bis-(2-

hydroxyethyl) terephthalate is by direct esterification of terephthalic acid with ethylene glycol as described in U.S. Pat. No. 3,050,533. In this method the by-product of the reaction is water which is distilled from the reaction product. Polyesters produced from the above starting materials may be produced similarly  
5 under conventional conditions well known to the skilled artisan. Conventional processes for the preparation of polyesters may also be found in U.S. patents 4,568,720 and 5,552,512. The polyester layer preferably comprises polyester copolymers selected from aliphatic and aliphatic/aromatic polyesters having a molecular weight of from about 10,000 to about 100,000. Some of the above  
10 polyesters are commercially available and the others can be easily prepared by those skilled in the art using similar, usual means.

The polyester layer may include another polymer to facilitate straight tearing, such as a nylon polymer. In one embodiment, the polyester layer comprises a  
15 blend of polyethylene terephthalate and nylon MXD6.

The sealant layer is preferably attached to the nylon or polyester layer by coextrusion, or lamination via an intermediate adhesive layer. Of these, lamination is the most preferred. The sealant layer is preferably a polyolefin, such  
20 as a polyethylene or polypropylene, or blends of one or more polyolefins. Other polyolefins may be employed, such as ethylene vinyl acetate, in particular when blended with a polyethylene. Polyethylenes are particularly preferred. Non-limiting examples of suitable materials for the polyethylene films are low density polyethylene (LDPE), linear low density polyethylene (LLDPE), linear medium  
25 density polyethylene (LMDPE), linear very-low density polyethylene (VLDPE), linear ultra-low density polyethylene (ULDPE), high density polyethylene (HDPE). Of these, the most preferred is low density polyethylene.

Any suitable adhesive may be employed. Such adhesives include polyurethanes, epoxies, polyesters, acrylics, anhydride modified polyolefin and blends thereof. Modified polyolefin compositions have at least one functional moiety selected  
5 from the group consisting of unsaturated polycarboxylic acids and anhydrides thereof. Such unsaturated carboxylic acid and anhydrides include maleic acid and anhydride, fumaric acid and anhydride, crotonic acid and anhydride, citraconic acid and anhydride, itaconic acid an anhydride and the like. The adhesive layer may also optionally comprise a colorant, an ultraviolet light absorber or both. The  
10 adhesive layer may be applied by coating, sputtering, coextrusion and the like. Alternatively, one or more adhesive polymers may be directly blended or coextruded into other layers of the film, thus providing adhesion while minimizing the number of layers in the film.

15 The straight-tear films of the invention may further comprise an oxygen barrier layer, preferably an ethylene vinyl alcohol copolymer layer, between the nylon and polyethylene layers. Such copolymers suitable for use in the present invention can be prepared by the methods disclosed in U.S. patents 3,510,464; 3,560,461; and 3,585,177.

20 The ethylene vinyl alcohol copolymer can be hydrolyzed from ethylene vinyl acetate copolymer. The degree of hydrolysis can range from 85 to 99.5%. The ethylene vinyl alcohol copolymer preferably contains from about 10 to about 65 mol percent ethylene, and more preferably from about 25 to about 50 mol percent  
25 ethylene. Copolymers of lower than about 10 mol percent ethylene tend to be difficult to extrude while those above 65 mol percent ethylene have reduced oxygen barrier performance, as described in U.S. patent 3,595,740.



Useful ethylene vinyl alcohol copolymers suitable for the present invention are commercially available from a variety of sources. For example, Kuraray of Japan produces an ethylene vinyl alcohol copolymer under the designation "EP-E" which has about 44% ethylene, a number average molecular weight of about 29,500 and melting point of 164°C. Other manufacturers produce suitable ethylene vinyl alcohol copolymers. One suitable copolymer has about 32% ethylene with a melting point of 183°C. Another grade has about 29% ethylene, a number average molecular weight of about number average 22,000 and a melting point of about 188°C. Another described in U.S. patent 4,252,169 has 40% ethylene, a number average molecular weight of about 26,000 and a melting point of 164°C. The number average molecular weight can be measured by osometry.

Ethylene vinyl alcohol copolymers suitable for use in the invention preferably exhibit good oxygen barrier property such as an oxygen permeability of < 1 cc.mil/100 in<sup>2</sup> /day in 100 % oxygen at 25°C.

It is also within the scope of the invention that the straight-tear films may comprise additional layers suitable for the purposes of the invention. For example, the films may further include a moisture barrier layer between the nylon and polyethylene layers. Also, in the preferred embodiment of the invention, a metal foil layer is attached to each straight-tear film on a surface of each nylon layer opposite the adhesive layer. Preferably, this metal foil layer is an aluminum foil. This aluminum foil layer may be printed with any design or indicia as a manufacturer may desire to label the product contained within the package.

Each of the polyethylene films, nylon films, polyester films, optional ethylene vinyl alcohol film, and adhesive layers may optionally also include one or more conventional additives whose uses are well known to those skilled in the art. The use of such additives may be desirable in enhancing the processing of the compositions as well as improving the products or articles formed therefrom. 5 Examples of such include: oxidative and thermal stabilizers, lubricants, release agents, flame-retarding agents, oxidation inhibitors, oxidation scavengers, dyes, pigments and other coloring agents, ultraviolet light absorbers and stabilizers, organic or inorganic fillers including particulate and fibrous fillers, reinforcing agents, nucleators, plasticizers, as well as other conventional additives known to 10 the art. Such may be used, for example, in amounts of up to about 10 % by weight of the overall composition. Representative ultraviolet light stabilizers include various substituted resorcinols, salicylates, benzotriazole, benzophenones, and the like. Suitable lubricants and release agents include stearic acid, stearyl 15 alcohol, and stearamides. Exemplary flame-retardants include organic halogenated compounds, including decabromodiphenyl ether and the like as well as inorganic compounds. Suitable coloring agents including dyes and pigments include cadmium sulfide, cadmium selenide, titanium dioxide, phthalocyanines, ultramarine blue, nigrosine, carbon black and the like. Representative oxidative and thermal stabilizers include the Period Table of Element's Group I metal 20 halides, such as sodium halides, potassium halides, lithium halides; as well as cuprous halides; and further, chlorides, bromides, iodides. Also, hindered phenols, hydroquinones, aromatic amines as well as substituted members of those above mentioned groups and combinations thereof. Exemplary plasticizers include 25 lactams such as caprolactam and lauryl lactam, sulfonamides such as o,p-toluenesulfonamide and N-ethyl, N-butyl benylnesulfonamide, and combinations of any of the above, as well as other plasticizers known to the art.

One noteworthy characteristic of the films of this invention is that they exhibit excellent gas barrier properties, particularly oxygen barrier properties. Oxygen permeation resistance or barrier may be measured using the procedure of ASTM  
5 D-3985. In general, the films of this invention have an oxygen transmission rate (OTR) at 90% relative humidity (RH) of less than about  $1.0 \text{ cm}^3/100 \text{ in}^2$  ( $645 \text{ cm}^2$ )/24 hrs/Atm at  $25^\circ\text{C}$  using 100% oxygen, and preferably less than about  $0.5 \text{ cm}^3/100 \text{ in}^2$  ( $645 \text{ cm}^2$ )/24 hrs/Atm at  $25^\circ\text{C}$ .

10 Preferably a blend or combination of nylon polymers is produced by a melt extrusion of the nylon components. The composition may be formed by dry blending solid particles or pellets of each of the nylon components and then melt blending the mixture in a suitable mixing means such as an extruder, a roll mixer or the like. Typical melting temperatures range from about  $200^\circ\text{C}$  to about  
15  $270^\circ\text{C}$ , preferably from about  $210^\circ\text{C}$  to about  $260^\circ\text{C}$ . Blending is conducted for a period of time required to attain a substantially uniform blend. Such may easily be determined by those skilled in the art.

The multilayered straight-tear films of the invention may be formed by any  
20 conventional technique for forming films, including coextrusion and extrusion lamination. The preferred method for making multilayer film is by coextrusion. For example, the material for the individual layers, as well as any optional layers, are fed into infeed hoppers of the extruders of like number, each extruder handling the material for one or more of the layers. The melted and plasticated streams  
25 from the individual extruders are fed into a single manifold co-extrusion die. While in the die, the layers are juxtaposed and combined, then emerge from the

die as a single multiple layer film of polymeric material. After exiting the die, the film is cast onto a first controlled temperature casting roll, passes around the first roll, and then onto a second controlled temperature roll, which is normally cooler than the first roll. The controlled temperature rolls largely control the rate of cooling of the film after it exits the die. In another method, the film forming apparatus may be one which is referred to in the art as a blown film apparatus and includes a multi-manifold circular die head for bubble blown film through which the plasticized film composition is forced and formed into a film bubble which may ultimately be collapsed and formed into a film. After the formation of the coextruded films, the films are then biaxially oriented. These orientation processes may be by several methods, including sequential and simultaneous orientation. In the sequential process the films are first oriented in one direction, for example the machine direction, after which they are oriented in the normal direction, for example the transverse direction. In the simultaneous orientation process the films are oriented in both the machine and transverse directions at the same time. A blown film process may also be used to biaxially orient the film, where the blown unoriented film is subsequently oriented in both the machine and transverse direction by expanding the solidified polymer "tube" at temperatures below the melting points of the polymers used to compose the film. In each of the above instances the oriented films are preferably subsequently heat set at elevated temperatures as a means of controlling the films shrinkage properties. Processes of coextrusion to form film laminates are generally known. Alternatively the individual layers may first be formed into sheets and then laminated together under heat and pressure with or without intermediate adhesive layers.

25

Lamination techniques are well known in the art. Typically, laminating is done by positioning the individual layers on one another under conditions of sufficient

heat and pressure to cause the layers to combine into a unitary film. For example, the nylon film, polyethylene film, optional ethylene vinyl alcohol film and adhesive layers are positioned on one another, and the combination is passed through the nip of a pair of heated laminating rollers by techniques well known in the art. Lamination heating may be done at temperatures ranging from about 120 ° C. to about 175 ° C., preferably from about 150 ° C. to about 175 ° C., at pressures ranging from about 5 psig (0.034 MPa) to about 100 psig (0.69 MPa), for from about 5 seconds to about 5 minutes, preferably from about 30 seconds to about 1 minute.

10

Films produced according to the present invention should be oriented by stretching or drawing the films at draw ratios of from about 1.1:1 to about 10:1 in at least one direction, and preferably at a draw ratio of from about 2:1 to about 5:1 in at least one direction. The term "draw ratio" as used herein indicates the increase of dimension in the direction of the draw. Therefore, a film having a draw ratio of 2:1 has its length doubled during the drawing process. Generally, the film is drawn by passing it over a series of preheating and heating rolls. The heated film moves through a set of nip rolls downstream at a faster rate than the film entering the nip rolls at an upstream location. The change of rate is compensated for by stretching in the film. Such films may be stretched or oriented in any desired direction using methods well known to those skilled in the art. The film may be stretched biaxially in both the longitudinal direction and the transverse direction. Straight tear films may be formed by a judicious selection of nylon or polyester polymer types, molecular weight and degree of orientation. In general, a straight tear film propagates a tear in the film along a straight line which does not wander more than about 3 mm transversely from a tear line which is parallel to the margin edges 12, 14 and zipper 18 of the enclosure. One useful

25

straight tear nylon film comprises a blend of nylon 6 and nylon MXD6 and is commercially available from Idemitsu of Tokyo, Japan

The thickness of each of the straight-tear films preferably range from about 0.05  
5 mils (1.3 ( $\mu\text{m}$ )) to about 50 mils (1270 ( $\mu\text{m}$ )), and more preferably from about  
0.05 mils (1.3 ( $\mu\text{m}$ )) to about 10 mils (254 ( $\mu\text{m}$ )). Most preferably, each straight-  
tear film has a thickness of less than about 5 mils (127 $\mu\text{m}$ ). While such  
thicknesses are preferred as providing a readily flexible film, it is to be understood  
that other film thicknesses may be produced to satisfy a particular need and yet  
10 fall within the scope of the present invention.

Once first and second straight-tear films of the invention are formed, a reclosable  
zipper 18 comprising first and second zipper tracks is formed below and  
substantially parallel to the top edge of the films. The zipper tracks may be  
15 formed in a number of conventional ways. The may be formed by passing the  
straight-tear films through a mold such that complementary tracks are formed.  
They may be formed by coextruding a polymer through die having the shape of  
complementary tracks and onto a film layer. The tracks may also be formed by  
extrusion of a polymer through the same die as one of the film layers, with the die  
20 shaped to form complementary tracks on coextruded layers. Additionally, the  
tracks may be formed by extruding a polymer through a die and solidifying the  
polymer, followed by attaching the tracks to the films with heat or with an  
adhesive. Suitable adhesives include those described above. These techniques  
are intended to be non-exclusive and any means known in the art for forming  
25 zipper tracks may be used.

In the preferred embodiment of the invention, the first and second complementary zipper tracks are located at an inner area of the package and extend between and are spaced from the left and right edges of the films, terminating at left and right end points. Generally, the zipper tracks comprise flexible complementary  
5 polymeric strips that are capable of releasably engaging each other, the first zipper track having a male rib and groove configuration and the second zipper track having a female rib and groove configuration. Such zippers are well known in the art for use with food storage bags and can be seen, for example, in U.S. patents 5,067,208, 5,896,627, and 5,482,375. The strips may be formed of any suitable  
10 polymeric material as is known in the art, which includes but is not limited to the nylon homopolymers and copolymers listed above or blends and mixtures thereof, polypropylene, polyethylene and polystyrene and the like.

Following application of the zipper tracks, a moveable slider 20 is attached to the  
15 tracks such that the slider 20 is capable of engaging and disengaging the tracks of the zipper 18 between the first and second end points of the tracks. The slider 20 engages the tracks by pressing the complementary tracks together when it slides along the length of the zipper. The slider 20 may be attached to the zipper using techniques known in the art, such as those shown in U.S. patents 5,067,208,  
20 5,896,627, 5,924,173 and 6,148,588. The slider is preferably formed from a single piece of molded polymer. Suitable polymers are known in the art and non-exclusively include nylon homopolymers and copolymers and blends thereof, polypropylene, polyethylene and polystyrene and the like.

25 Once the slider is attached, the first and second straight-tear films are adjoined by sealing the opposing left and right edges and a bottom edge of each film together such that the polyethylene layers are attached together, forming an enclosure. The

films may be attached either by thermally sealing them together or by using an adhesive. Most preferably they are adjoined by thermal sealing. The films are sealed together at the left, right and bottom edges, forming a left margin 12, a right margin 14 and a bottom margin 16. As can be seen in Figures 1 and 2, the margins extend for a distance away from the bottom, left and right edges of the films toward a center of the films. As can also be seen from the figures, the left margin 12 and the right margin 14 extend to the left and right end points of the zipper tracks. The thickness of each of the left, right and bottom margins is not intended to be limiting to the invention and may be as desired. The formation of the margins creates a removable tear strip 22 above the zipper 18 and between the left margin 12 and right margin 14, as seen in Figure 1.

After the films are sealed together, a left nodule 24 is formed at the intersection of the left zipper end point and the left margin 12 and a right nodule 26 is formed at the intersection of the right zipper end point and the right margin 14. These nodules are preferably heat sealed areas formed with a welder or heat bar that melts through each of the first and second straight-tear films.

After the nodules are formed, the enclosure may be filled with a product, such as a liquid or solid food product. The zipper is then preferably closed and the top edge of the films sealed together above the zipper. The top edge is preferably thermally sealed using heat and pressure or sealed alternatively using an adhesive as described above. Of these, thermal sealing is preferred. As shown in Figure 1, the reclosable package of the invention may further preferably comprise tear notches 34 and 36 along the top edge of the adjoined films directly above each of the left and right nodules. In this embodiment, the tear notches 34 and 36 facilitate the straight tearing of the films along a locus of points in one of two



substantially straight perpendicular lines in response to an applied force sufficient to propagate a tear in the films. Tear notches are well known in the art and facilitate the tearing of the films. These may also comprise a polymeric strip, a polymeric tab or a notch formed by making two small cuts in the films along the top edge directly above each of the left and right nodules.

In use, the films are torn from the top left corner of the tear strip 22 down a locus of points along the left margin 12 in a direction of arrow 28 until to left nodule 24 is reached. At left nodule 24, the tearing direction is turned to the direction of arrow 30 perpendicular to direction 28, and the films are the torn together along a locus of points across the film above the zipper 18 to right nodule 26. At the right nodule 26, the tearing direction is turned to a direction of arrow 32 perpendicular to direction 30 and parallel to direction 28. The films are torn together along right margin 14 to the top edge of the films, completely removing tear strip 22. After the tear strip is removed, the portions of the left margin 12 and right margin 14 above the zipper 18 remain, and the closed zipper 18 is revealed. This can be seen in Figure 2. The package may then be opened by sliding the slider 20 along the zipper 18 to disengage the interlocked zipper tracks, revealing the product within the enclosure.

This product and process avoids the need for microperforating or laser scoring of the films to facilitate tearing of the films. These steps are undesirable because they compromise the integrity of the packaging by allowing microbes and other dangerous organisms to penetrate the package and reach the product stored therein. By avoiding these techniques, optimal integrity of the bag and product are maintained, as well as saving the extra cost involved with applying these techniques. Therefore, a low cost, high quality product is achieved.

While the present invention has been particularly shown and described with reference to preferred embodiments, it will be readily appreciated by those of  
5 ordinary skill in the art that various changes and modifications may be made without departing from the spirit and scope of the invention. It is intended that the claims be interpreted to cover the disclosed embodiment, those alternatives which have been discussed above and all equivalents thereto.

What is claimed is:

1. A reclosable film package comprising:
  - a) first and second overlapping straight-tear films capable of propagating a tear along a locus of points in one of two substantially straight perpendicular lines in response to an applied force sufficient to propagate a tear in the films, the films  
5 being sealed together at top, bottom, left and right edges defining an enclosure, the enclosure having sealed bottom, left and right margins extending for a distance away from the bottom, left and right edges toward a center of the films; each film comprising in order from an outside portion of the enclosure to an  
10 inside portion of the enclosure:
    - i. a nylon or polyester layer;
    - ii. optionally, an adhesive layer; and
    - iii. a sealant layer;
  - b) a reclosable zipper substantially parallel with and positioned below the top  
15 edge of the films and extending between left and right end points located at the left and right margins; said zipper comprising a first track on the first straight-tear film and a second track on the second straight-tear film, which first and second tracks are adapted to releasably engage each other;
  - c) a slider moveably attached to said tracks for engaging and disengaging the  
20 tracks between the end points;
  - d) left and right nodules positioned at the left and right end points; and
  - e) a tear propagation line extending from the left nodule to the right nodule substantially parallel along the zipper, and a tear propagation line extending from each of the left and right nodules substantially parallel along the left and right  
25 margins to the top edge of the films, defining a removable tear strip between the left and right margins and above the zipper.

2. The reclosable film package of claim 1 wherein an adhesive layer is present between the nylon or polyester layer and the sealant layer.
3. The reclosable film package of claim 1 wherein each straight-tear film further  
5 comprises an oxygen barrier layer between the nylon or polyester layer and the sealant layer.
4. The reclosable film package of claim 1 wherein each straight-tear film further  
10 comprises an ethylene vinyl alcohol layer between the nylon or polyester layer and the polyethylene layer.
5. The reclosable film package of claim 1 wherein at least one straight-tear film comprises a nylon layer.
- 15 6. The reclosable film package of claim 5 wherein the nylon layer comprises a nylon selected from the group consisting of nylon 6, nylon MXD6 and combinations thereof.
7. The reclosable film package of claim 6 wherein the nylon layer comprises a  
20 blend of nylon 6 and nylon MXD6.
8. The reclosable film package of claim 1 wherein at least one straight-tear film comprises a polyester.
- 25 9. The reclosable film package of claim 8 wherein said polyester comprises polyethylene terephthalate.

10. The reclosable film package of claim 1 wherein said sealant layer is a polyolefin.
11. The reclosable film package of claim 10 wherein said polyolefin is a polyethylene.
12. The reclosable film package of claim 11 wherein the polyethylene layer comprises a polyethylene selected from the group consisting of low density polyethylene, linear low density polyethylene, linear medium density polyethylene, linear very-low density polyethylene, linear ultra-low density polyethylene, high density polyethylene and combinations thereof.
13. The reclosable film package of claim 12 wherein said polyethylene is low density polyethylene.
14. The reclosable film package of claim 2 wherein the adhesive layer comprises a polyolefin.
15. The reclosable film package of claim 2 further comprising a metal foil layer attached to a surface of each nylon or polyester layer opposite the adhesive.
16. The reclosable film package of claim 15 wherein said foil comprises an aluminum foil.
17. The reclosable film package of claim 1 further comprising left and right tear notches adjacent to the left and right margins and along the top edge of the films.

18. The reclosable film package of claim 1 wherein each film has a thickness of about 10 mils or less.
19. The reclosable film package of claim 1 wherein the package contains a  
5 product.
20. The reclosable film package of claim 19 wherein the package contains food.
21. The reclosable film package of claim 1 wherein the first and second tracks  
10 and the slider are formed from a polymeric material.
22. A reclosable film package comprising:
- a) first and second overlapping straight-tear films capable of propagating a tear  
15 along a locus of points in one of two substantially straight perpendicular lines in response to an applied force sufficient to propagate a tear in the films, the films being sealed together at top, bottom, left and right edges defining an enclosure, the enclosure having sealed bottom, left and right margins extending for a distance away from the bottom, left and right edges toward a center of the films; each film comprising in order from an outside portion of the enclosure to an  
20 inside portion of the enclosure:
- i. a nylon layer;
  - ii. an adhesive layer; and
  - iii. a polyethylene layer;
- b) a reclosable zipper substantially parallel with and positioned below the top  
25 edge of the films and extending between left and right end points located at the left and right margins; said zipper comprising a first track on the first straight-tear

- film and a second track on the second straight-tear film, which first and second tracks are adapted to releasably engage each other;
- c) a slider moveably attached to said tracks for engaging and disengaging the tracks between the end points;
- 5 d) left and right nodules positioned at the left and right end points; and
- e) a tear propagation line extending from the left nodule to the right nodule substantially parallel along the zipper, and a tear propagation line extending from each of the left and right nodules substantially parallel along the left and right margins to the top edge of the films, defining a removable tear strip between the
- 10 left and right margins and above the zipper.
23. The reclosable film package of claim 22 wherein said nylon layer comprises a blend of nylon 6 and nylon MXD6.
- 15 24. A process for forming a reclosable film package comprising:
- a) forming first and second straight-tear films by attaching a nylon or polyester layer to a sealant layer optionally via an intermediate adhesive layer, said films having top, bottom, left and right edges;
- b) forming first and second zipper tracks below and parallel to the top edge of the
- 20 films, said tracks having left and right end points and said tracks releasably engaging each other;
- c) attaching a moveable slider to the tracks such that the slider is capable of engaging and disengaging the tracks between left and right end points;
- d) adjoining the first and second straight-tear films by sealing the respective left,
- 25 right and bottom edge of each film together such that the sealant layers are attached together, and forming left, right and bottom margins, thereby forming an enclosure; and

e) forming a left nodule at an intersection of a left zipper end point and the left margin, and forming a right nodule at an intersection of a right zipper end point with the right margin.

5 25. The process of claim 24 further comprising attaching the nylon or polyester layer and the sealant layer via an adhesive.

26. The process of claim 24 further comprising the steps:

f) filling the enclosure with a product;

10 g) engaging the first and second zipper tracks; and

g) sealing a top edge of the films above the zipper.

27. The process of claim 24 further comprising attaching an oxygen barrier layer between the nylon and sealant layers prior to step (b).

15

28. The process of claim 25 further comprising attaching a metal foil layer to a surface of each nylon or polyester layer opposite the adhesive layer of each straight-tear film prior to step (b).

20 29. The process of claim 24 wherein the nylon or polyester layer comprises a nylon selected from the group consisting of nylon 6, nylon MXD6 and combinations thereof.

25 30. The process of claim 29 wherein the nylon or polyester layer comprises a blend of nylon 6 and nylon MXD6.



31. The process of claim 24 wherein the sealant layer is a polyethylene.

32. The process of claim 31 wherein the polyethylene layer comprises a polyethylene selected from the group consisting of low density polyethylene, linear low density polyethylene, linear medium density polyethylene, linear very-  
5 low density polyethylene, linear ultra-low density polyethylene, high density polyethylene and combinations thereof.

33. The process of claim 25 wherein the adhesive layer comprises a polyolefin.

10

34. The process of claim 24 further comprising forming left and right tear notches adjacent to the left and right margins and along the top edge of the films .

35. The process of claim 26 wherein the product comprises food.

15

36. The process of claim 24 wherein the nylon or polyester layers and the sealant layers are attached by coextrusion.

37. The process of claim 24 wherein the nylon or polyester layer and the sealant

20 layers are attached by lamination.

25

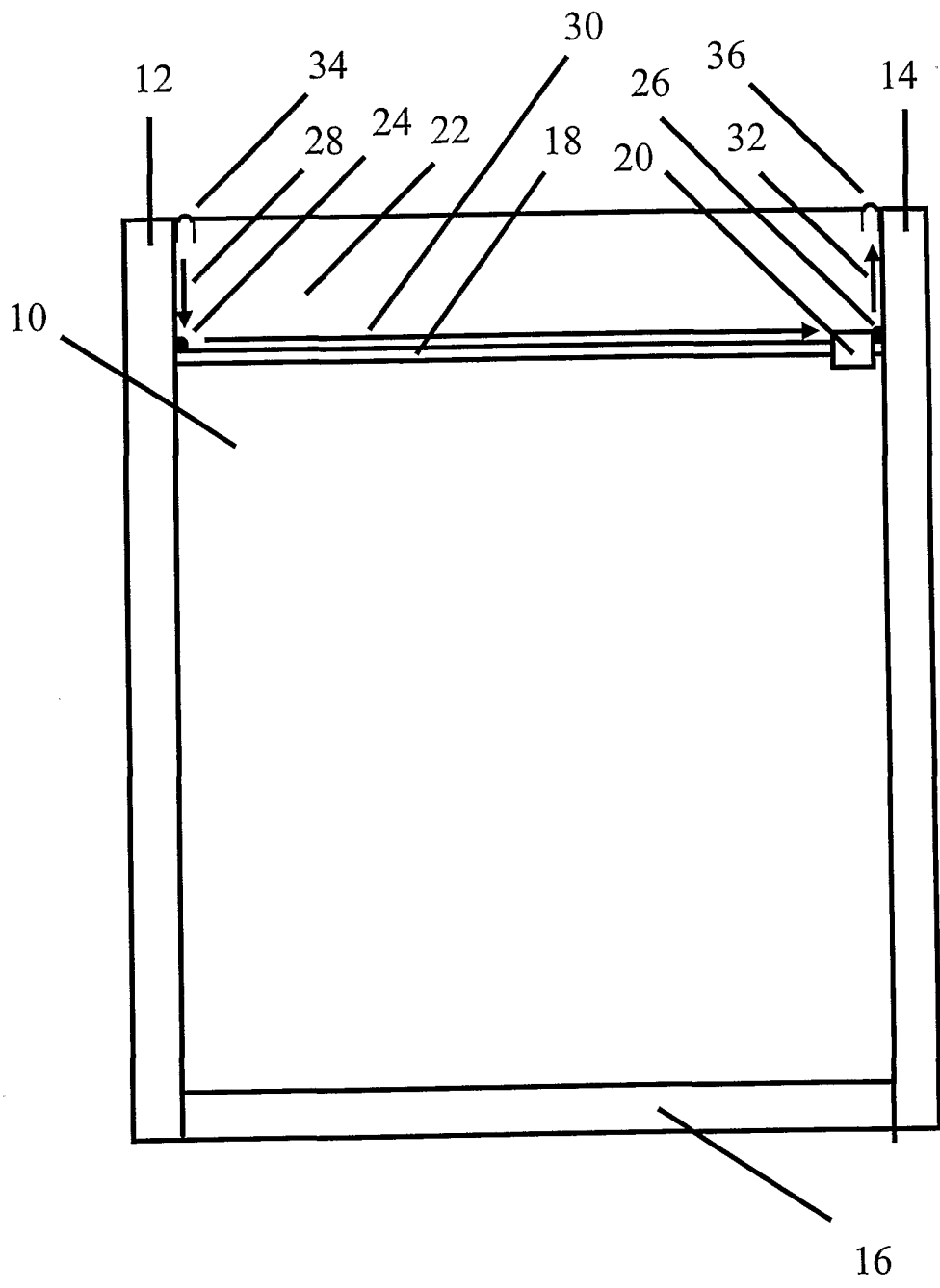


FIG. 1

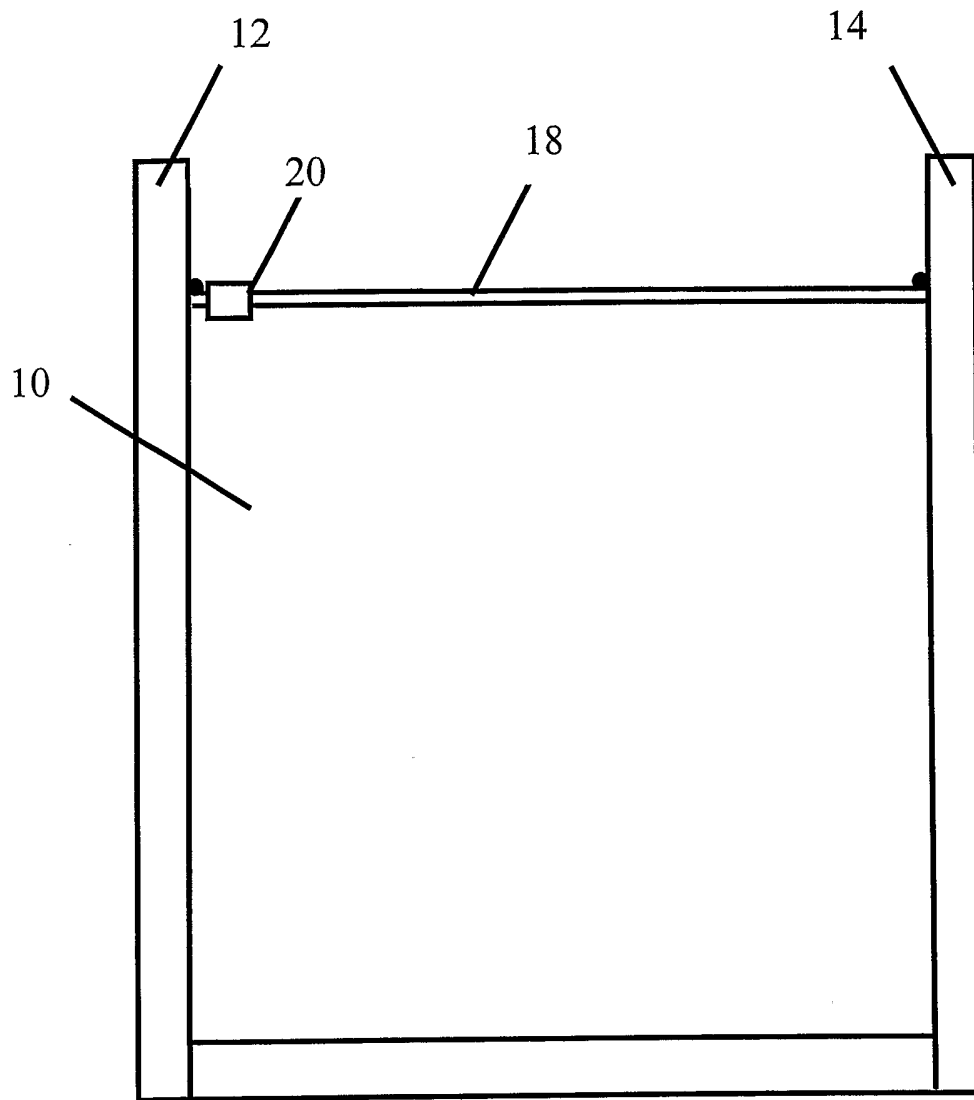


FIG. 2

INTERNATIONAL SEARCH REPORT

Inter. Application No  
PCT/US 02/15442

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 B65D33/25 B65D75/58 B65D65/40

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 B65D B32B

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	EP 1 142 500 A (REYNOLDS CONSUMER PROD) 10 October 2001 (2001-10-10) figure 11	1-37
A	EP 0 573 782 A (EASTMAN KODAK CO) 15 December 1993 (1993-12-15) page 5; table column 2, line 2	1-37
A	US 6 206 571 B1 (OLIN ALAN D) 27 March 2001 (2001-03-27) the whole document	1-37
A	US 5 603 995 A (TAKUBO TOYOKAZU ET AL) 18 February 1997 (1997-02-18) the whole document	1-37

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

20 August 2002

Date of mailing of the international search report

20. 09. 2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

William Helin

## INTERNATIONAL SEARCH REPORT

Int	l Application No
	PCT/US 02/15442

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1142500	A	10-10-2001	EP 1142500 A2	10-10-2001
EP 0573782	A	15-12-1993	CA 2093170 A1 EP 0573782 A2 JP 6047858 A	14-11-1993 15-12-1993 22-02-1994
US 6206571	B1	27-03-2001	US 2001010737 A1	02-08-2001
US 5603995	A	18-02-1997	JP 6144451 A AU 679004 B2 AU 5052893 A DE 69316712 D1 DE 69316712 T2 DE 69324827 D1 DE 69324827 T2 DE 69324828 D1 DE 69324828 T2 EP 0597650 A1 EP 0731033 A2 EP 0731034 A2 EP 0731035 A2 ES 2111719 T3 JP 3244842 B2 JP 6191540 A US 5645905 A	24-05-1994 19-06-1997 19-05-1994 05-03-1998 14-05-1998 10-06-1999 16-09-1999 10-06-1999 16-09-1999 18-05-1994 11-09-1996 11-09-1996 11-09-1996 16-03-1998 07-01-2002 12-07-1994 08-07-1997