

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
23 February 2006 (23.02.2006)

PCT

(10) International Publication Number  
**WO 2006/019798 A1**

- (51) International Patent Classification<sup>7</sup>: **B32B 27/34**, 27/32
- (21) International Application Number:  
PCT/US2005/024823
- (22) International Filing Date: 13 July 2005 (13.07.2005)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
10/890,777 14 July 2004 (14.07.2004) US
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- (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, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, 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), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, 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).
- Published:**  
— *with international search report*
- 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.*

(54) Title: HIGH BARRIER ANTIFOG LAMINATE FOR CASE READY MEAT PACKAGING

(57) Abstract: Multilayered packaging films having good antifog performance that are suitable for use in food packaging. One multilayered film comprises at least one nylon layer having a silicone oil blended therein or coated on a surface thereof, and also comprises a barrier film that includes a sealant film having an antifog composition either contained within at least part of the sealant film or is coated on a surface of the sealant film. The silicone oil effectively blocks the migration of the antifog composition into an adjacent nylon layer when the multilayered film is stored in roll form.



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## HIGH BARRIER ANTIFOG LAMINATE FOR CASE READY MEAT PACKAGING

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### BACKGROUND OF THE INVENTION

#### FIELD OF THE INVENTION

The invention relates to packaging films. More particularly, the invention  
10 pertains case ready packaging films having good antifog performance that are  
suitable for use in meat packaging.

#### DESCRIPTION OF THE RELATED ART

Containers have long been used to store perishable foods, such as meats, fruits  
15 and vegetables, prior to sale in the marketplace to consumers. Maximizing the  
time in which the food remains preserved in the containers minimizes the  
amount of spoilage.

The environment around which the food is preserved is an important factor in  
20 the preservation process. It is important that the food is maintained at an  
adequate temperature, while also controlling the molecular and chemical  
content of the gases surrounding the food. By providing an appropriate gas  
content to the environment surrounding the food, the food can be better  
preserved when maintained at the proper temperature or even when it is  
25 exposed to variations in temperature. This gives the food producer some  
assurance that the food will be in an acceptable condition when it reaches the  
consumer. Preferred modified atmosphere packaging systems for foods,  
including raw meats, exposes these foods to extremely low levels of oxygen  
because it is well known that the freshness of meat can be preserved longer

under anaerobic conditions than under aerobic conditions.

levels of oxygen minimizes the growth and multiplication of aerobic bacteria.

Additionally, modified atmosphere packaging can involve high levels of

oxygen, e.g. 80%, combined with nitrogen and/or carbon dioxide. The gases

5 in these combinations do not favor bacterial growth but allow the raw meat to maintain a preferred red color that is acceptable to the consumer.

It is also important that the packaging exhibit good resistance to the formation of condensation inside the package on a surface of the film. This is known in

10 the art as an antifog property. Multilayered films for modified atmosphere packaging having such antifog properties are well known and are commonly used when packaging food products having a high moisture content, such as fresh meats, and when it is important for the product to be clearly visible to the consumer. For example, U.S. patents 5,766,772, 5,567,533 and 5,520,764  
15 describe multi-layer heat-shrinkable films endowed with antifog properties having a different structure from this invention.

To produce a film exhibiting this antifog property, an antifog component is typically blended with or coated onto a sealant film such as a polyethylene

20 film. This antifog-polyethylene component then forms a part of a multilayered packaging film, such as a nylon packaging film, that may also incorporate an oxygen barrier polymer layer such as ethylene vinyl alcohol. However, one significant problem associated with such known multilayered films having this antifog component is that the antifog component tends to be drawn toward  
25 polar materials, such as nylon, and away from the non-polar polyethylene.

This is particularly a problem when the film is rolled up after manufacture such that the antifog layer or antifog containing polyethylene layer is brought into direct contact with an adjacent nylon layer. This causes the antifog component to migrate out of its existing polyethylene layer and into the nylon

layer, compromising the performance of the nylon layer as the antifog property of the film. Therefore, it would be desirable to provide a multilayered packaging film having good antifog performance and having an antifog component which does not migrate into adjacent nylon layers when stored. The present invention provides such a solution to this need.

### SUMMARY OF THE INVENTION

The invention provides a multilayered film comprising:

- 10 a) an oriented first nylon layer having first and second surfaces; and
  - b) a barrier film attached to the second surface of the first nylon layer via a first adhesive tie layer, which barrier film comprises in order:
    - i. a second nylon layer having first and second surfaces;
    - ii. a silicone oil blended in said second nylon layer;
    - 15 iii. an oxygen barrier layer having first and second surfaces, with its first surface being attached to the second surface of said second nylon layer;
    - iv. a third nylon layer having first and second surfaces, with its first surface being attached to the second surface of said oxygen barrier layer;
    - 20 v. a silicone oil blended in said third nylon layer;
    - vi. a second adhesive tie layer having first and second surfaces, with its first surface on the second surface of the third nylon layer; and
    - vii. a sealant film having first and second surfaces, with its first surface on the second surface of the second adhesive tie layer, which sealant film comprises at least one polyethylene layer, and which at least one polyethylene layer either contains an antifog composition therein or has an antifog composition coated on a surface thereof;
- wherein the second surface of the first nylon layer and the first surface of the

second nylon layer are facing each other.

The invention also provides a multilayered film comprising:

- a) an oriented first nylon 6 layer having first and second surfaces;
- 5 b) a barrier film attached to the second surface of the first nylon 6 layer via a first adhesive tie layer, which barrier film comprises in order:
  - i. a second nylon 6 layer having first and second surfaces;
  - ii. a silicone oil blended in said second nylon 6 layer;
  - iii. an ethylene vinyl alcohol layer having first and second surfaces,  
10 with its first surface being attached to the second surface of said second nylon 6 layer;
  - iv. a third nylon 6 layer having first and second surfaces, with its first surface being attached to the second surface of said ethylene vinyl alcohol layer;
  - 15 v. a silicone oil blended in said third nylon 6 layer;
  - vi. a second adhesive tie layer having first and second surfaces, with its first surface on the second surface of the third nylon layer; and
  - vii. a sealant film having first and second surfaces, with its first surface on the second surface of the second adhesive tie layer, which sealant  
20 film comprises at least one polyethylene layer, and which at least one polyethylene layer either contains an antifog composition therein or has an antifog composition coated on a surface thereof;

wherein the second surface of said first nylon 6 layer and the first surface of said second nylon 6 layer are facing each other.

25 The invention further provides a multilayered film comprising:

- a) an outer film which comprises:
  - i. a first nylon layer having first and second surfaces;
  - ii. an oxygen barrier layer having first and second surfaces, with its  
30 first surface being attached to said second surface of said first nylon

layer;

iii. a second nylon layer having first and second surfaces, with its first surface being attached to said second surface of said oxygen barrier

layer; and

5 b) an inner film which comprises:

i. a third nylon layer having first and second surfaces, which third nylon layer has a silicone oil blended therein;

10 ii. a first adhesive tie layer having first and second surfaces, with its first surface being attached to the second surface of said third nylon layer; and

15 iii. a sealant film having first and second surfaces, with its first surface on the second surface of the first adhesive tie layer, which sealant film comprises at least one polyethylene layer, and which at least one polyethylene layer either contains an antifog composition therein or has an antifog composition coated on a surface thereof;

and wherein said outer film and said inner film are attached together via a second adhesive tie layer such that the second surface of said second nylon layer is attached to the first surface of said third nylon layer.

20 The invention still further provides a process for forming a multilayered film comprising:

a) forming a first oriented nylon layer having first and second surfaces;

b) forming a barrier film which comprises:

25 i. forming a second nylon layer having first and second surfaces, which second nylon layer has a silicone oil blended therein;

ii. attaching an oxygen barrier layer having first and second surfaces to said second nylon layer, with its first surface being attached to the second surface of said second nylon layer;

iii. attaching a third nylon layer having first and second surfaces to said

oxygen barrier layer, with its first surface being attached to the first surface of said oxygen barrier layer, which third nylon layer has a silicone oil blended therein;

iv. attaching a sealant film having first and second surfaces to said third nylon layer, with its first surface on the second surface of the third nylon layer, which sealant film comprises at least one polyethylene layer, and which at least one polyethylene layer either contains an antifog composition therein or has an antifog composition coated on a surface thereof; said sealant film being attached to said third nylon layer via a second adhesive tie layer; and

c) attaching said first oriented nylon layer to said barrier film via a first adhesive layer, such that the second surface of said first nylon layer and the first surface of said second nylon layer are facing each other.

The invention also provides a process for forming a multilayered film comprising:

a) forming an outer film which comprises:

- i. a first nylon layer having first and second surfaces;
- ii. an oxygen barrier layer having first and second surfaces, with its first surface being attached to said second surface of said first nylon layer;
- iii. a second nylon layer having first and second surfaces, with its first surface being attached to said second surface of said oxygen barrier layer; and

b) forming an inner film which comprises:

- i. a third nylon layer having first and second surfaces, which third nylon layer has a silicone oil blended therein;
- ii. a first adhesive tie layer having first and second surfaces, with its first surface being attached to the second surface of said third nylon layer; and

- iii. a sealant film having first and second surfaces,  
on the second surface of the adhesive tie layer, which sealant film  
comprises at least one polyethylene layer, and which at least one  
polyethylene layer either contains an antifog composition therein or has  
5 an antifog composition coated on a surface thereof; and  
c) attaching said outer film to said inner film via a second adhesive tie layer  
such that the second surface of said second nylon layer is attached to the first  
surface of said third nylon layer.

10 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention provides multilayered packaging films having good antifog  
properties wherein the antifog composition does not migrate into adjacent  
polar film layers. The films of the invention also exhibit excellent oxygen  
barrier properties.

- 15 In the production of the first multilayered film of the invention, an oriented  
first nylon layer is attached to a multilayered, coextruded barrier film via a first  
adhesive tie layer. The barrier film comprises in order: i) a second nylon  
layer having first and second surfaces; ii) a silicone oil blended in said second  
20 nylon layer; iii) an oxygen barrier layer having first and second surfaces, with  
its first surface being attached to the second surface of said second nylon layer;  
iv) a third nylon layer having first and second surfaces, with its first surface  
being attached to the second surface of said oxygen barrier layer; v) a silicone  
oil blended in said third nylon layer; vi) a second adhesive tie layer having first  
25 and second surfaces, with its first surface on the second surface of the third  
nylon layer; and vii. a sealant film having first and second surfaces, with its  
first surface on the second surface of the second adhesive tie layer, which  
sealant film comprises at least one polyethylene layer, and which at least one  
polyethylene layer either contains an antifog composition therein or has an

antifog composition coated on a surface thereof. Additionally, the first surface of the first nylon layer and the first surface of the second nylon layer are facing each other.

- 5 Each of the nylon layers of the invention may comprise the nylon materials described herein. Nylons are conventionally used in the art of multilayered packaging films. Suitable nylons within the scope of the invention non-exclusively include homopolymers or copolymers selected from aliphatic polyamides and aliphatic/aromatic polyamides having a molecular weight of  
10 from about 10,000 to about 100,000. General procedures useful for the preparation of polyamides are well known to the art. Such include the reaction products of diacids with diamines. 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  
20 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



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,  
sulfone, 4,4'-diaminodiphenylmethane, alkylated diamines such as 2,2-  
dimethylpentamethylenediamine, 2,2,4-trimethylhexamethylenediamine, and  
2,4,4 trimethylpentamethylenediamine, as well as cycloaliphatic diamines,  
5 such as diaminodicyclohexylmethane, and other compounds. Other useful  
diamines include heptamethylenediamine, nonamethylenediamine, and the  
like.

Useful polyamide homopolymers include poly(4-aminobutyric acid) (nylon 4),  
10 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), poly(12-aminododecanoic  
acid) (nylon 12), nylon 4,6, poly(hexamethylene adipamide) (nylon 6,6),  
15 poly(hexamethylene sebacamide) (nylon 6,10), poly(heptamethylene  
pimelamide) (nylon 7,7), poly(octamethylene suberamide) (nylon 8,8),  
poly(hexamethylene azelamide) (nylon 6,9), poly(nonamethylene azelamide)  
(nylon 9,9), poly(decamethylene azelamide) (nylon 10,9),  
poly(tetramethylenediamine-co-oxalic acid) (nylon 4,2), the polyamide of n-  
20 dodecanedioic acid and hexamethylenediamine (nylon 6,12), the polyamide of  
dodecamethylenediamine and n-dodecanedioic acid (nylon 12,12) and the  
like. Useful aliphatic polyamide copolymers include  
caprolactam/hexamethylene adipamide copolymer (nylon 6,6/6),  
hexamethylene adipamide/caprolactam copolymer (nylon 6/6,6), trimethylene  
25 adipamide/hexamethylene azelaamide copolymer (nylon trimethyl 6,2/6,2),  
hexamethylene adipamide-hexamethylene-azelaamide caprolactam copolymer  
(nylon 6,6/6,9/6) and the like. Also included are other nylons which are not  
particularly delineated here. Of these polyamides, preferred polyamides

include nylon 6, nylon 6,6, nylon 6/6,6 as well as mixtures  
most preferred polyamide is nylon 6.

Aliphatic polyamides used in the practice of this invention may be obtained  
5 from commercial sources or prepared in accordance with known preparatory  
techniques. For example, poly(caprolactam) can be obtained from Honeywell  
International Inc., Morristown, New Jersey under the trademark CAPRON®.

Exemplary of aliphatic/aromatic polyamides include

10 poly(tetramethylenediamine-co-isophthalic acid) (nylon 4,I),  
polyhexamethylene isophthalamide (nylon 6,I), hexamethylene  
adipamide/hexamethylene-isophthalamide (nylon 6,6/6I), hexamethylene  
adipamide/hexamethylene-terephthalamide (nylon 6,6/6T); poly (2,2,2-  
trimethyl hexamethylene terephthalamide), poly(m-xylylene adipamide)  
15 (MXD6), poly(p-xylylene adipamide), poly(hexamethylene terephthalamide),  
poly(dodecamethylene terephthalamide), polyamide 6T/6I, polyamide  
6/MXDT/I, polyamide MXDI, and the like. Blends of two or more  
aliphatic/aromatic polyamides can also be used. Aliphatic/aromatic polyamides  
can be prepared by known preparative techniques or can be obtained from  
20 commercial sources. Other suitable polyamides are described in U.S. patents  
4,826,955 and 5,541,267, which are incorporated herein by reference.

The first nylon layer is an oriented film which is attached to the barrier film  
such that the first nylon layer is facing the second nylon layer. The first nylon  
25 layer may be either uniaxially or biaxially oriented through techniques which  
are well known in the art. Preferably, the first nylon layer is biaxially oriented.  
The first nylon layer may comprise any of the polyamide materials described  
above. In the preferred embodiment of the invention, each of the nylon layers  
preferably comprise nylon 6, nylon 66, nylon 666 or a combination thereof.

Most preferably, the nylon layers of the multilayered films preferably comprise nylon 6. Each of the nylon layers of the films described herein may comprise the same or a different nylon composition.

- 5 In the preferred embodiment of the aforescribed multilayered film, the second and third nylon layers of the barrier film are additionally blended with a silicone oil lubricant. This silicone oil may generally comprise any surface active lubricant which is preferably comprised of a polydimethylsiloxane material. The preferred silicone oils suitable for use in the present invention
- 10 are food grade silicone oils. These are preferably a clear fluid, with a wide range of viscosities, ranging from about 0.65 cSt up to about 100,000 cSt., are essentially non-toxic and present a low environmental hazard. Additionally, these are very thermally stable materials that have low surface tension and a minimal viscosity variation of from about -40 °C to about 204°C. Silicone oils
- 15 are also available in industrial and medical grades.

- The food grade polydimethylsiloxane silicone oils are preferably 100% active silicone fluids that are inert, nontoxic and non-carbonizing. They generally have number average molecular weights ranging from about 7,500 to about
- 20 106,000. In the preferred embodiment of the invention, the food grade silicone oils used have viscosities ranging from about 50 cSt to about 1,000 cSt.

- While the silicone oil is blended with the nylon material, once the nylon-oil
- 25 blend is formed into a layer, the oil typically blooms to a surface of the nylon layer. Accordingly, it has been found that when the multilayered films of the invention are produced and rolled up for storage, the silicone oil will prevent the antifog composition from migrating out of the sealant film and into an adjacent nylon layer. The silicone oil may be applied using techniques that are

well known in the art. In the preferred embodiment of the silicone oil component is blended together with the nylon component to form a nylon blend, prior to forming the nylon into a layer, via well known extrusion techniques described in detail below. Alternately, a silicone oil may be coated  
5 onto the outer surface of the nylon layer. Suitable coating methods include dip coating, meniscus coating, roller coating, doctor blade coating, and the like which are well known in the art.

Positioned between the second nylon layer and the third nylon layer of this  
10 multilayered film is an oxygen barrier layer. The oxygen barrier layer preferably is an ethylene vinyl alcohol layer. Ethylene vinyl alcohol compounds are well known in the art and readily commercially available. Copolymers of ethylene and vinyl alcohol suitable for use in the present invention can be prepared, for example, by the methods disclosed in U.S.  
15 patents 3,510,464; 3,560,461; 3,847,845; 3,595,740 and 3,585,177. The ethylene vinyl alcohol copolymer can be a hydrolyzed ethylene vinyl acetate copolymer. The degree of hydrolysis can range from about 85% to about 99.5%. The ethylene vinyl alcohol copolymer preferably contains from about 15 to about 65 mol percent ethylene and more preferably about 25 to about 50  
20 mol percent ethylene. Copolymers of lower than 15 mol percent ethylene tend to be difficult to extrude while those above 65 mol percent ethylene have reduced oxygen barrier performance. The term "ethylene/vinyl alcohol copolymer" or "EVOH" is intended to comprise also the hydrolyzed or saponified ethylene/vinyl acetate copolymers and refers to a vinyl alcohol  
25 copolymer having an ethylene comonomer, which may be obtained, for example, by the hydrolysis of an ethylene/vinyl acetate copolymer or by chemical reaction of ethylene monomers with vinyl alcohol.

Positioned on a second surface of the third nylon layer is a high clarity, heat

sealable polyolefin sealant film which may or may not be a sealant film is preferably comprised of polyethylene, and has an antifog composition that is either combined with the polyethylene or coated on a surface of the sealant film opposite the nylon layer. Non-limiting examples of suitable polyethylenes are low density polyethylene (LDPE), linear low density polyethylene (LLDPE), linear medium density polyethylene (LMDPE), linear very-low density polyethylene (VLDPE), linear ultra-low density polyethylene (ULDPE), metallocene linear low density polyethylene (m-LLDPE) high density polyethylene (HDPE). Of these, the most preferred is a low density polyethylene, particularly linear low density polyethylene.

The antifog composition prevents condensation on the film when used to package products such as fresh meats, vegetables, etc. Non-limiting examples of antifog compositions are glycerol monoesters of a saturated or unsaturated fatty acid having from about 8 to about 20 carbon atoms, glycerol diesters of a saturated or unsaturated fatty acid having from about 8 to about 20 carbon atoms and ionic surfactants having phosphate, sulfate or quaternary amine functional end groups. Also suitable as antifog compositions are surfactants including anionic, cationic, nonionic and amphoteric surfactants. Suitable ionic surfactants have phosphate, sulfate or quaternary amine functional end groups. Other antifog compositions include sorbitan esters of aliphatic carboxylic acids, glycerol esters of aliphatic carboxylic acids, esters of other polyhydric alcohols with aliphatic carboxylic acids, polyoxyethylene compounds, such as the polyoxyethylene sorbitan esters of aliphatic carboxylic acids and polyoxyethylene ethers of higher aliphatic alcohols. Preferred antifog compositions are glycerol monooleate, glycerol monostearate, sorbitan esters and blends thereof. When the antifog composition is incorporated into the sealant film, it is blended into the polyethylene composition preferably in an amount of from about 0.1 weight percent to about 5 weight percent. When

the antifog composition is coated on the sealant film it is provided with a coating weight of from about 0.2 to about 0.6 g/m<sup>2</sup>. Suitable antifog compositions are described, for example, in U.S. patent 5,766,772.

5 The first and second nylon layers of this multilayered film, as well as the third nylon layer and the sealant film, are preferably attached together via an intermediate adhesive tie layer. Suitable adhesive materials include polyurethanes, epoxies, polyesters, acrylics, anhydride modified polyolefin and blends thereof. Modified polyolefin compositions have at least one functional moiety preferably selected 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 and anhydride the like. The adhesive layers may also optionally comprise a colorant, an ultraviolet light absorber or both. The adhesive layers may be applied directly onto either of the adjacent layers by any appropriate means in the art, such as by coating. Suitable coating techniques are described above.

The invention also provides a multilayered film which comprises an outer film attached to an inner film, wherein the outer film comprises i) a first nylon layer having first and second surfaces; ii) an oxygen barrier layer having first and second surfaces, with its first surface being attached to said second surface of said first nylon layer; iii) a second nylon layer having first and second surfaces, with its first surface being attached to said second surface of said oxygen barrier layer; and wherein inner film comprises i) a third nylon layer having first and second surfaces, which third nylon layer has a silicone oil blended therein; ii) a first adhesive tie layer having first and second surfaces, with its first surface being attached to the second surface of said third nylon layer; and iii) a sealant film having first and second surfaces, with its first surface on the

second surface of the first adhesive tie layer, which sealant film contains at least one polyethylene layer, and which at least one polyethylene layer either contains an antifog composition therein or has an antifog composition coated on a surface thereof; and wherein said outer film and said inner film are attached together via a second adhesive tie layer such that the second surface of said second nylon layer is attached to the first surface of said third nylon layer. Each of the nylon layers, the oxygen barrier layer, the adhesive tie layers, the silicone oil and the sealant film preferably comprise the same materials as described herein with respect to the first multilayered film of the invention.

Each of the nylon layers, oxygen barrier layers, adhesive layers or sealant films of the multilayered films of the invention 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. 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 the art. Such may be used in amounts, for example, 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 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 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 lactams such as caprolactam and lauryl lactam, sulfonamides such as o,p-toluenesulfonamide and N-ethyl, N-butyl benzylsulfonamide, and combinations of any of the above, as well as other plasticizers known to the art.

Each of the layers of the barrier film described above are preferably joined together by coextrusion. Additionally, each of the component layers of said outer and inner films are preferably joined together by coextrusion. In the coextrusion process, for example, the polymeric material for the individual layers are fed into infeed hoppers of a like number of extruders, each extruder handling the material for one or more of the layers. In the preferred embodiment of the invention, this technique is used to form a blend of the nylon material and the silicone oil. Preferably, the silicone oil is added to melted nylon at about 100 ppm to about 200 ppm, more preferably from about 125 ppm to about 175 ppm, and most preferably from about 140 ppm to about 160 ppm. The melted and plasticated streams 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. Additional rolls may be employed. In a 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. Processes of coextrusion to form film and sheet laminates are generally known. Typical coextrusion techniques are described in U.S. patents 5,139,878 and 4,677,017.

Alternately, individual films may first be formed as separate layers and then laminated together under heat and pressure with or without intermediate adhesive layers. 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. Typically the outermost nylon layer of a film of the invention and the antifog composition containing sealant film will be positioned on one another such that each of the antifog composition layer and the silicone oil layer are facing outward, 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.

25

In a preferred embodiment of the first multilayered film of the invention, the individual layers of the barrier film are coextruded, while the first nylon film is preferably laminated to the barrier film such that the first nylon layer is attached to the second nylon layer. The first and second nylon layers are

preferably attached by lamination via a first intermediate adl  
discussed above. In a preferred embodiment of the second multilayered film  
of the invention, the individual layers of each of the outer film and the inner  
film are coextruded, while the outer film is preferably laminated to the inner  
5 film via a first intermediate adhesive tie layer such that said second nylon layer  
is facing the third nylon layer.

In the first multilayered film of the invention described herein, it is preferred  
that the first nylon layer is either monoaxially or biaxially oriented prior to  
10 being attached to the barrier film, preferably being biaxially oriented. The  
second and third nylon layers and the sealant film are preferably unoriented,  
but may be either monoaxially or biaxially oriented. For the purposes of the  
present invention the term draw ratio is an indication of the increase in the  
dimension in the direction of draw. Preferably, in the present invention the  
15 first nylon layer is drawn to a draw ratio of from 1.5:1 to 5:1 uniaxially in at  
least one direction, i.e. its longitudinal direction, its transverse direction or  
biaxially in each of its longitudinal and transverse directions. Preferably, the  
first nylon layer is simultaneously biaxially oriented, for example orienting a  
plasticized film in both the machine and transverse directions at the same. This  
20 results in dramatic improvements in clarity strength and toughness properties.  
Alternately, the nylon layers may be unoriented cast nylon.

It is also within the scope of the invention that the individual nylon layers of  
the multilayered film be subjected to a corona treatment in order to improve  
25 the adhesion to other layers. A corona treatment is a process in by which a  
layer of material is passed through a corona discharge station giving the  
surface of the layer a charge that improves its ability to bond to an adjacent  
layer. However, this step is not required. If conducted, it is preferably done  
immediately after extrusion of the layer or film.

In the preferred embodiment of the second multilayered film of the invention described herein, each of the first and second nylon layers of the outer film are preferably uniaxially or biaxially oriented, more preferably biaxially oriented.

5 Said orientation may be conducted prior to joining said first and second nylon layers of the outer film with the oxygen barrier layer, or each component layer of said outer film may be oriented together. Further, the inner film may be either an oriented or unoriented film.

10 Optionally, the overall multilayered films may be either uniaxially or biaxially oriented in a manner and in an amount indicated above. However, it is preferred that none of the individual layers or overall films of the invention are heat set so that they are shrinkable both in both the transverse and longitudinal directions. In this case, other individual layers may or may not have been  
15 oriented already.

Although each layer of each of the multilayer film structures may have different thicknesses, the thickness of each of the nylon layers is preferably from about 1  $\mu\text{m}$  to about 25  $\mu\text{m}$ , more preferably from about 3  $\mu\text{m}$  to about 8  
20  $\mu\text{m}$ , and most preferably from about 4  $\mu\text{m}$  to about 6  $\mu\text{m}$ . In an embodiment where the silicone oil is coated onto its corresponding nylon layer, the silicone oil coating preferably has a thickness of from about 1  $\mu\text{m}$  to about 25  $\mu\text{m}$ , more preferably from about 2  $\mu\text{m}$  to about 8  $\mu\text{m}$ , and most preferably from about 3  $\mu\text{m}$  to about 5  $\mu\text{m}$ . The thickness of the ethylene vinyl alcohol layer is  
25 from about 1  $\mu\text{m}$  to about 25  $\mu\text{m}$ , preferably from about 2  $\mu\text{m}$  to about 8  $\mu\text{m}$  and more preferably from about 3  $\mu\text{m}$  to about 5  $\mu\text{m}$ . The thickness of the sealant film is preferably from about 1  $\mu\text{m}$  to about 50  $\mu\text{m}$ , more preferably from about 10  $\mu\text{m}$  to about 30  $\mu\text{m}$ , and most preferably from about 12  $\mu\text{m}$  to about 25  $\mu\text{m}$ . If a multicomponent sealant film is included rather than an

individual antifog containing polyethylene layer, the thick  
multicomponent sealant film is preferably within this range. The overall  
thickness of either of the multilayered films is preferably from about 1  $\mu\text{m}$  to  
about 50  $\mu\text{m}$ , more preferably from about 10  $\mu\text{m}$  to about 30  $\mu\text{m}$ , and most  
5 preferably from about 12  $\mu\text{m}$  to about 25  $\mu\text{m}$ . While such thicknesses are  
preferred, it is to be understood that other film thicknesses may be produced to  
satisfy a particular need and yet fall within the scope of the present invention.

The oxygen transmission rate (OTR) of the multilayered films of the invention  
10 may be determined via the procedure of ASTM D-3985. In the preferred  
embodiment, the multilayered films according to this invention has an OTR of  
less than about 1 cc/100 in<sup>2</sup>/day or less at 65% relative humidity at 20°C and  
more preferably less than 0.1 cc/100 in<sup>2</sup> per day at 65% relative humidity at 20  
°C.

15 The multilayered films of the invention are preferably heat shrinkable,  
generally by an amount of from about 2% to about 30%, more preferably from  
about 10% to about 20 % in its length, or its width or each of its length and  
width. To provide a tightly adhering lid for a tray, for example, the film only  
20 need to exhibit shrinkage on the order of about 2 to about 3%. However, in  
order to have the film also form (unrestrained) about the side of the tray,  
higher shrinkage in the film is desirable.

The multilayered films may further have printed indicia on at least one of the  
25 nylon layers. Since such printing is on an internal surface of the structure, it  
will not rub off when the surface is contacted.

Preferably the film has a haze of about 10 % or less and a clarity of about 93%  
or higher as measured by ASTM D1003.

The multilayered films may be formed as a web and stored as a roll. It has been found that the unique structures of the inventive films are particularly effective in preventing the migration of the antifog material from the polyethylene of the sealant film to an adjacent nylon layer when in roll form. More particularly, it has been unexpectedly found that the use of a silicone oil lubricant effectively blocks the migration of the antifog. It has also been found that a biaxially oriented first nylon layer or outer film is effective in preventing migration of the antifog composition into and adjacent, biaxially oriented nylon films. Therefore, the invention is useful for a wide variety of structures formed with a wide variety of materials, in order to insure excellent antifog performance.

The multilayered films are useful for forming a food package including a container, such as a tray, having an open portion and the multilayered film sealing the open portion. Such a structure is generally referred to a lidding or packaging film. Such containers are suitable for packaging a variety of raw meats such as beef, pork, poultry, and veal, among others. A packaged food may comprises the food package and a food product such as a meat in the food package.

The container may have enclosed side walls, a floor and an top opening defining a central cavity wherein the open top optionally has a substantially flat peripheral rim. The multilayered film surrounds the container and is heat shrunk and heat sealed to it such that the antifog composition is on the open portion (facing inward) and the first nylon layer is facing away from the open portion of the container. The container may comprise a material such as cardboard, paperboard, boardstock, a plastic and combinations thereof. Preferred plastics include any one of several thermosetting or thermoplastic

resins any of which are capable of sealing to the lidding materials include acrylonitrile, an acrylic polymer, polyethylene terephthalate (PET) or copolymers thereof, polyvinyl chloride, polycarbonate, polystyrene and polypropylene. In use the multilayered film is positioned around the open portion and is caused to shrink, e.g. by the application of heat, by a sufficient amount to seal the open portion of the container.

The invention further contemplates additional layers being attached to the multilayered films either before or after attaching the first and second nylon layers or the outer and inner films. For example, additional nylon layers may be attached to either the first or second nylon layers, or additional polyethylene or polyolefin layers may be added to the sealant film. In such embodiments, each of the additional layers are preferably attached by coextrusion, but may also be attached by lamination with or without an intermediate adhesive layer.

It is also within the intended scope of the invention that any of the individual nylon layers of the invention may have a silicone oil blended therein. The silicone oil is preferably the same oil as is present in the other nylon layers of described herein. The invention, however, is not limited solely to the particular embodiments that are disclosed.

The following non-limiting examples serve to illustrate the invention.

#### EXAMPLES

In each of the following examples, a monolayer film of Huntsman Linear Low Density Polyethylene (Rexcell L3103) containing 25% of an antifog masterbatch (5% active antifog agent) was laminated to a variety of different polyamide monolayer films. The lamination was done by pressing the films together at room temperature in a GBC3500 desktop laminator. This cold

lamination simulates the contact that a polyamide film would  
antifog containing film wound in a roll. After a given number of days, the  
polyethylene film was removed and sealed to a 5"x7" polyethylene tray  
containing a pad of tissue paper soaked with 30 mils of water. The tray was  
5 placed inside a refrigerator and the extent of condensation buildup on the film  
surface was noted after a set period of time (5 hours). The degree of  
condensation and antifog performance rating is described in Table 1. A score  
of above 8 is acceptable. The results are described in Table 2.

10

TABLE 1

| Grade | Antifog Performance                                                |
|-------|--------------------------------------------------------------------|
| 0     | Fine fog across entire surface. Difficult to view product          |
| 2     | Small droplets ( 1 - 2 mm). Product somewhat obscured.             |
| 4     | Medium droplets ( 2 - 4 mm).                                       |
| 6     | Large drops ( > 4 mm).                                             |
| 8     | Moisture visible but fairly uniform w/some texture or large drops. |
| 10    | Indistinguishable from dry film over entire package.               |

TABLE 2

| Polyamide Film        | Containing<br>Silicone<br>Oil | Before<br>Lamination (In<br>Roll, form for<br>0 days) | In Roll<br>for 2<br>days | In Roll<br>for 4<br>days | In Roll<br>for 6<br>days |
|-----------------------|-------------------------------|-------------------------------------------------------|--------------------------|--------------------------|--------------------------|
| Nylon 6<br>(B100ZP)   | No                            | 8                                                     | 6                        | 5                        | 4                        |
| Nylon 6<br>(B100QP)   | Yes                           | 9                                                     | 6                        | 8                        | 9                        |
| Nylon 666<br>(CA73QP) | Yes                           | 8                                                     | 7                        | 9                        | 9                        |

- 5 The examples show the enhanced antifog performance after lamination and roll storage of the laminates using silicone oil additives.

While the present invention has been particularly shown and described with reference to preferred embodiments, it will be readily appreciated by those of  
 10 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 multilayered film comprising:

a) an oriented first nylon layer having first and second surfaces; and

b) a barrier film attached to the second surface of the first nylon layer via a

5 first adhesive tie layer, which barrier film comprises in order:

i. a second nylon layer having first and second surfaces;

ii. a silicone oil blended in said second nylon layer;

iii. an oxygen barrier layer having first and second surfaces, with its  
first surface being attached to the second surface of said second nylon  
10 layer;

iv. a third nylon layer having first and second surfaces, with its first  
surface being attached to the second surface of said oxygen barrier  
layer;

v. a silicone oil blended in said third nylon layer;

15 vi. a second adhesive tie layer having first and second surfaces, with its  
first surface on the second surface of the third nylon layer; and

vii. a sealant film having first and second surfaces, with its first surface  
on the second surface of the second adhesive tie layer, which sealant  
film comprises at least one polyethylene layer, and which at least one  
20 polyethylene layer either contains an antifog composition therein or has  
an antifog composition coated on a surface thereof;

wherein the second surface of the first nylon layer and the first surface of the  
second nylon layer are facing each other.

25 2. The film of claim 1 further comprising a silicone oil blended in said first  
nylon layer.

3. The film of claim 1 wherein said sealant film comprises at least one  
polyolefin layer.

4. The film of claim 1 wherein the antifog composition is contained within said sealant film.
- 5 5. The film of claim 1 wherein said antifog composition is coated on a surface of said sealant film.
6. The film of claim 1 wherein each of said nylon layers each independently comprise nylon 6, nylon 66, nylon 6/6,6, nylon 6,6/6 or combinations thereof.
- 10 7. The film of claim 1 wherein said first nylon layer comprises nylon 6.
8. The film of claim 1 wherein said first nylon layer comprises either nylon 6/6,6 or nylon 6,6/6.
- 15 9. The film of claim 1 wherein said silicone oil comprises a surface active lubricant.
10. The film of claim 1 wherein said silicone oil comprises a
- 20 polydimethylsiloxane material.
11. The film of claim 1 wherein said sealant film comprises a polyethylene layer selected from the group consisting of ultra low density polyethylene, low density polyethylene, linear low density polyethylene, metallocene linear low density polyethylene, medium density polyethylene, high density polyethylene
- 25 and combinations thereof.
12. The film of claim 1 wherein said sealant film comprises a linear low density polyethylene.

13. The film of claim 1 wherein each of said first and said second adhesive tie layers are selected from the group consisting of polyurethanes, epoxies, polyesters, acrylics, anhydride modified polyolefins and combinations thereof.

5

14. The film of claim 1 wherein said oxygen barrier layer comprises an ethylene vinyl alcohol polymer.

15. The film of claim 1 wherein said antifog composition comprises one or more materials selected from the group consisting of glycerol monoesters of a saturated or unsaturated fatty acid having from about 8 to about 20 carbon atoms, glycerol diesters of a saturated or unsaturated fatty acid having from about 8 to about 20 carbon atoms; ionic surfactants having phosphate, sulfate or quaternary amine functional end groups; and sorbitan esters.

15

16. The film of claim 1 wherein said first nylon layer is biaxially oriented.

17. The film of claim 1 further comprising printed indicia on at least one nylon layer.

20

18. The film of claim 1 which has an oxygen transmission rate of  $< 0.1 \text{ cc/100 in}^2 \text{ per day at } 65\% \text{ RH and } 20^\circ\text{C}$ .

19. A multilayered film comprising:

25

- a) an oriented first nylon 6 layer having first and second surfaces;
- b) a barrier film attached to the second surface of the first nylon 6 layer via a first adhesive tie layer, which barrier film comprises in order:
  - i. a second nylon 6 layer having first and second surfaces;
  - ii. a silicone oil blended in said second nylon 6 layer;

- iii. an ethylene vinyl alcohol layer having first and second surfaces, with its first surface being attached to the second surface of said second nylon 6 layer;
- iv. a third nylon 6 layer having first and second surfaces, with its first surface being attached to the second surface of said ethylene vinyl alcohol layer;
- v. a silicone oil blended in said third nylon 6 layer;
- vi. a second adhesive tie layer having first and second surfaces, with its first surface on the second surface of the third nylon layer; and
- vii. a sealant film having first and second surfaces, with its first surface on the second surface of the second adhesive tie layer, which sealant film comprises at least one polyethylene layer, and which at least one polyethylene layer either contains an antifog composition therein or has an antifog composition coated on a surface thereof;
- wherein the second surface of said first nylon 6 layer and the first surface of said second nylon 6 layer are facing each other.

20. The film of claim 19 further comprising a silicone oil blended in said first nylon 6 layer.

21. The multilayered film of claim 19 wherein said first nylon 6 layer is a biaxially oriented film.

22. A food package which comprises a container having an open portion and a multilayered film sealing the open portion, which multilayered film comprises the film of claim 1.

23. A packaged food which comprises the food package of claim 19 and a food product in the food package.

24. The packaged food of claim 23 wherein said food product comprises a meat.

5 25. A food package which comprises a container having an open portion and a multilayered film sealing the open portion, which multilayered film comprises the film of claim 19.

26. The multilayered film of claim 1 in roll form.

10

27. A multilayered film comprising:

a) an outer film which comprises:

- i. a first nylon layer having first and second surfaces;
- 15 ii. an oxygen barrier layer having first and second surfaces, with its first surface being attached to said second surface of said first nylon layer;
- iii. a second nylon layer having first and second surfaces, with its first surface being attached to said second surface of said oxygen barrier layer; and

20 b) an inner film which comprises:

- i. a third nylon layer having first and second surfaces, which third nylon layer has a silicone oil blended therein;
- ii. a first adhesive tie layer having first and second surfaces, with its first surface being attached to the second surface of said third nylon layer; and
- 25 iii. a sealant film having first and second surfaces, with its first surface on the second surface of the first adhesive tie layer, which sealant film comprises at least one polyethylene layer, and which at least one polyethylene layer either contains an antifog composition therein or has

an antifog composition coated on a surface thereof;  
and wherein said outer film and said inner film are attached together via a  
second adhesive tie layer such that the second surface of said second nylon  
layer is attached to the first surface of said third nylon layer.

5

28. The film of claim 27 further comprising a silicone oil blended in at least  
one of said first and second nylon layers.

10

29. The film of claim 27 further comprising a silicone oil blended in both of  
said first and second nylon layers.

30. The film of claim 27 wherein the antifog composition is contained within  
said sealant film.

15

31. The film of claim 27 wherein said antifog composition is coated on a  
surface of said sealant film.

20

32. The film of claim 27 wherein said nylon layers each independently  
comprise nylon 6, nylon 66, nylon 6/6,6, nylon 6,6/6 or combinations thereof.

33. The film of claim 27 wherein said nylon layers comprise nylon 6.

25

34. The film of claim 27 wherein said silicone oil comprises a surface active  
lubricant.

35. The film of claim 27 wherein said silicone oil comprises a  
polydimethylsiloxane material.

36. The film of claim 27 wherein said sealant film comprises a polyethylene

layer selected from the group consisting of ultra low density density polyethylene, linear low density polyethylene, metallocene linear low density polyethylene, medium density polyethylene, high density polyethylene and combinations thereof.

5

37. The film of claim 27 wherein said sealant film comprises a linear low density polyethylene.

10

38. The film of claim 27 wherein said first and second adhesive tie layers are selected from the group consisting of polyurethanes, epoxies, polyesters, acrylics, anhydride modified polyolefins and combinations thereof.

15

39. The film of claim 27 wherein said oxygen barrier layer comprises an ethylene vinyl alcohol polymer.

20

40. The film of claim 27 wherein said antifog composition comprises one or more materials selected from the group consisting of glycerol monoesters of a saturated or unsaturated fatty acid having from about 8 to about 20 carbon atoms, glycerol diesters of a saturated or unsaturated fatty acid having from about 8 to about 20 carbon atoms; ionic surfactants having phosphate, sulfate or quaternary amine functional end groups; and sorbitan esters.

25

41. The film of claim 27 wherein said first nylon layer film is uniaxially oriented or biaxially oriented.

42. The film of claim 27 wherein said first nylon layer is biaxially oriented.

43. The film of claim 27 which has an oxygen transmission rate of  $< 0.1 \text{ cc/100 in}^2$  per day at 65% RH and 20°C.

44. A process for forming a multilayered film comprising:

a) forming a first oriented nylon layer having first and second surfaces;

b) forming a barrier film which comprises:

- 5 i. forming a second nylon layer having first and second surfaces,  
which second nylon layer has a silicone oil blended therein;
- ii. attaching an oxygen barrier layer having first and second surfaces  
to said second nylon layer, with its first surface being attached to the  
second surface of said second nylon layer;
- 10 iii. attaching a third nylon layer having first and second surfaces to said  
oxygen barrier layer, with its first surface being attached to the second  
surface of said oxygen barrier layer, which third nylon layer has a  
silicone oil blended therein;
- iv. attaching a sealant film having first and second surfaces to said  
15 third nylon layer, with its first surface on the second surface of the third  
nylon layer, which sealant film comprises at least one polyethylene  
layer, and which at least one polyethylene layer either contains an  
antifog composition therein or has an antifog composition coated on a  
surface thereof; said sealant film being attached to said third nylon  
20 layer via a second adhesive tie layer; and

c) attaching said first oriented nylon layer to said barrier film via a first  
adhesive layer, such that the second surface of said first nylon layer and the  
first surface of said second nylon layer are facing each other.

25 45. The process of claim 44 further comprising blending a silicon oil in said  
first nylon layer.

46. The process of claim 44 wherein said barrier film is formed by  
coextrusion.

47. The process of claim 44 wherein said first oriented nylon layer and said barrier film are attached by lamination.

5 48. The process of claim 44 wherein the first oriented nylon layer is biaxially oriented.

49. A process for forming a multilayered film comprising:

a) forming an outer film which comprises:

- 10 i. a first nylon layer having first and second surfaces;  
ii. an oxygen barrier layer having first and second surfaces, with its first surface being attached to said second surface of said first nylon layer;  
iii. a second nylon layer having first and second surfaces, with its first  
15 surface being attached to said second surface of said oxygen barrier layer; and

b) forming an inner film which comprises:

- i. a third nylon layer having first and second surfaces, which third nylon layer has a silicone oil blended therein;  
20 ii. a first adhesive tie layer having first and second surfaces, with its first surface being attached to the second surface of said third nylon layer; and  
iii. a sealant film having first and second surfaces, with its first surface on the second surface of the adhesive tie layer, which sealant film  
25 comprises at least one polyethylene layer, and which at least one polyethylene layer either contains an antifog composition therein or has an antifog composition coated on a surface thereof; and

c) attaching said outer film to said inner film via a second adhesive tie layer such that the second surface of said second nylon layer is attached to the first

surface of said third nylon layer.

50. The process of claim 49 further comprising a silicone oil blended in at least one of said first and second nylon layers.

5

51. The process of claim 49 further comprising a silicone oil blended in both of said first and second nylon layers.

10

52. The process of claim 49 wherein each of said outer film and said inner film are formed by coextrusion.

53. The process of claim 49 wherein said outer film and inner film are attached by lamination.

# INTERNATIONAL SEARCH REPORT

Inter. Application No  
PCT/US2005/024823

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 B32B27/34 B32B27/32

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 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, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category * | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                 | Relevant to claim No.       |
|------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|
| X          | US 2004/053063 A1 (PORTER SIMON J ET AL)<br>18 March 2004 (2004-03-18)<br><br>claims; examples<br>paragraphs '0008! - '0046!<br>paragraphs '0047! - '0065!<br>paragraphs '0068! - '0076!                                           | 27,<br>31-43,<br>49, 52, 53 |
| X, Y       |                                                                                                                                                                                                                                    | 1-53                        |
| Y          | US 2003/170409 A1 (PORTER SIMON J ET AL)<br>11 September 2003 (2003-09-11)<br>paragraphs '0009! - '0050!<br>paragraphs '0051! - '0081!; claims;<br>examples<br>claims 29, 31, 32<br>paragraphs '0079!, '0080!<br><br>-----<br>-/-- | 1-53                        |

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

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

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

Date of the actual completion of the international search

27 September 2005

Date of mailing of the international search report

07/10/2005

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## INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US2005/024823

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages                                                                         | Relevant to claim No. |
|------------|------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A          | US 6 447 892 B1 (HATLEY EARL L ET AL)<br>10 September 2002 (2002-09-10)<br>abstract<br>column 2, line 45 - column 6, line 30;<br>claims; examples<br>----- | 1-53                  |
| A          | US 2002/197425 A1 (WOLF JOHN R ET AL)<br>26 December 2002 (2002-12-26)<br>* Comparative Example 1 *                                                        | 1-53                  |
| A          | US 2003/148123 A1 (MUSCO CARLO E ET AL)<br>7 August 2003 (2003-08-07)<br>the whole document<br>-----                                                       | 1-53                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

II

Initial Application No

PCT/US2005/024823

| Patent document<br>cited in search report |    | Publication<br>date |    | Patent family<br>member(s) |  | Publication<br>date |
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| US 2003170409                             | A1 | 11-09-2003          | AU | 2003213745 A1              |  | 22-09-2003          |
|                                           |    |                     | CA | 2477788 A1                 |  | 18-09-2003          |
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