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- (71) **Applicant (for all designated States except US):** **CRYO-VAC, INC.** [US/US]; 100 Rogers Bridge Road, Building A, Duncan, South Carolina SC 29334-0464 (US).
- (72) **Inventors; and**
- (71) **Applicants (for US only):** **FORLONI, Roberto** [IT/IT]; Via Montenero 14, I-20017 Rho (MI) (IT). **HAXHI, Aida** [IT/IT]; Via Treviso 7, I-15121 Alessandria (IT). **NE-PLENBROEK, Tonny** [NL/NL]; Schoutenkampweg 16, Soest (NL). **CANTONI, Roberto** [IT/IT]; Via Cassanese 194, I-20090 Segrate (MI) (IT). **GHIRARDI, Alessandra** [IT/IT]; Via Sapri 41, I-20156 Milano (IT).
- (74) **Agent:** **FRAIRE, Cristina**; c/o PONZELLINI GIOIA E ASSOCIATI S.R.L., Via Mascheroni, 31, I-20145 Milano (IT).

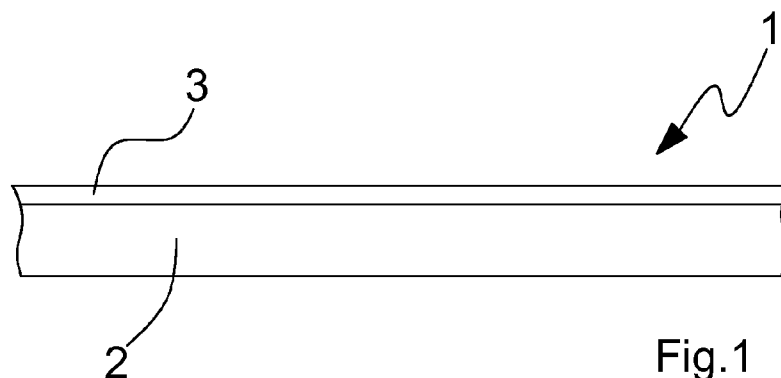
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(54) **Title:** ANTIFOG COATING COMPOSITION, COATED POLYESTER FILM, METHOD FOR ITS MANUFACTURE AND PACKAGE



**Fig. 1**

(57) **Abstract:** A coated polyester film obtainable by coating a polyester film with a coating composition comprising at least an anti-fog additive, a cationic polysaccharide and a suitable diluent. The film is peelable when sealed to polyester containers. The packages so obtained are particularly suitable for fresh red meat and fish packaging.

## Description

### Technical field

The invention relates to a coated polyester film, preferably to a biaxially oriented coated polyester film, having at least a heat-sealable surface comprising a polyester resin, said film being obtainable by coating said at least one surface with a coating composition comprising at least an antifog additive and at least a cationic polysaccharide. The coated film is endowed with antifog properties, is peelable when sealed to polyester containers or films and it is also sealable through contaminants. The invention further relates to a method for producing the coated film and to its use as a lidding, wrapping or skin film in food packaging operations.

### Background Art

Polyester films are commonly used as lidding films, in particular for ovenable containers, and for case-ready market, particularly for fresh red meat and fish packaging. These packaging systems comprise a rigid or foam container. Materials suitable for the container are either solid or foamed and, usually, comprise crystalline polyethylene terephthalate (CPET) or amorphous polyethylene terephthalate (APET). To improve the heat-sealability of these containers with the lidding films, the container often comprises a layer of amorphous polyesters (typically APET) as the food contact layer. Biaxially oriented PET is generally employed as the lidding film. To improve the heat-sealability of the lidding film to the container, often the lidding film also comprises a heat-sealable layer of lower melting or amorphous polyester, for example polyethylene terephthalate glycol (PETg) can be used. Usually, the biaxially oriented polyester films suitable for these applications are heat-set, i.e. non-heat-shrinkable or low-shrinkable materials.

Refrigerated food items are often displayed to consumers by resting the food item in a tray and covering the top of the tray with a transparent plastic film wrap. Typically, the food tray will have a perimeter lip extending above the stored food item so that the plastic film covering the top of the tray does not touch most of the packaged food. In this arrangement, the consumer may see clearly through the plastic wrap to view the food item stored in the package.

Upon refrigeration of a food item packaged in this manner, a "fog" may form on the inner, food-contact or food-side surface of the film, especially if the packaged food item

has a high moisture content. The term "fog" describes the collection of small moisture droplets that condense on the inner side of the film wrap. Unfortunately, these water droplets may cloud the inner surface of the film and thus obstruct or disrupt the view through the film resulting in a negative consumer perception because of the inability to see clearly the packaged food through the plastic film wrap.

There have been several approaches to reduce the negative effects of fogging. One approach involves dispersing one or more antifog agents, i.e. agents able to prevent the buildup of moisture drops on a surface, into the plastic film resin during processing of the film. Once in the film resin, the antifog agent tends to migrate to the surface of the film and raise the surface tension of the film. As a result, the water on the film surface tends to form a relatively continuous film-like, transparent sheet of water rather than a fog.

Another approach to minimize the negative effects of fogging on a film involves applying an antifog coating directly to the plastic film's inner, food-side surface. Although this approach adds the expense of an additional coating step, it provides the benefit of applying the antifog agent to the film surface where it is most effective at reducing fogging.

These packaging films must be antifog in order to guarantee the pack appearance of the package and good see-through quality for consumer inspection. Several antifog additives are known in the art and can be applied with different techniques, among them coating being the most suitable one for polyester films.

Another important property of the package required by the final consumer is peelability: the force required to open the package must be comfortable for the consumer but still strong enough in order to avoid the accidental opening of the package during transportation, handling and storage of the same. Nowadays the peelability of the lid from the container is an important feature requested by most customers, to facilitate pack opening to final consumers. So far, peelability has been imparted to packaging films by admixing further resins in the sealant layer. In order to reduce the sealing strength, thereby facilitating the removal of the film from the container or from a substrate by hand, blends of the polyester resin of the heat-sealable layer with 3 to 40% by weight, more frequently 15 to 25 % by weight of an appropriate thermoplastic resin, have been usually used. Suitable thermoplastic resins that contribute to lowering the sealing strength of a polyester sealant layer of a film are polyamides, polystyrenes, in

particular styrene-butadiene block copolymers, ionomers, ethylene/unsaturated carboxylic acid copolymers, like ethylene/(meth)acrylic acid copolymers and ethylene/cyclic olefin copolymers, like ethylene/norbornene copolymers. These resins have low compatibility with the polyester resin layer and the resulting phase separation confers the desired peelability but has negative effects on the film optical properties.

It has now been found that by applying a composition comprising at least an antifog additive and at least a cationic polysaccharide to the heat-sealable surface of a polyester packaging film, both antifog and peelability properties are achieved. Further, it has also been observed that the coated film so obtained can successfully be sealed to a suitable container or to itself even in case contaminants are present on the sealing surfaces.

Cationic polysaccharides are described for use in compositions for personal care, in particular for hair applications, and in compositions for fabric cleaning and/or fabric care. Cationic polysaccharides are defined as polysaccharides containing a cationic group. The cationic charge on the cationic polysaccharide may be derived from ammonium groups, guanidium groups, sulfonium groups, phosphonium groups, bound transition metals, and other positively charged functional groups. A cationic group may be connected to the polysaccharide via an ether or an ester linkage.

Suitable polysaccharide polymers may be cellulose-based, pectin-based, starch-based, natural gum-based. Examples of starch-based polysaccharides are starches from rice, wheat, corn, tapioca or potato.

Cationic starches are well known and used in the field of paper manufacture to increase the fibres and fillers retention and to improve the physical properties of the paper. However, in Applicant's knowledge, cationic polysaccharides have never been used in connection with sealable packaging films, in particular with polyester sealable packaging films.

These cationic starches are prepared by the reaction of the starch molecule with reagents enabling the introduction of a positively charged group. The chemical bond may be of the ether or the ester type.

At present, the majority of cationic starches on the market are prepared by means of nitrogen containing reagents. The reagent used may be based on a primary, secondary or tertiary amine or on a quaternary ammonium salt. The cationic starches may also be "amphoterised" by introducing anionic substituents into the starch. In this case, the

amphoteric products are both cationic and anionic. Typically, the anions are phosphate or phosphonate groups.

GB2063282 describes a process for the cationization of starch, cationic starches so prepared and their use in different industrial fields: paint, varnish and ink industry, the plaster industry, ceramic industry, agriculture etc. US5891305, US4613407 and US8088209 describe the use of cationic additives for the manufacture of paper. EP1358806 describes a coating composition comprising at least one starch, at least one insolubiliser and optionally a plasticizer, such composition being coated onto food service bowls in order to provide water and oil resistance.

#### **Disclosure of the invention**

It is therefore a first object of the present invention a parent composition, namely a precursor of a coating composition, comprising at least an antifog additive, at least a cationic polysaccharide and no diluent.

A second object of the present invention is a coating composition comprising at least an antifog additive, at least a cationic polysaccharide and a suitable diluent.

A third object of the present invention is a coated polyester film, preferably a biaxially oriented coated polyester film, said film being obtainable by coating a suitable polyester film with a coating composition comprising at least an antifog additive, a cationic polysaccharide and a suitable diluent.

A fourth object of the present invention is a method for the manufacture of a coated polyester film, preferably a biaxially oriented coated polyester film, said method comprising the step of

- a) extruding a polyester film; and
- b) coating at least a surface of the film with a coating composition comprising at least an antifog additive, a cationic polysaccharide and a suitable diluent.

A fifth object of the present invention is a package comprising the coated polyester film of the invention and a product, optionally placed into a container.

The term “ polyester” is used herein to refer to both homo-and co-polyesters, wherein homo-polyesters are defined as polymers obtained from the condensation of hydroxyacids or lactones or of one dicarboxylic acid with one diol and co-polyesters are defined as polymers obtained from the condensation of one or more dicarboxylic acids with one or more diols. Among polyesters, biodegradable polyesters are also included, in particular aliphatic and aromatic polyesters.

Example of biodegradable polyesters are: polyglycolide (PGA) and its copolymers with caprolactone, lactide or trimethylene carbonate, polylactide (PLA) , poly(lactide-co-glycolide) (PLGA), Poly(butylene succinate) (PBS) and poly(ethylene succinate), poly(butylene adipate-co-terephthalate) (PBAT).

A suitable PLA is commercialized for example under the tradename of NatureWorks® by CargillDow. A suitable PBAT is sold as Ecoflex® by BASF, Eastar Bio® by Eastman Chemical, Origo-Bi® by Novamont.

Polyesteramides may also be used such as those commercialised by Bayer under the tradename BAK®.The first object of the present invention is a parent composition comprising at least an antifog additive, at least a cationic polysaccharide and no diluent.

The first object of the present invention is a parent composition, namely a precursor of a coating composition, comprising at least an antifog additive, at least a cationic polysaccharide and no diluent.

The parent composition does not comprise diluents, i.e. does not comprise diluents in an amount sufficient to disperse or dissolve at least partially the components.

With the term “ diluent(s)” solid or liquid inert compounds – namely compounds which are not active per se but are useful in diluting or dissolving the ingredients of a composition - are meant. Diluents preferably are liquid diluents, more preferably are solvents (i.e. compounds able to dissolve at least partially, the components), even more preferably are polar solvents, such as water, alcohols, glycols etc, most preferably the diluent is water, or their admixtures.

The parent composition according to the first object of the present invention may consist of at least an antifog additive and at least a cationic polysaccharide.

The ratio by weight between the antifog additive and the cationic polysaccharide in the present parent composition is generally comprised between 1:20 and 20:1, preferably between 1:10 and 10:1, more preferably between 1:7 and 7:1, even more preferably between 1:5 and 5:1, most preferably between 2:1 and 1:2.

Upon dilution with a suitable diluent(s) and, optionally, by addition of further components, the parent composition furnishes the coating composition according to the second object of the present invention.

Accordingly to the second object of the present invention, the coating composition comprises at least an antifog additive, at least a cationic polysaccharide and a suitable diluent, wherein said antifog is in an amount from 0.1% to 5.0% by weight and said

cationic polysaccharide in an amount from 0.1% to 3.5% with respect to the total weight of the composition.

Preferably, said coating composition is a liquid composition, such as a solution, a suspension, an emulsion or a colloidal dispersion, more preferably is a solution or an emulsion, even more preferably is an aqueous solution.

In case of a liquid composition, the diluent is preferably a liquid solvent.

In a preferred embodiment, the liquid coating composition of the present invention comprises at least an antifog additive in an amount from 0.1% to 2.0 %, more preferably from 0.5 % to 1.5% and at least a cationic polysaccharide in an amount from 0.15% to 3%, even more preferably from 0.2% to 1.0% together with the selected diluent, preferably with water.

All the above percentages are percentages by weight calculated with respect to the total weight of the coating composition.

In the above coating composition other additives may also be present to impart better properties for instance to improve the stability of the composition, its sprayability, its adhesion to the surface after coating etc...

In one embodiment the coating composition of the present invention comprises an amount by weight of cationic polysaccharide(s) equal or lower than the amount by weight of antifog additive(s).

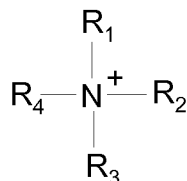
In another embodiment the amount by weight of cationic polysaccharide(s) is higher than the amount by weight of antifog additive(s).

Suitable antifog additives for the present parent and coating compositions are non-ionic surfactants selected among polyhydric alcohol fatty acid esters, higher fatty acid amines, higher fatty acid amides, polyoxyethylene ethers of higher fatty alcohols, and ethylene oxide adducts of higher fatty acid amines or amides. Among these, polyhydric alcohol fatty acid esters, polyoxyethylene ethers of higher fatty alcohols and glycerin fatty acid esters are preferred. Among them, polyhydric alcohol fatty acid esters, commonly known as Spans, or their ethoxylated derivatives Tweens, such as Tween 80 (ethoxylated sorbitan mono-oleate, vegetal origin) or Tween 20 (polyoxyethylene (20) sorbitan monolaurate) are particularly preferred.

Other particularly preferred antifog additives for use in the present composition are Glucopon® 650 EC (an alkyl polyglycosides from Cognis Deutschland GmbH&Co) and Rhodasurf® 870/H-20 (an ethoxylated fatty alcohol from Rhoda).

As defined herein, a cationic polysaccharide is a polysaccharide containing at least a cationic group. The cationic charge on the cationic polysaccharide may be derived from ammonium groups, guanidium groups, sulfonium groups, phosphonium groups, bound transition metals, and other positively charged functional groups.

A preferred cationic group is a quaternary ammonium group according to the formula



wherein each R1, R2, R3 and R4 is independently a lower alkyl or a lower hydroxyalkyl group. Preferably each R1, R2, R3 and R4 is independently a C1-C6 alkyl or a C1-C6 hydroxyalkyl group. More preferably, R1, R2 and R3 are identical C1-C4 alkyl groups and R4 is a C3-C6 hydroxyalkyl group. Even more preferably, R1, R2 and R3 are methyl groups and R4 is a C3-C6 hydroxyalkyl group. Most preferably the cationic group is a quaternary 2-hydroxy-3-(trimethylammonium)propyl group.

A cationic group may be preferably connected to the polysaccharide via an ether or an ester linkage.

The polysaccharide component of the cationic polysaccharide is a polymer comprising monosaccharide units linked by glycosidic linkages. The monosaccharide unit may be an aldose or a ketose of 5 or 6 carbon atoms. The polysaccharide may be a homopolysaccharide or a heteropolysaccharide, it may be linear or branched, and/or it may contain substituents, and/or it may be hydrophobically modified.

Suitable polysaccharide polymers may be cellulose-based, pectin-based, starch-based, natural gum-based.

Examples of cellulose-based polysaccharides are hydroxyethylcellulose, hydrophobically modified hydroxyethylcellulose, ethyl hydroxyethyl cellulose, hydrophobically modified ethyl hydroxyethyl cellulose, hydroxypropylcellulose or sodium carboxymethylcellulose.

Examples of starch-based polysaccharides are starches from rice, wheat, corn, tapioca or potato.

Examples of natural gum-based polysaccharides are polygalactomannans like guar gums or locust bean gums, polygalactans like carrageenans, polyglucans like xanthan gums, polymannuronates like alginate. Preferred natural gums are based on guar gum.



Preferred cationic polysaccharides are cationic guar gums such as Guar gum 2-hydroxy-3-(trimethylammonium)propyl ether chloride and Guar gum 2-hydroxypropyl, 2-hydroxy-3-(trimethylammonio) propyl ether chloride. Suitable cationic guar gums are sold under the trade name Jaguar by Rhodia. Also preferred are cationic starches such as (3-Chloro-2-Hydroxypropyl)Trimethylammonium Chloride modified starch. Suitable cationic starches are sold for example under the tradenames HI-CAT or VECTOR by Roquette.

The starch may be a partially hydrolysed starch and it further may contain substituents and/or it may be hydrophobically modified. Cationic starches modified with a 2-hydroxy-3-(trimethylammonium) propyl group, such as 2-hydroxy-3-(trimethylammonium)propyl ether chloride modified starch are preferred. Suitable cationic starches are sold under the tradenames Vector by Roquette, SolsaCAT by PT. Starch Solution International Kawasan, CATO by National Starch & Chemical, Mermaid by Shikishima Starch and Excell by Nippon Starch Chemical.

Particularly preferred cationic polysaccharides for the present invention are cationic starches. Commercially available and preferred grades are sold under tradenames VECTOR SC 20157 (Roquette) and VECTOR IC 27216 (Roquette).

Cationic starches may be combined with certain anions, such as silicate and/or phosphonate and/or phosphate and/or ethylenediaminetetraacetate (EDTA) and/or methylglycinediacetate (MGDA) and/or nitrilotriacetate (NTA) and/or iminodisuccinate (IDS) and/or hydroxide and/or citrate and/or gluconate and/or lactate and/or acetate anions.

The cationic starches used for the present invention can be obtained by any process, in aqueous or other solvent medium or in the dry phase, such process enabling one or a number of nitrogenous group(s) of electropositive nature to be fixed to the starch or a mixture of starches of any nature and origin.

The degree of substitution (DS), representing the number of cationic groups, typically ranges from about 0.01 to 5%, preferably from 0.03% to 2%.

The cationic starches used according to the invention can moreover be of "polycationic" nature, such as those described EP406837 and US429444.

Suitable liquid diluents, preferably solvents, for the liquid composition of the present invention comprise water, alcohols, glycol ethers and paraffines, water being the most preferred.

The liquid composition can be prepared by adding the selected amount of the antifog additive(s) and the selected amount of the cationic polysaccharide(s) into the selected amount of solvent in a tank; if water is used, the composition is kept under mechanical stirring preferably up to dissolution or emulsification of the components, at a temperature typically from about 40°C to about 50°C before being applied onto the film of the present invention using techniques known in the art such as coating, wiping, spraying or dipping.

In a preferred embodiment, water is used as solvent and the resulting liquid composition comprises from 0.4% to 1.5%, from 0.4 to 1.3% by weight of the antifog additive and from 0.1 to 1.1 %, 0.1 to 0.4 % by weight of cationic polysaccharide.

In a most preferred embodiment, water is used as solvent and the liquid composition comprises from 0.5 to 1.3%, from 0.5 to 1.1% by weight of the antifog additive and from 0.2 to 0.9%, from 0.2 to 0.3% by weight of the cationic polysaccharide.

In one embodiment, the coating composition consists of from 0.4% to 1.5%, preferably from 0.5 to 1.3 %, from 0.5 to 1.1% by weight of the antifog additive, from 0.1 to 1.1 %, preferably from 0.2 to 0.9 %, from 0.2 to 0.3% by weight of the cationic polysaccharide, and water up to the balance.

In one embodiment, the coating composition comprises 0.5% by weight of the antifog additive, 0.3% by weight of the cationic polysaccharide and water.

In another embodiment, the coating composition comprises 1.1% by weight of the antifog additive, 0.2 or 0.8% by weight of the cationic polysaccharide and water.

In a further embodiment, the coating composition comprises 1.0% by weight of the antifog additive, 0.4 or 0.8% by weight of the cationic polysaccharide and water.

In an additional embodiment, the coating composition comprises 1.5% by weight of the antifog additive, 0.4 % by weight of the cationic polysaccharide and water.

In one embodiment, the coating composition consists of 0.5% by weight of the antifog additive, 0.3% by weight of the cationic polysaccharide and water up to the balance.

In another embodiment, the coating composition consists of 1.1% by weight of the antifog additive, 0.2 or 0.8% by weight of the cationic polysaccharide and water up to the balance.

In a further embodiment, the coating composition consists of 1.0% by weight of the antifog additive, 0.4 or 0.8% by weight of the cationic polysaccharide and water up to the balance.

[0001] In an additional embodiment, the coating composition consists of 1.5% by weight of the antifog additive, 0.4 % by weight of the cationic polysaccharide and water up to the balance.

In a preferred embodiment, the cationic polysaccharide is 2-hydroxy-3-(trimethylammonium)propyl ether chloride modified starch and the antifog additive is ethoxylated sorbitan mono-oleate or polyoxyethylene (20) sorbitan monolaurate.

The composition can comprise more than one antifog additive and more than one cationic polysaccharide.

A third object of the present invention is a coated polyester film 1, as shown in figure 1, preferably a biaxially oriented coated polyester film, said film being obtainable by coating a suitable polyester film 2 with a coating composition 3 comprising at least an antifog additive and at least a cationic polysaccharide.

The present polyester film comprises a surface coating, wherein said coating comprises a composition comprising at least an antifog additive and at least a cationic polysaccharide.

Preferably said coating consists of at least an antifog additive and at least a cationic polysaccharide.

The total thickness of the inventive coated polyester film may vary within wide limits. It is preferably from 3 to 100  $\mu\text{m}$ , in particular from 5 to 80  $\mu\text{m}$ , preferably from 10 to 70  $\mu\text{m}$ , even more preferably from 15 to 50  $\mu\text{m}$ . The thickness of the coating is generally lower than 5  $\mu\text{m}$ , preferably lower than 2  $\mu\text{m}$ , more preferably lower than 1  $\mu\text{m}$ .

Typically, for tray lidding applications, the films of the present invention have no or negligible shrink at temperatures below 140°C. The shrink (in each direction) is generally at most 15% at temperatures up to 100°C, up to 120°C, and even up to 140°C.

Usually the shrink (in each direction) does not exceed 20% over the common heat-sealing temperature range of polyester films, namely in the range of from 140 to 200°C. The shrink generally does not exceed 20% (in each direction) at 180°C, at 160°C, and even at 150°C.

However, for other packaging applications, for instance in case of wrapped products or bags, different values of free shrink and/or of shrinking temperatures can be recommendable. Tailored shrink behaviour can be imparted to the present film by the

skilled in the art through a suitable selection of process parameters, especially through appropriate orientation and/or annealing settings.

The coated polyester film object of the present invention is obtainable by coating a suitable polyester film with the coating composition previously described.

With a suitable “ polyester film ” a mono or multilayer film comprising a major amount of polyesters, preferably an amount higher than 50%, 60%, 70%, 80%, 90% or 95% with respect to the total weight of the polymer resins of the film, more preferably consisting of one or more polyesters, is meant.

The suitable polyester film may have one or both the two outer surfaces particularly suitable to be sealed. In the present description that surface is generally identified as sealing or sealant or sealable surface. In case of monolayer films both the surfaces are equally heat sealable; in case of a multilayer structure, said sealing surface is generally the outer surface of an external layer, named heat sealing or sealant or sealable layer, whose composition is tailored to allow a particularly advantageous and smooth sealability of the whole film.

In a first embodiment, the suitable polyester film to be coated according to the present invention is a monolayer polyester structure where the single layer acts as heat-sealable and structural layer and comprises an amorphous polyester resin optionally blended with a crystalline polyester, the term “ crystalline ” being used herein to indicate that the resin has a definite melting temperature. The amorphous polyester guarantees the heat-sealability of the film.

The heat-sealable layer or monolayer comprises at least a first amorphous polyester resin and optionally a further polyester resin.

Said amorphous polyester is characterized by a T<sub>g</sub> value lower than 115°C, preferably lower than 95°C, even more preferably lower than 85°C.

Suitable amorphous polyester resins are those deriving from an aliphatic diol and a cycloaliphatic diol with one or more dicarboxylic acids, preferably an aromatic dicarboxylic acid. Preferred amorphous polyesters are co-polyesters of terephthalic acid with an aliphatic diol and a cycloaliphatic diol, particularly ethylene glycol and 1,4-dicyclohexanedimethanol. The preferred molar ratios of the cycloaliphatic diol to the aliphatic diol are in the range from 10:90 to 60:40, preferably in the range from 20:80 to 40:60, more preferably from 30:70 to 35:65. Specific examples of particularly preferred amorphous polyester are PETG Eastar® 6763, sold by Eastman (glass transition

temperature 81°C, density 1.27 g/cc) and Embrace sold by Eastman Chemical, (glass transition temperature 70.6°C, density 1.32 g/cc).

A blend of two or more amorphous polyesters is also suitable for the heat-sealable layer or monolayer of the film of the present invention.

Suitable further polyesters are those deriving from an aliphatic diol, preferably ethylene glycol and one or more aromatic dicarboxylic acid, preferably terephthalic acid.

Polyethylene terephthalate and its copolyesters are preferred. Specific examples include Eastapak Copolyester 9921 sold by Eastman and Ramapet N180 sold by Indorama.

The amount of the first amorphous polyester in the heat-sealable layer or monolayer of the film according to the present invention is preferably at least 30% by weight with respect to the total weight of the heat-sealable layer or monolayer, preferably at least 50% by weight, even more preferably at least 80%.

The amount of the further polyester in the heat-sealable layer or monolayer of the film according to the present invention is generally at most 70% by weight with respect to the total weight of the heat-sealable layer or monolayer, preferably at most 50% by weight, even more preferably at most 20%.

In a preferred embodiment the heat-sealable layer or monolayer of the film of the present invention only comprises an amorphous polyester.

Preferably said amorphous polyester derives from an aliphatic diol and a cycloaliphatic diol with one or more dicarboxylic acids, preferably an aromatic dicarboxylic acid selected among those deriving from an aliphatic diol and a cycloaliphatic diol with one dicarboxylic aromatic acid, more preferably with terephthalic acid.

In a preferred embodiment, a suitable film of the present invention comprises a heat-sealable layer 2a and a base layer 2b, both layers comprising a polyester. In this case, the film has a two-layer structure, as shown in figure 2.

The heat-sealable layer can have a thickness up to about 25  $\mu\text{m}$ , preferably up to about 15  $\mu\text{m}$ , more preferably between about 0.5  $\mu\text{m}$  and 10  $\mu\text{m}$ , and even more preferably between about 0.5  $\mu\text{m}$  and 7  $\mu\text{m}$ .

Mixtures or blends of homo- and/or co-polyesters can be used for the base layer.

Suitable polyester for the base layer are, for example, polyesters of ethylene glycol and terephthalic acid, i.e. poly(ethylene terephthalate) (PET). Preference is given to polyesters which contain ethylene units and include, based on the dicarboxylate units,

at least 90 mol%, more preferably at least 95 mol %, of terephthalate units. The remaining monomer units are selected from other dicarboxylic acids or diols. Suitable other aromatic dicarboxylic acids are preferably isophthalic acid, phthalic acid, 2,5-, 2,6- or 2,7-naphthalenedicarboxylic acid. Of the cycloaliphatic dicarboxylic acids, mention should be made of cyclohexanedicarboxylic acids (in particular cyclohexane-1,4-dicarboxylic acid). Of the aliphatic dicarboxylic acids, the (C<sub>3</sub>-C<sub>19</sub>)alkanedioic acids are particularly suitable, in particular succinic acid, sebacic acid, adipic acid, azelaic acid, suberic acid or pimelic acid.

Suitable other aliphatic diols are, for example aliphatic diols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, 1,3-butane diol, 1,4-butane diol, 1,5-pentane diol, 2,2-dimethyl-1,3-propane diol, neopentyl glycol and 1,6-hexane diol, and cycloaliphatic diols such as 1,4-cyclohexanedimethanol and 1,4-cyclohexane diol, optionally heteroatom-containing diols having one or more rings.

Suitable amorphous polyester resins for use in the base layer are co-polyesters of terephthalic acid with an aliphatic diol and a cycloaliphatic diol, preferably ethylene glycol and 1,4-cyclohexanedimethanol. A preferred polymer is PETG Eastar® 6763 sold by Eastman.

The thickness of the base layer represents at least 50% of the overall thickness of the multi-layer film of the invention, from 50 to 90% of the overall thickness being preferred. In another preferred embodiment, the polyester film of the invention has a three layer structure, as shown in figure 3. In this structure, a second outer or abuse layer 2c is present. Said abuse layer 2c is directly adhered to one side of the base layer 2b while the heat sealing layer 2a is directly adhered to the other side. Preferably said abuse layer comprises a major amount of a polyester, in particular more than 50%, 60%, 70%, 80%, 90%, more preferably consists of a polyester homo- and/or co-polyesters as previously defined can also be used for the outer or abuse layer, alone or in admixtures. Said polyester is generally selected according to its mechanical, thermal, optical and surface properties which have to be suitable for the final applications. In particular the abuse layer has an important role in conferring stiffness, puncture resistance, thermal resistance, glossy appearance, transparency and printability to the final structure. For instance suitable polyesters for the abuse layer are RAMAPET N180 (by Indorama, density 1.4 g/cc, IV 0.8 mPas) or EASTAPAK COPOLYESTER 9921 (by Eastman Chemical, copolyester of PET).

The second outer or abuse layer can have a thickness up to about 25  $\mu\text{m}$ , preferably up to about 15  $\mu\text{m}$ , more preferably between about 0.5  $\mu\text{m}$  and 10  $\mu\text{m}$ , and even more preferably between about 0.5  $\mu\text{m}$  and 7  $\mu\text{m}$ .

The film of the present invention can further comprise a gas-barrier layer comprising well known gas-barrier resins and their blends. For example, ethylene-vinyl alcohol copolymers (EVOH), polyamides and acrylonitrile-based copolymers can be cited. Once the gas-barrier resin has been selected, its thickness will be set to provide for the desired permability properties.

Additional layers, such as for instance tie layers, to improve interlayer adhesion, may be present in the film.

Tie layers may be disposed between the respective layers in case where a sufficient adhesion is not ensured between adjacent layers. The adhesive resin may preferably comprise one or more polyolefins, one or more modified polyolefins or a blend of the above. Specific, not limitative, examples thereof may include: ethylene-vinyl acetate copolymers, ethylene-(meth)acrylate copolymers, ethylene-  $\alpha$ -olefin copolymers, any of the above modified with carboxylic or preferably anhydride functionalities, elastomers, and a blend of these resins.

One or more of the layers of the film of the present invention may contain any of the additives conventionally employed in the manufacture of polymeric films. Thus, agents such as pigments, lubricants, anti-oxidants, radical scavengers, oxygen scavengers, UV absorbers, thermal stabilisers, anti-blocking agents, surface active agents, slip aids, optical brighteners, gloss improvers, viscosity modifiers may be incorporated as appropriate.

In particular, to improve the processing of the film in high speed packaging equipment slip and/or anti-blocking agents may be added to one or both of the outer layers. The additives may be added in the form of a concentrate in a polyester carrier resin. The amount of additive is typically in the order of 0.2 to 5% by weight of the total weight of the layer.

The film of the present invention can be extruded by means well known in the art; in case of multilayer structures, i.e. a film comprising more than one layer, coextrusion equipments are used, where each resin is extruded through an extruder and all the layers are joined into the extrusion die. Typically, for polyester films, flat die is used.

The film of the present invention is, preferably, also oriented. A tubular or, preferably, flat film orientation process can be used to produce a biaxially oriented film.

In a tubular process, also known as “double bubble” process, simultaneous biaxial orientation is obtained by extruding a thermoplastic resin tube which is subsequently quenched, reheated and then expanded by internal gas pressure to induce transverse orientation, and withdrawn at a rate which will induce longitudinal orientation. An example of equipment suitable for this technique is disclosed by US4841605.

In a flat film process, the film-forming thermoplastic resins are extruded through a T-die and rapidly quenched upon a chill roll to ensure that the resins are quenched to the amorphous state.

In order to improve the adhesion of the film on the chill roll electrostatic pinning can be used, as known in the art and as described in US5494619.

Orientation is then, optionally, effected by flat stretching, simultaneously or sequentially, the quenched extrudate at a temperature above the glass transition temperature of the thermoplastic resins.

In the sequential flat orientation method a flat, quenched extrudate is firstly oriented in one direction, usually the longitudinal direction, i.e. the forward direction through the film stretching machine, and then in the transverse direction. Longitudinal stretching of the extrudate is conveniently carried out over a set of rotating rolls (MDO), which rotate at different speeds. At least one of the first pairs of rolls is heated, for example by inner circulation of hot oil. Transverse stretching is usually carried out in a tenter apparatus (TDO), which comprises a certain number of heating zones and suitable stretching means.

To produce the film of the invention the polymers for the base layer, for the heat-sealable outer layer and, where appropriate, for the second outer layer are fed to separate extruders. The melts are extruded through a multilayer T-die and quenched over a chill roll. Longitudinal stretching (MDO) of the extrudate is conveniently carried out at a temperature range from 60 to 120° C, preferably from 70 to 100°C.

In the transverse stretching (TDO), the temperatures of the film are in the range from 90° C (preheating zone) to 130° C (stretching zone), preferably from 90°C (preheating zone) to 110°C (stretching zone).



The longitudinal stretching ratio is in the range from 2.0:1 to 5.0:1, preferably from 2.3:1 to 4.8:1. The transverse stretching ratio is generally in the range from 2.4:1 to 6.0:1, preferably from 2.6:1 to 5.5:1.

In the simultaneous flat orientation method a flat, quenched extrudate is simultaneously oriented in both the longitudinal and in the transverse direction through a simultaneous tenter apparatus.

Said extrudate is fed to the pre-heating zone of a simultaneous tenter apparatus, with or without a prior passage through an IR heated oven. The temperature of the oven in said pre-heating zone, the length thereof and the time spent by the traveling web in said zone (i. e. the web speed) can suitably be varied in order to bring the sheet up to the desired temperature for bi-axial orientation. In a preferred embodiment the orientation temperature is comprised between about 90 °C and about 140 °C and the temperature of the pre-heating zone is kept between about 90 °C and about 150 °C. In said pre-heating zone the sheet is clipped but it is not yet stretched. Thereafter, the resulting hot, optionally irradiated, and clipped sheet is directed to the stretching zone of the simultaneous tenter. Any simultaneous stretching means can be used in said zone. Preferably however the clips are propelled throughout the opposed loops of the tenter frame by means of a linear synchronous motor. A suitable line for simultaneous stretching with linear motor technology has been designed by Bruckner GmbH and advertised as LISIM line. An alternative line for simultaneous stretching of the extruded flat tape is the Andritz line, based on a pantograph, equipped with two separated monorails on each side of the orientation unit. The configuration of the tenter can be varied depending on the stretching ratios desired.

The temperature in the stretching zone is kept close to the selected orientation temperature.

In case, annealing is carried out at a temperature of from 140 to 220° C, the temperature depending on the desired shrink. Subsequently, the film is wound up in a customary manner.

Following said optional annealing or heat-setting step the film is transferred to a cooling zone where generally air, either cooled or kept at the ambient temperature, is employed to cool down the film. The temperature of said cooling zone is therefore typically comprised between about 20° C and about 40° C. At the end of the line, the edges of the film, that were grasped by the clips and have not been oriented, are trimmed off and

the obtained bi-axially oriented, heat-shrinkable or heat-set film is then wound up, with or without prior slitting of the film web to the suitable width.

To improve the adhesion of the solution to the surface of the film, the heat sealable surface of the film is treated or modified to change the surface energy of the film. Surface treatments and modifications include: i) mechanical treatments, such as corona treatment, plasma treatment, and flame treatment, and ii) primer treatment. Surface treatments and modifications are known to those of skill in the art. Among them, the preferred one is corona treatment.

The polyester film can be coated with the coating composition of the first object by means of several techniques well known in the art, for example by brushing, dipping, press molding, electrostatic application, coating or spraying the coating composition onto the heat-sealable side of the film, thus providing the coated film of the present invention

A fourth object of the present invention is a method for the manufacture of a coated polyester film, preferably a biaxially oriented coated polyester film, said film being obtainable by coating a suitable polyester film with a coating composition comprising at least an antifog additive, at least a cationic polysaccharide and a diluent..

The method comprises the steps of:

- a) extruding the polyester film; and
- b) coating at least a surface of the film so obtained with a coating composition comprising at least an antifog additive and at least a cationic polysaccharide.

The method may further comprise in any order, the steps of

- c) biaxially orienting the film; and/or
- d) treating the sealant surface of the polyester film by corona treatment, plasma treatment, flame treatment or primer treatment.

In one preferred embodiment the manufacture method comprises all the steps above (refer to figure 4) according to the following sequence:

- a) extruding the suitable polyester film;
- c) biaxially orienting said extrudate;
- d) treating the sealant surface of the polyester film by corona treatment, plasma treatment, flame treatment or primer treatment;
- b) coating the film so obtained with a coating composition comprising at least an antifog additive and at least a cationic polysaccharide

In another embodiment (refer to figure 5) the manufacture method comprises all the steps above according to the following sequence

- a) extruding the suitable polyester film;
- d) treating the sealant surface of the film to change its surface energy by corona treatment, plasma treatment, flame treatment or primer treatment;
- b) coating the film so obtained with a coating composition comprising at least an antifog additive and at least a cationic polysaccharide;
- c) biaxially orienting said extrudate.

The application of the coating composition (step b) to give the coated film of the present invention, may be carried out either by an in-line method involving application during the manufacture of the polyester film or by an off-line coating method involving application after the manufacture of the polyester film.

In the preferred embodiment, the film is coated after the orientation step.

To improve the adhesion of the solution to the surface of the film, the heat-sealable side of the film may be treated or modified to change the surface energy of the film (step d). Surface treatments and modifications include: i) mechanical treatments, such as corona treatment, plasma treatment, and flame treatment, and ii) primer treatment. Surface treatments and modifications are known to those of skill in the art. Among them, the preferred one is corona treatment. Control methods known in the art are available to check if the surface treatment was efficient in order to modify the surface tension of the film. For example, surface tension test pens by Sherman Treaters can be used and ASTM D2578 can be followed.

In a preferred embodiment of the manufacture method, the film is treated or modified to change the surface energy of the film before applying the coating.

The suitable polyester films can be coated with the coating composition of the second object to give the coated polyester films of the present invention by means of several techniques well known in the art, for example by brushing, wiping, dipping, press molding, electrostatic application, coating or spraying the coating composition onto the heat-sealable surface of the film.

In a preferred embodiment, the film is coated by spraying an aqueous composition onto the heat-sealable surface of the film in a continuous process during which the film moves at a substantially steady speed. The composition to be sprayed is fed to several nozzles through a pump and is applied onto the film preferably kept in vertical position.

After the spraying, the film is allowed to pass under a spreading roll and then into a drying oven, kept at temperature preferably between 80°C and 95°C, typically 90°C for some seconds. The residence time of the film into the oven will depend on the film line speed. This speed is set-up taking into consideration the oven dimensions, the oven temperature, the film shrinkability, the drying efficiency and can be easily defined through a routine experimentation. Commercially systems are available to implement this spraying process, for instance those sold by WEKO.

Spraying doses for the manufacture of the coated film of the present invention are comprised from 0.1 to 8 ml/m<sup>2</sup>, 0.5 to 7 ml/m<sup>2</sup>, 0.5 to 5 ml/m<sup>2</sup>, 1 to 3 ml/m<sup>2</sup>.

In the preferred embodiment, the spraying dose is comprised between 1.5 ml/m<sup>2</sup> and 2.5 ml/m<sup>2</sup>.

In another preferred embodiment, the film is applied by coating the composition according to the second object of the present invention onto the heat-sealable surface of the film in a continuous process during which the film moves at a substantially steady speed.

In a preferred embodiment the sealant layer of the film is treated before applying the coating in order to increase its surface tension.

The liquid compositions can be advantageously prepared by adding the selected amount of the antifog additive into a tank containing the pre-heated water and keeping this mixture under mechanical stirring up to the dissolution of the antifog into the water. Afterwards, the selected amount of the cationic polysaccharide can be added into the tank keeping the mixture under mechanical stirring up to dissolution of the cationic polysaccharide. Preferably the mixture is kept at temperature higher than ambient temperature, for ex. 40°C.

In a preferred embodiment, the compositions so prepared are loaded into the tank of a station of flexography printing equipment under continuous stirring.

As well known for the skilled in the art, the application roller of the flexography printing equipment (called Anilox) can be selected depending on the amount of coating that has to be applied onto the films. The anilox roller rotates into the tank containing the composition and allows depositing this composition onto a rubber photopolymer roller which releases the coating onto the film surface. After the coating, the drying temperature at the printing station and into the tunnel has to be adjusted depending on

the line speed, on the coating thickness, as well known to the skilled in the art. The coated film can then be edge trimmed and collected in rolls in a further slitting step.

Alternatively, rotogravure technique may be used, where an engraved cylinder rotates in a tank containing the composition according to the second object of the present invention and releases the composition directly to the sealant side of the film. The engraved cylinder is selected by the skilled in the art, depending on the composition characteristics and on the amount of coating to be applied on the surface of the film.

In another embodiment, the film is coated by wiping the composition according to the second object of the present invention onto the heat-sealable surface of the film.

Coating and spraying process are preferred.

Coating process as described is the most preferred.

For particular packaging applications, it may be advantageous applying the coating composition of the present invention onto both the outer surfaces of the suitable polyester film. In such a case, the resulting coated films will show the advantageous properties of smooth peelability, antifog and sealability through contamination on both sides of the film.

A fifth object of the present invention is a package 10 comprising the coated polyester film of the invention and a product, optionally placed into a container.

In one embodiment (figure 6) said package 10 comprises a container 12, a product 11 placed into the container and a lid 13 formed from the coated polyester film of the invention sealed onto the container.

In another embodiment (figure 7) said package 10 comprises a container 12, a product 11 placed into the container and the coated polyester film 1 of the invention wrapped around and suitably sealed to itself.

In another embodiment (figure 8) said package 10 comprises a bag or a pouch 14 and a product 11 packaged into said bag or pouch, wherein the bag or pouch is formed by sealing the coated polyester film of the invention to itself.

Self-sealing includes fin and/or lap seals. Suitable manufacturing processes include HFFS and VFFS processes, processes commonly known in the art of packaging.

In another embodiment (figure 9), said package 10 is formed by flexible top and a bottom webs 15, 16 sealed circumferentially and enclosing a product 11, being both the webs made of the coated polyester film of the present invention.

In another embodiment (figure 10), said package 10 comprises a bottom substrate 17, a product 11 placed onto said bottom substrate and the coated polyester film 1 of the invention draped over said product and sealed onto the surface of the bottom substrate all around the product (vacuum skin packaging or VSP applications).

Preferably the product packaged according to the fifth object of the present invention is a food product, preferably fresh meat or fish.

Depending on the peculiar kind of package and on the nature of the product, the internal atmosphere can be suitably modified or removed or replaced by tailored gas admixtures, as well known in the art of packaging.

In case of tray lidding applications, the coated film of the present invention forms peelable seals with polyester-based materials, in particular with both APET and CPET containers.

Typically, the surface of the container in contact with the product, i.e. the surface involved in the formation of the seal with the lidding film, comprises a polyester resin. Examples of suitable containers for the package of the invention are CPET, APET or APET/CPET containers. Such containers can be foamed or non-foamed, i.e. solid.

The package is produced by techniques well-known to those skilled in the art. Once the food to be packaged has been introduced into the container, the coated polyester film of the invention is sealed onto the peripheral flange of the container using temperature and/or pressure according to conventional techniques and equipment. The coated film is placed on the container such that the heat-sealable coated layer is in contact with the surface of the container. Sealing is carried out by means of a heated frame at temperatures of from 140 to 220°C, 170 to 200°C at a pressure of 2 to 8 bar, 4 to 7 bar. Sealing times are typically in the order of 0.01 to 2.0 seconds, more frequently 0.5 to 1.0 seconds. The heat generated by the sealing frame, regardless of short sealing times, also promotes the shrinkage of the film, if heat-shrinkable, in both directions without distortion of the container to give a taut hermetically sealed lid.

The coated polyester film, preferably the biaxially oriented coated polyester film, of the present invention can be advantageously used in different packaging applications, preferably in food packaging applications.

Examples of possible packaging applications of said films are tray lidding, in particular case ready packages, wrapping of products - as such or placed into rigid trays - , manufactured for instance by Horizontal Form Fill Seal (HFFS) technology, bags-

comprising different seales such as end seals, transversal seals etc, pouches, prepared for examples with Vertical Form Fill Seal (VFFS) equipments, flexible packaging and - as a top web - in vacuum skin (VSP) applications.

### **EXAMPLES**

The present invention will be illustrated by some examples, however it is not to be intended as limited to these examples.

The coated biaxially oriented polyester films prepared according to the following Examples and Comparative Examples were evaluated by the test methods described below.

FREE SHRINK (%): it is the percent dimensional change in a 10 cm x 10 cm specimen of film when subjected to a selected heat; it has been measured following ASTM Standard Test Method D 2732, immersing the specimen for 5 seconds in a heated oil bath at 120°C and 140°C.

PEEL TEST (score).

The films reported in the Examples 1-6 and Comparative Examples 1-10 were sealed using a SealPac A7 inside cut machine along the flange of MAPET Faerch Trays coded 2260019008. The sealing temperature was 190°C, the sealing time was 1.0 sec and the sealing pressure was 5.8 bar. The packages had a tab (excess of film) to facilitate the opening of the package. No products were placed inside the packages.

The films reported in the Examples 7-8 were sealed using a Mondini E340 machine onto MAPET II Faerch Tray coded 2232-1B applying the sealing conditions reported in Table 5. The packages had a tab (excess of film) to facilitate the opening of the package.

The films reported in the Examples 9-11 were tested for their seal properties against a flat bottom sheet, the bottom sheet having the following composition:

- sealant layer of 20 microns, 98% Artenius Xcel M (PETG copolyester resin, Neopentylglycol-ethyleneglycol terephthalate copolymer; CAS No.: 26780-49-4, density 1.29 g/cc) and 2% SUKANO G DC S503 supplied by Sukano (see Table 1 for parameters);
- base layer of 380 microns of 100% Artenius PET Global supplied by Artenius UK Ltd (polyethylene terephthalate, density 1.33 g/cc, melting point 245°C, intrinsic viscosity 0.82 dl/g). The sheet was obtained by flat coextrusion.

Both the film and the flat bottom sheet were cut at dimension of 15 cm x 15 cm and superimposed, keeping aligned their respective longitudinal and transversal directions. Ten samples of top and bottom coupled film for each of the films of Examples 9 to 11 were prepared for each panelist.

Each sample was put in the sealing machine (Audion 460 MSIDK) and sealed with a single either longitudinal or transversal central seal across the whole length or wide of the sample. In particular, for each of the tested films (Ex. 9 – 11), in a first set of 5 samples, the seal was longitudinal, in a second set of other 5 samples transversal, for a total of 30 samples, being 15 longitudinally and other 15 transversally sealed. The sealing conditions applied were the same in terms of time, temperature and equipment used.

The sealing temperature was 190°C and the sealing time was 0.5 sec. The seal was 0.8 cm wide and 15 cm long (across the total length of the samples). The sealed specimens so obtained were then manually opened as described below and the peelability performance of each film, reported in Table 6, was expressed as an average of the peelability results judged by the three panelists, opening each 5 longitudinally and 5 transversally sealed samples. Both the longitudinal and the transversal seals resulted peelable.

For all the examples and comparative examples, the peelability of the packages or of the samples was evaluated through a panel test giving the following scores:

- “ strong/no peel seal” when the seal strength was judged too strong by the panelist;
- “ peel seal” if the seal strength was considered comfortable enough for an easy opening but still able to keep hermeticity by the panelist;
- “ weak seal” if the seal strength was considered low and insufficient to keep hermeticity by the panelist.

Five packages for each example of Table 3 below were opened by each of the three panelists. The average score was reported for each example.

#### HERMETICITY TEST

Hermeticity of the seals was evaluated according to an internal test. The packages were manufactured on a Mondini E340 machine at different sealing temperatures and times as reported in Table 5. Some films according to the present invention were sealed onto MAPET II Faerch trays coded 2232-1B (1523-30). In a first testing set called “ clean” , the films were sealed onto the tray keeping the tray flange in clean (i.e. non-



contaminated) conditions; in a second testing set called “ contaminated” , the films were sealed onto the tray after contaminating the tray flange with beef exudates.

The packages so obtained were put in a closed water tank. Vacuum was created in the headspace of the water tank and the value of the pressure (bar) inside the tank when bubbles start to escape the closed packages was recorded. 50 packages were tested for each sealing condition and the average pressure value was recorded.

The packs fit for use have to stand at least to -0.30 bar both under clean and contaminated sealing conditions.

#### ANTIFOG TEST (score)

A packaging film is defined as “ antifog” if its internal surface allows the droplets of water to lay as a smooth and uniform layer allowing visual inspection of the packaged product.

An internal test method was used to evaluate the antifog performance of the coated film. 250 ml of water were placed in a 900 ml glass vessel. The film was then secured through a rubber band tightly over the vessel; the sealant side of the film was placed towards the water without being into contact with the liquid. The vessel was then placed in a refrigerated cooler at 2-4°C. Three vessels were prepared for each example of Table 3.

The specimens so prepared were then observed after 24 hours and scored by three panelists according to the following rating scale, ordered from very poor to excellent antifog properties:

- score 1 for opaque layer of small fog droplets;
- score 2 for opaque or transparent layer of large droplets;
- score 3 for complete layer of large transparent droplets;
- score 4 randomly distributed or large transparent droplets;
- score 5 transparent film without visible water.

The final antifog score is the average of three panelists judgment.

#### SURFACE TENSION

Surface tension test pens by Sherman Treaters were used and ASTM D2578 was followed.

The polyester film structure used for the Examples 1-11 and the Comparative Examples 1-10 is reported in Table 1.

Table 1

layer	Polymer				Parameters			
	Trade name	Supplier	Chemical Nature	percentage (% wt)	Parameter	Value	Units	thickness (µm)
1	Embrace	Eastman Chem.	PETg	99,5	Density	1,32	g/cm <sup>3</sup>	6,6
					Glass Transition	70,6	°C	
					Vicat softening point	68,9	°C	
	Sukano G DC S503	Sukano	AntiBlock and Slip in PETg - SiO <sub>2</sub> 6 %, Wax 10%	0,5	Apparent density	1,2	g/cm <sup>3</sup>	
2	Estar PETG 6763	Eastman Chem.	PETg	100	Vicat softening point	82	°C	19,8
					Density	1.27	g/cm <sup>3</sup>	
					Glass Transition	81	°C	
					Melt Flow Rate (200°C / 05.00 kg (G))	2.8	g/10 min	
3	Eastapak	Eastman	copolyester	98	Viscosity Solution (Brookfield method)	0.75	mPA. sec	6,6
					Density	1,4	g/cm <sup>3</sup>	

	Copolyester 9921	Chem.	of PET		Melting Point	255	°C	
	Sukano Gdc S503	Sukano	AntiBlock and Slip PETg - SiO <sub>2</sub> 6 %, Wax 10%	2,0	Apparent density	1,2	g/cm <sup>3</sup>	
					Vicat softening point	82	°C	

PET g = Polyethylene Terephthalate/Glycol

For all the examples which follow, the diluent used was water.

Preparation of the examples 1-6 and comparative examples 1-10 (sprayed).

A three-layer film having the composition reported in Table 1 and a total thickness of 33  $\mu$  m was coextruded through a 3-layer feedblock. The three layers were then distributed through a flat die, having a multimanifold system. The melt out of the die was quenched onto a chill rolls; electrostatic pinning was applied to increase the contact between melt and chill roll kept at 19°C.

The so formed cast film was then biaxially oriented. The stretching was done simultaneously on a tenterframe, at ratios of 3.8:1 in both MD and TD directions, and at temperatures of 98°C in the preheating zones and 96°C in the stretching zones. Before oven exit, the film was annealed at a temperature of 145°C.

Bioriented film was finally cooled, edge trimmed, and wound into mill logs. The film exhibited a free shrink of:

- 3% in longitudinal direction and 1% in transversal direction at 120°C;
- 10% in longitudinal direction and 7% in transversal direction at 140°C.

The films of Examples 1-6 and Comparative examples 2-4 were corona treated using a two-unit corona treater each having power 20KW. The surface tension of the corona-treated film, evaluated after 24h from the corona treatment, was 50 dyne/cm, while the non-treated film had a surface tension of 44 dyne/cm.

The components used to prepare the coating aqueous compositions for the examples and comparative examples are reported in Tables 2 and 3:

Table 2

Component:	Tradename	Supplier	info	
antifog	TWEEN 80	CRODA	Polysorbate 80	ethoxylated sorbitan mono-oleate, vegetal

				origin
antifog	TWEEN 20	CRODA	CAS 9005-64-5	polyoxyethylene (20) sorbitan monolaurate, density 1.10 g/ml.
Cationic polysaccharide	VECTOR SC 20157 (20% ww aq. sol.)	Roquette Freres	starch, 2-hydroxy-3- (trimethylammonium) propyl ether, chloride	Viscosity 2500 mPa.sec
				Degree of Substitution 0.16 (1.2%N)
Cationic polysaccharide	VECTOR IC 27216 (28% ww aq. sol.)	Roquette Freres	starch, 2 -hydroxy- 3 - (trimethylammonium)- propyl ether, chloride	Viscosity 4000 mPa.sec
				Degree of Substitution 0.04 (0.4%N)

Water was pre-heated and kept at temperature of 40°C in a tank and then the antifog additive and/or the cationic polysaccharides were added, depending on the coating compositions under preparation. For all the examples and the comparative examples, mechanical stirring was used to facilitate the dissolution of the components.

For Examples 1 to 6 the liquid compositions were prepared by adding first the selected amount of the antifog additive into the tank containing the pre-heated water. This mixture was then kept under mechanical stirring up to the dissolution of the antifog into the water. Afterwards, the selected amount of the cationic polysaccharide was added into the tank containing the water and the antifog additive. The composition was kept at 40°C under mechanical stirring up to dissolution of the cationic polysaccharide.

The compositions so prepared were sprayed onto the film sealant surface, in amounts of 0.5- 2.5 ml/sqm by using a WEKO system. The aqueous compositions were sprayed onto the heat-sealable surface of the film in a continuous process during which the film moved at a speed of 30 m/min. The coating compositions to be sprayed were fed to several nozzles through a pump and applied onto the film kept in vertical position. After the spraying, the film was allowed to pass under a spreading roll and then into a drying oven, kept at 90°C for about 4 seconds.

Table 3 reports the details of the tested compositions and the obtained results in terms of antifog and peelability properties of the sprayed films.

Preparation of the examples 7-8 (coated).

The film composition and layer thickness were identical to those reported in Table 1. The same procedure was followed as described for previous examples for the film manufacturing with the following changes:

- the temperature for the preheating and stretching zones was 96°C;
- the annealing temperature was 160°C;
- the films were corona treated using a single-unit corona treater having power 3KW.

The films so obtained exhibited a free shrink of:

- 0% in longitudinal direction and 0% in transversal direction at 120°C;
- 5% in longitudinal direction and 5% in transversal direction at 140°C.

The components used to prepare the coating aqueous compositions for these examples are reported in Tables 2 and 4.

The liquid compositions were prepared by adding first the selected amount of the antifog additive into the tank containing the pre-heated water. This mixture was then kept under mechanical stirring up to the dissolution of the antifog into the water. Afterwards, the selected amount of the cationic polysaccharide was added into the tank containing the water and the antifog additive. The composition was kept at 40°C under mechanical stirring up to dissolution of the cationic polysaccharide.

The compositions so prepared were loaded into the tanks of a station of flexography printing equipment.

The coating step was performed using six-station Flessotecnica press. Only one press station was used to apply the coating compositions reported in Table 4 onto the film. As known in the art of printing, for this kind of equipment, each press station comprised a pump connected to a tank.

Each specific coating composition, for each of the examples 7 and 8 reported in Table 4 and prepared according to the procedure as before described, was put in 25 liters tank and kept under continuous stirring.

The sealant layer of the film was corona treated on the printing press before applying the coating. The generator was set-up to get a surface tension of the film of 52 dynes/cm.

The coating was applied using:

- an Anilox roller 100 lines per cm, volume 14 cc<sup>3</sup> per sqm;
- a photopolymer Aquaflex Optima thickness 2.54 mm.

Press running speed was 46 m/min; the drying temperature at printing station and tunnel was 115°C. The coated film was then edge trimmed and the rolls so obtained were used for the testing evaluation. Tables 4 and 5 report the details of the tested compositions and the results so obtained in terms of antifog, peelability and hermeticity properties of the films.

#### Preparation of the examples 9-11 (wiped).

The same procedure described for examples 7 and 8 was followed for the film preparation, but the films were not corona-treated before the coating step. The liquid compositions were prepared by adding first the selected amount of the antifog additive into a beaker containing the pre-heated water. This mixture was then kept under mechanical stirring up to the dissolution of the antifog into the water. Afterwards, the selected amount of the cationic polysaccharide was added into the beaker containing the water and the antifog additive. The composition was kept at 40°C under mechanical stirring up to dissolution of the cationic polysaccharide. The films were cut in equal square-shaped pieces of area 144 sqcm (12 cm x 12 cm). The film pieces were placed on a bench and the prepared compositions were applied onto internal layer of the films by wiping with a cotton pad. The cotton pad (pre-cut 5 cm x 5 cm square shaped) was put on the top of the neck of a 100 ml plastic bottle containing the tested solution and soaked by rotating the bottle twice. The cotton pad is then wiped onto the sealant side of the film, once in both L and T directions. The wiped films were weighted before and immediately after the wiping step with a high precision analytical balance. The averaged wiped amount was 2.0 gram per sqm. The compositions used for the wiping step, the peel and antifog results were reported in table 6.

As can be seen from the data reported in Table 3, the films coated with the composition only comprising the antifog (comparative 1) did not show peel seal, while the films coated with the composition only comprising the cationic polysaccharide (comparatives 2 – 4) did not show acceptable antifog scores and exhibited weak seal.

Another surprising effect of the coated film of the present invention is its ability to be sealed also through contaminants, such as blood or other organic exudates, without significantly impairing the seal strength, as clearly shown by the data in Table 5.

The results reported in Tables 3 to 6 clearly demonstrate that different coating processes can be advantageously used, obtaining a good balance of hermeticity, peelability and antifog properties. In particular, the composition according to the present invention has a positive effect on the sealing in terms of peelability during the package opening, keeping good hermeticity in both clean and contaminated sealing conditions.

Table 3- sprayed films

Examples:	antifog additive Tween 80 (% wt)	cationic starch <sup>1</sup> (% wt)	sprayed amount (ml/m <sup>2</sup> )	film corona treated	Antifog score at 24h	peel panel test
comparative 1	3,1	0,0	2	no	4,5	strong/no peel seal
comparative 2	0,0	0,2	2,5	yes	2	weak seal
comparative 3	0,0	0,4	1,5	yes	1,5	weak seal
comparative 4	0,0	0,4	2,5	yes	2	weak seal
comparative 5	1,1	0,2	1,5	no	3,5	strong/no peel seal
comparative 6	1,1	0,2	2	no	3,5	strong/no peel seal
comparative 7	1,1	0,2	2,5	no	3,5	strong/no peel seal
comparative 8	0,5	0,3	1,5	no	3	strong/no peel seal
comparative 9	0,5	0,3	2	no	3	strong/no peel seal
comparative 10	0,5	0,3	2,5	no	3	strong/no peel seal
example 1	1,1	0,2	1,5	yes	3	peel seal
example 2	1,1	0,2	2	yes	4	peel seal

example 3	1,1	0,2	2,5	yes	4,5	peel seal
example 4	0,5	0,3	1,5	yes	3	peel seal
example 5	0,5	0,3	2	yes	3,5	peel seal
example 6	0,5	0,3	2,5	yes	4	peel seal

Key: (1) = the % by weight refers to the cationic starch per se. The cation starch used in these trials is available on the market as a 20% ww aqueous solution (Vector SC 20157)

Table 4- coated films

Examples:	antifog additive Tween 80 (% wt)	cationic starch <sup>1</sup> (% wt)	film corona treated	Antifog score at 24h
example 7	1,1	1,1	yes	5
example 8	1,1	0,8	yes	4,5

Key: (1) = the % by weight refers to the cationic starch per se. The cation starch used in these trials is available on the market as a 20% ww aqueous solution (Vector SC 20157)

Table 5- coated films

Example	Sealing temperature and time	Sealing condition	Pressure avg value (bar)	Peel panel test
8	165 °C 0,5 sec.	Clean	-0,32	peel seal
		Contaminated	-0,32	peel seal
	175 °C 0,5 sec.	Clean	-0,37	peel seal
		Contaminated	-0,34	peel seal
	185 °C 0,5 sec.	Clean	-0,33	peel seal
		Contaminated	-0,34	peel seal
7	165 °C 0,5 sec.	Clean	-0,29	peel seal
		Contaminated	-0,29	peel seal
	175 °C 0,5 sec.	Clean	-0,3	peel seal
		Contaminated	-0,3	peel seal
	185 °C 0,5 sec.	Clean	-0,34	peel seal
		Contaminated	-0,34	peel seal



Table 6 - wiped films

Examples	antifog additive (%wt)	cationic starch (%wt)	wiping amount (g/m <sup>2</sup> )	film corona treated	Antifog score at 24h	peel panel test
example 9	1.0% Tween 80	0.4% <sup>2</sup>	2	no	4.5	peel seal
example 10	1.0% Tween 80	0.8% <sup>2</sup>	2	no	4.5	peel seal
example 11	1.5% Tween 20	0.4% <sup>1</sup>	2	no	4.5	peel seal

Key: the % by weight refers to the cationic starch per se. The cation starch used in these trials is available on the market as a: (2) 28% ww aqueous solution (Vector IC 27216) and (1) 20% ww aqueous solution (Vector SC 20157)

The surprising combined effect of the antifog additive and the polysaccharide allows obtaining both peelable and antifog film. It was then found that it is possible to balance the antifog on one side and the peelability and hermeticity properties on the other side by varying the ratio between the antifog additive and the cationic polysaccharide. Depending on the container used and its sealant composition, on the coated film used and its sealant composition and on the packaged product, the best coating composition comprising the antifog and the cationic polysaccharide can be tailored. Another surprising effect of the coated film of the present invention is its ability to be sealed also through contaminants, such as blood or other organic exudates, without significantly impairing the seal strength.

### Claims

- 1) A parent composition comprising at least an antifog additive, at least a cationic polysaccharide and no diluent.
- 2) The composition according to claim 1 wherein the weight ratio between said antifog additive and said cationic polysaccharide is comprised between 1: 20 and 20:1, preferably between 1:10 and 10:1, more preferably between 1:7 and 7:1, even more preferably between 1:5 and 5:1, most preferably between 2:1 and 1:2.
- 3) A coating composition comprising the parent composition according to claims 1 or 2 and a suitable diluent, wherein said parent composition comprises at least an antifog additive and at least a cationic polysaccharide, wherein said antifog additive is in an amount from 0.1% to 5.0% and said cationic polysaccharide in an amount from 0.1% to 3.5% by weight.
- 4) The composition according to anyone of claims 1 to 3 wherein the weight ratio between said antifog additive and said cationic polysaccharide is higher than one.
- 5) The composition according to anyone of claims 1 to 3 wherein the weight ratio between said antifog additive and said cationic polysaccharide is equal or lower than one.
- 6) The coating composition according to anyone of claims 3 to 5 wherein the diluent is liquid, preferably the diluent is water.
- 7) The coating composition according to any one of claims 3 to 6 comprising said antifog additive from 0.1% to 2.0 %, preferably from 0.5 % to 1.5% and said cationic polysaccharide in an amount from 0.15% to 3 %, preferably from 0.2 % to 1.0% by weight.
- 8) The coating composition according to any one of claims 3 to 7 consisting of from 0.4% to 1.5% of the antifog additive, from 0.1 to 1.1 % by weight of the cationic polysaccharide and of water as diluent up to the balance.
- 9) The composition according to any one of claims 1 to 8 wherein said antifog additive is a non-ionic surfactant selected among polyhydric alcohol fatty acid esters, higher fatty acid amines, higher fatty acid amides, polyoxyethylene ethers of higher fatty alcohols, and ethylene oxide adducts of higher fatty acid amines or amides, preferably among polyhydric alcohol fatty acid esters, polyoxyethylene ethers of higher fatty alcohols and glycerin fatty acid esters, more preferably among polyhydric alcohol fatty acid esters and their ethoxylated derivatives.

- 10) The composition according to any one of claims 1 to 9 wherein said cationic polysaccharide has at least a cationic group selected among ammonium, guanidium, sulfonium, phosphonium groups, bound transition metals, and other positively charged functional groups, preferably among quaternary ammonium groups, and wherein the polysaccharide polymer is selected among celluloses, pectins, starches and natural gums, preferably starches.
- 11) The composition according to any one of claims 1 to 10 wherein the antifog additive is ethoxylated sorbitan monooleate or polyoxyethylene (20) sorbitan monolaurate and the cationic polysaccharide comprises at least a 2-hydroxy-3-(trimethylammonium) propyl group, preferably is a 2-hydroxy-3-(trimethylammonium) propyl ether chloride modified starch.
- 12) A coated polyester film comprising at least one surface coating, wherein said surface coating comprises a composition according to claims 1 or 2.
- 13) The film according to claim 12 wherein said surface coating consists of a composition according to claims 1 or 2.
- 14) A coated polyester film, said film being obtainable by coating at least one surface of a polyester film with a coating composition according to any one of claims 3 to 11.
- 15) The film according to anyone of claims 12 to 14 which is biaxially oriented.
- 16) The film of claim 15 wherein the free shrink in each of LD (longitudinal) or TD (transversal) direction is at most 15% at temperatures below 100°C, below 120°C, and even below 140°C and does not exceed 20% in the temperature range of from 140 to 200°C, and at 180°C, at 160°C, and even at 150°C.
- 17) A method for the manufacture of a coated polyester film according to anyone of claims 12 to 16 said method comprising the step of
- a) extruding a polyester film; and
  - b) coating at least a surface of the film with a coating composition according to any one of claims 3 to 11.
- 18) The method of claim 17 further comprising, in any order, the steps of:
- c) biaxially orienting the film, and / or
  - d) treating the sealant surface of the film by corona treatment, plasma treatment, flame treatment or primer treatment.
- 19) The method according to claims 17 or 18 wherein said coating step is effected by spraying the coating composition according to any one of claims 3 to 11 onto at least

one of the sealing surface of the polyester film in amount from 0.1 to 8 ml/m<sup>2</sup>, 0.5 to 7 ml/m<sup>2</sup>, 0.5 to 5 ml/m<sup>2</sup>, 1 to 3 ml/m<sup>2</sup>, preferably from 1.5 ml/m<sup>2</sup> to 2.5 ml/m<sup>2</sup>.

20) The method according to claims 17 or 18 wherein the coating composition according to anyone of claims 3 to 11 is applied by flexography printing or rotogravure technique.

21) A package comprising the coated polyester film according to any one of claims 12 to 16 and a product, optionally placed into a container.

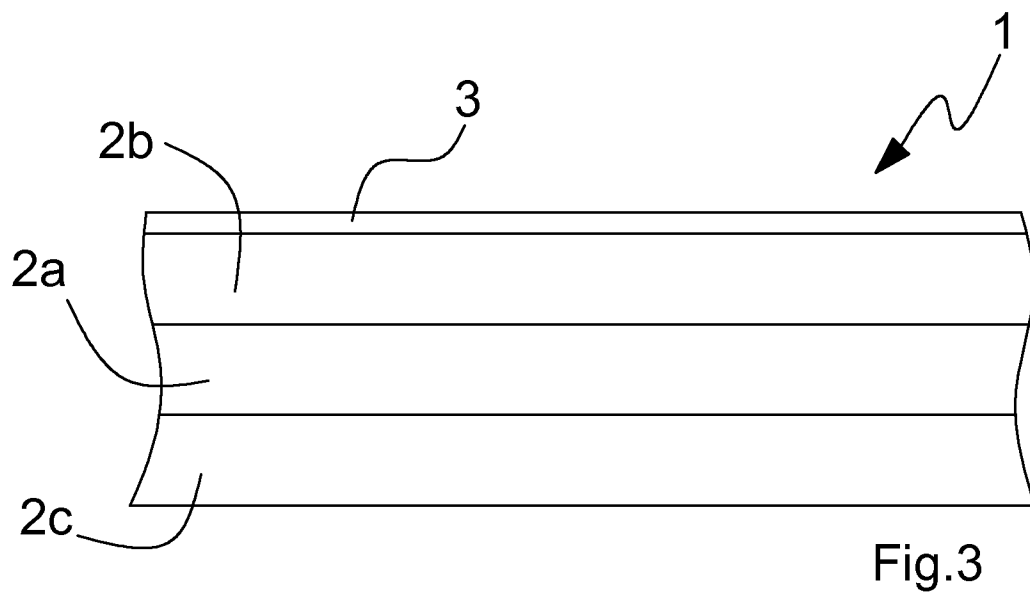
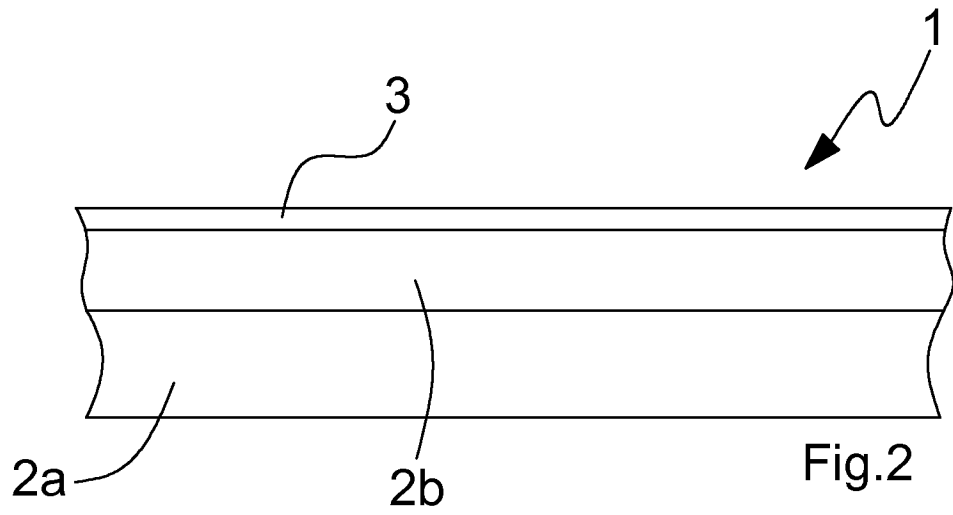
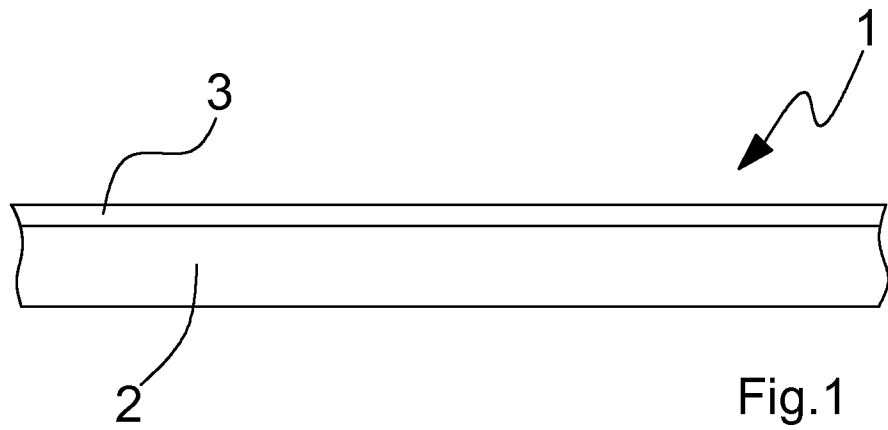
22) The package according to claim 21 wherein a polyester container is used

23) The package according to claims 21 or 22 wherein said package:

- i. comprises a container, a product placed in the container and a lid formed from the coated polyester film of anyone of claims 12 to 16 sealed onto the container; or
- ii. comprises a container, a product placed in the container and the coated polyester film of anyone of claims 12 to 16 wrapped around and suitably sealed to itself; or
- iii. comprises a bag or a pouch and a product packaged into said bag or pouch, wherein the bag or pouch is formed by self sealing the coated polyester film of anyone of claims 12 to 16, or
- iv. comprises a bottom substrate, a product placed onto said bottom substrate and the coated polyester film of anyone of claims 12 to 16 draped over said product and sealed onto the surface of the bottom substrate all around the product (VSP), or
- v. is formed by flexible top and a bottom webs sealed circumferentially and enclosing a product, being both the webs made of the coated polyester film of anyone of claims 12 to 16.

24) The package of anyone of claims 21 to 23 wherein said product is a food product, preferably fresh meat or fish.

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Fig.4

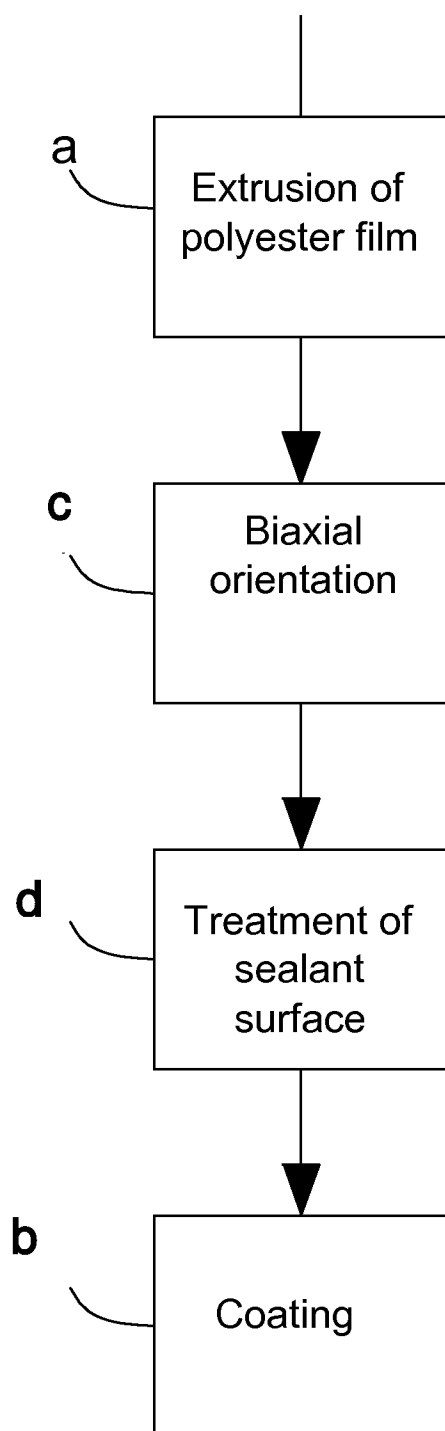
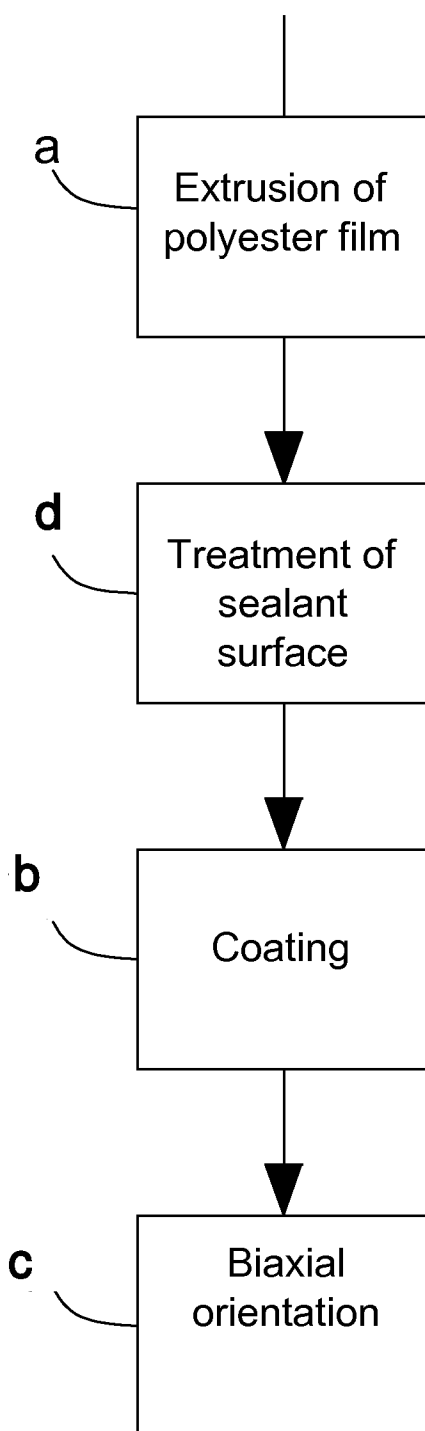


Fig.5



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Fig.6

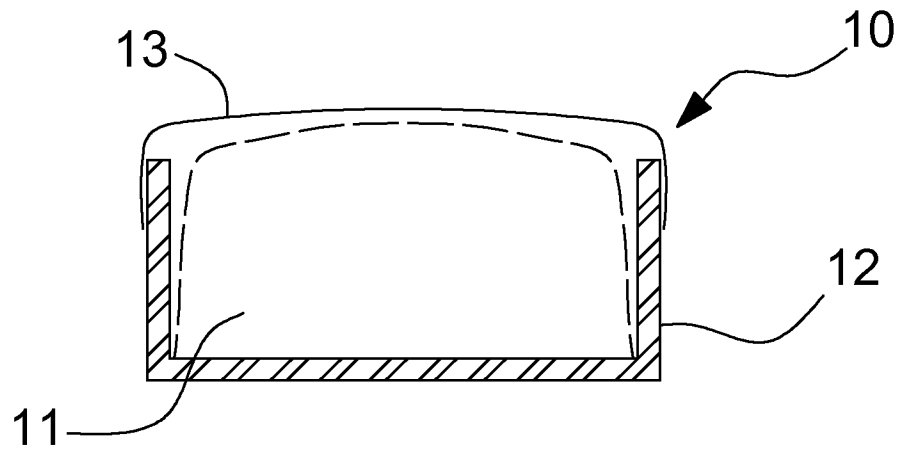


Fig.7

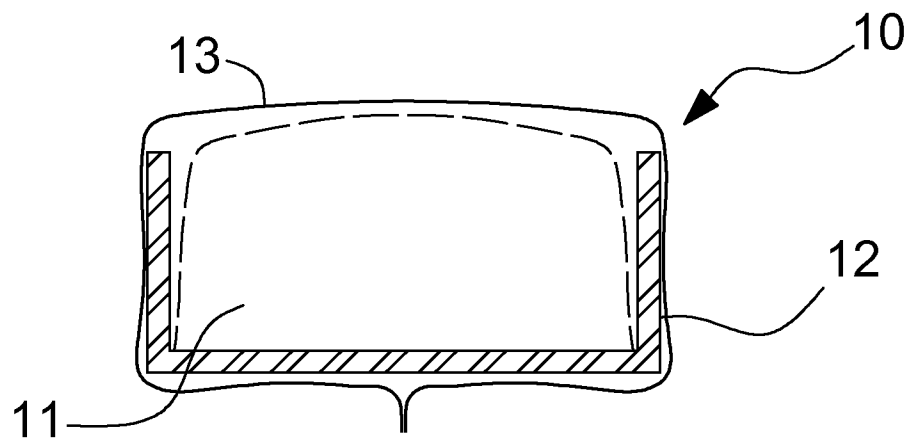


Fig.8

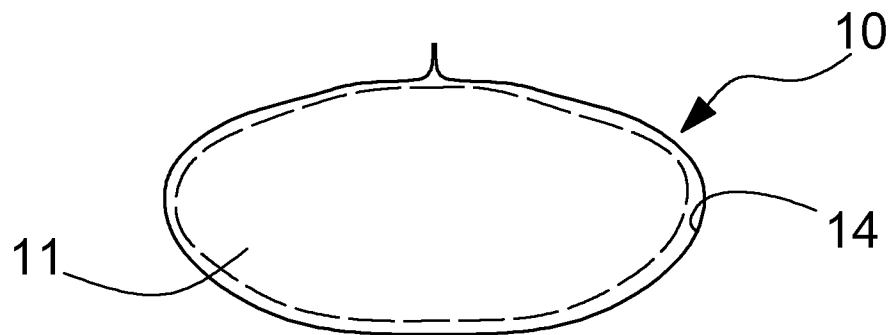


Fig.9



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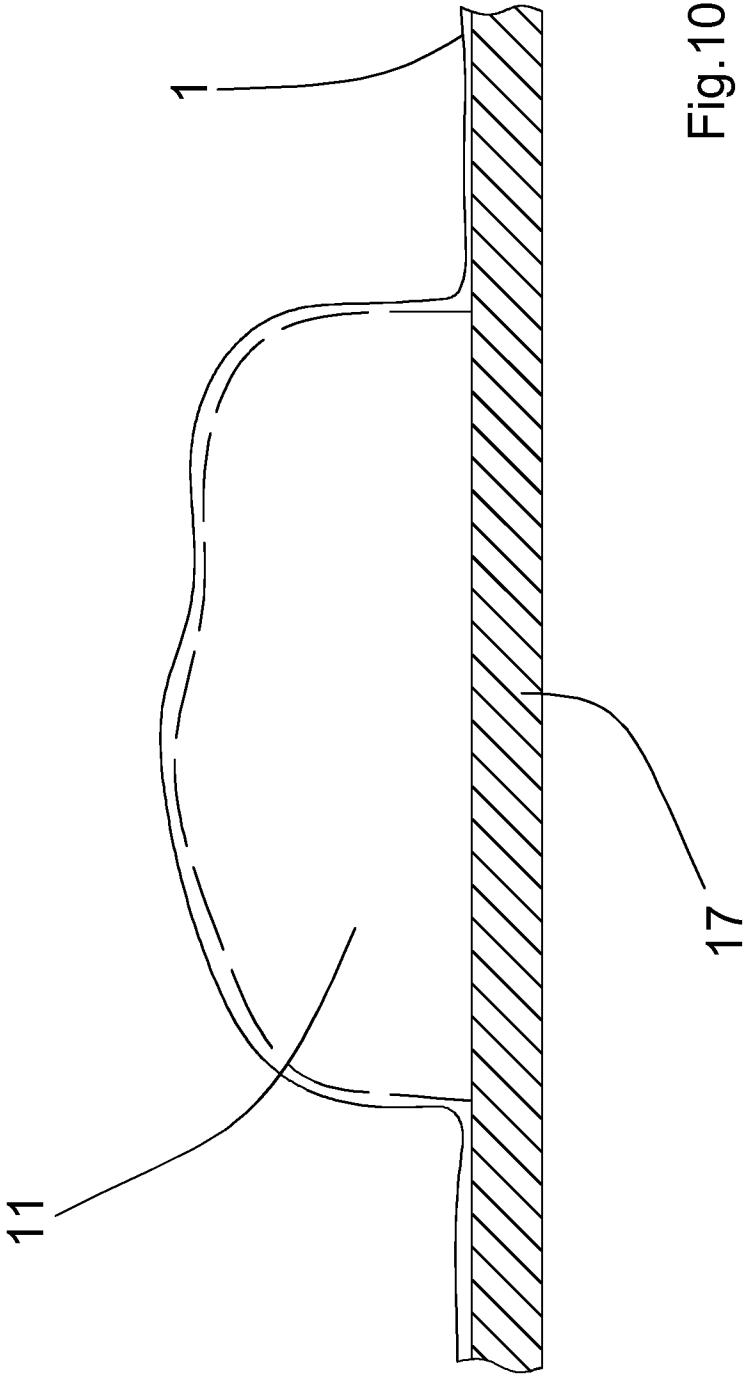


Fig. 10



## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2013/064305

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C08J5/18 C09D105/00 C09K3/18 C08L5/00  
ADD.

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08J C09D C09K C08L

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

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

EPO-Internal, WPI Data, CHEM ABS 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 5 773 595 A (WEUTHEN MANFRED [DE] ET AL) 30 June 1998 (1998-06-30) column 7, line 54 - column 8, line 67 column 8, line 53 - line 67 -----	1,2
X	EP 0 406 837 A2 (NAT STARCH CHEM INVEST [US]) 9 January 1991 (1991-01-09) cited in the application	3-24
Y	page 4, line 22 - page 5, line 52 page 25; example 6 -----	1-24
Y	CN 101 037 559 B (PETROCHINA CO LTD [CN] PETROCHINA CO LTD) 12 May 2010 (2010-05-12) claims 3,4 -----	1-24
	-/-	



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

7 December 2013

Date of mailing of the international search report

17/12/2013

Name and mailing address of the ISA/

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

Authorized officer

Mill, Sibel

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2013/064305

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 080 740 A1 (GUARDIAN INDUSTRIES [US]) 22 July 2009 (2009-07-22) page 2, paragraph 1 page 3, paragraph 2 -----	1-24
A	Anonymous: "Polysaccharide", Encyclopædia Britannica <sup>3</sup> 31 January 2001 (2001-01-31), XP002689371, Retrieved from the Internet: URL: <a href="http://www.britannica.com/EBchecked/to-pic/469090/polysaccharide">http://www.britannica.com/EBchecked/to-pic/469090/polysaccharide</a> [retrieved on 2012-12-17] the whole document -----	1-24

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP2013/064305

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1, 2(partially)  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

Continuation of Box II.2

Claims Nos.: 1, 2(partially)

Present claim 1 relates to an extremely large number of possible compositions. Support and disclosure in the sense of Article 6 and 5 PCT cannot be found in the application as originally filed, since no example of the parent composition (no diluent) is present as such. This is only an intermediate composition, which is not used as such.

Only a general disclosure is present on p. 4, l. 11-13 and p. 5, l. 14-15, which does not disclose the purpose or the meaning of such a parent composition. It is also not clear, whether such type of composition would be achievable (miscibility/stability of the phase comprising a non-ionic surfactant and a cationic polysaccharide as only components?) at all. The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1 and 2 (PCT Guidelines 9.19 and 9.23).

The search of claims 1-2 was restricted to those claimed compositions methods which appear to be supported, as in claim 9, where the antifog additive is defined as a non-ionic surfactant selected among polyhydric alcohol fatty acid esters, higher fatty acid amines, higher fatty acid amides, polyoxyethylene ethers of higher fatty alcohols, and ethylene oxide adducts of higher fatty acid amines or amides, which can comprise other components too, referred to otherwise than "diluent".

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/064305

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5773595	A	30-06-1998	DE 4413686 A1 26-10-1995
			EP 0756600 A1 05-02-1997
			ES 2121373 T3 16-11-1998
			JP 4018136 B2 05-12-2007
			JP H09512052 A 02-12-1997
			US 5773595 A 30-06-1998
			WO 9529183 A1 02-11-1995
EP 0406837	A2	09-01-1991	AU 613561 B2 01-08-1991
			AU 633221 B2 21-01-1993
			AU 639352 B2 22-07-1993
			AU 5794290 A 26-04-1991
			AU 8118991 A 31-10-1991
			AU 8119591 A 22-07-1991
			CA 2019675 A1 07-01-1991
			DE 69023055 D1 23-11-1995
			DE 69023055 T2 28-03-1996
			EP 0406837 A2 09-01-1991
			JP 2509739 B2 26-06-1996
			JP H0350201 A 04-03-1991
CN 101037559	B	12-05-2010	NONE
EP 2080740	A1	22-07-2009	NONE