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(54) Title: MULTILAYER HEAT-SEALABLE PACKAGING MATERIAL AND A SEALED PACKAGE MANUFACTURED THEREOF

(57) Abstract: The invention relates to a heat-sealable packaging material and a sealed package formed from the same, especially for packaging foodstuffs. The packaging material comprises a base layer of paper or board and polymeric heat-sealable layers on one side of the middle layer or, preferably, on both sides thereof. According to the invention, at least two layers containing polyamide (PA) are arranged on the packaging material to provide an oxygen barrier. The heat-sealable polymer can be a polyolefm, and, in addition, other polymeric barrier layers can be incorporated into the material to improve its oxygen, fat, and aroma tightness.

Multilayer heat-sealable packaging material and a sealed package manufactured thereof

The invention relates to the field of polymer-coated packaging materials that are heat sealed, whereby the structure comprises a layer that forms an oxygen barrier. Another object of the invention is a sealed package formed from such packaging material by heat sealing. The invention also relates to the utilization of the barrier properties of polyamide (PA) in a fibre-based packaging material.

Providing the fibre-based packaging material with a polymeric coating layer that softens or melts under the effect of heat enables the use of the material in packages, such as package containers and cartons, which are sealed by heat sealing. By means of the polymer coating that is heat sealed, the package can also be rendered liquid-tight. Depending on the product, food packages, in particular, are also required to protect the product against light and be oxygen and aroma-tight, which is achieved by means of suitably selected coating materials that are layered on the fibre base.

In conventional procedures, the fibre-based packaging material has been provided with an aluminium foil, which makes the package liquid-tight, oxygen-tight, and aroma-tight and also provides an effective protection against the penetration of visible light and UV radiation. However, as the aluminium foil is non-biodegradable, is susceptible to mechanical stress, complicates the recycling of the material and is also an expensive solution, it has increasingly been replaced by polymeric coating materials, of which the most important are ethylene vinyl alcohol copolymer (EVOH), polyamide (PA), and polyethylene terephthalate (PET). By combining these polymers with binders and heat-sealable polymers, multilayer boards have been provided, which have liquid, oxygen and aroma barrier properties almost comparable to those of aluminium, and also resistance to impacts, damages and moulding that is better than that of aluminium foil.

With developments towards increasingly thinner packaging materials, while the aluminium foil has been replaced with polymeric coating layers, there has been a disadvantage of an increasing permeability of oxygen and other gases of the packaging material. Exposure of packaged products to the oxygen in the air, e.g., oxidation of foodstuffs, decreases their preservability and lowers quality.

As an example of polymer-coated food packaging boards according to the prior art, patent specification EP 0630745 could be cited. This specification discloses boards with a fibre base that is provided with a heat-sealable polymer coating on both sides thereof, its material being, e.g., low density polyethylene LDPE or linear low density polyethylene LLDPE, and having a barrier layer placed between the fibre base and the heat-sealable layer. The patent discloses various barrier solutions, wherein the barrier layer in the structure comprises an EVOH or PET layer, or a blend containing EVOH and polyamide.

In polymer film applications, sandwich structures have been developed to embody a relatively large number of extremely thin layers, each of them contributing to the properties of the finished film, US2001/0010846 A1 being an example. Typically, such films are symmetrical, they are required to be transparent, bright, stretchable, shrinkable, and to have orientation, these properties being generally useless in paper and board applications. Generally, the lack of stiffness of the board layer in the polymer film structures also results in layer thicknesses, which are multi-fold compared to those used in board structures. In addition, joining them to the fibre base is a challenge in itself both in terms of the manufacturing technology and during the product life span. Hence, a simple repetition of the polymer film applications in paper coating is not a practical solution.

As an attempt to utilize some advantages of the sandwich structure and to avoid the equipment requirements of coextrusion, patent specifications have recently disclosed layers of blends. Published application US2002/0051873 is an example of this. It describes a packaging laminate, the single-layer polymer blend of which can be extrusion coated directly on top of a fibre-based base layer without tie layers.

Furthermore, there exists a need to find a product for packaging board applications, providing the desired properties by means of cost-effective materials. The raw materials used should be compatible with the base layer of chemical pulp fibre. Regarding the object that is packaged, demands are also directed at the materials; the object must not deteriorate (e.g., absorb odours) because of the packaging material, the package should improve its preservability, serve the storage and logistics, and offer a base for presenting the product specification and marketing communications, e.g., by printing. The recycling of the packing product after use should also be as simple as possible.

The purpose of the present invention is to provide a product that provides an improved oxygen barrier to paper and board applications in particular.

Another purpose of the invention is a product, wherein the properties of the oxygen barrier layer do not deteriorate when the structure is exposed to moisture.

A further purpose of the invention is to provide a technically alternative solution, its use providing advantages over these.

The idea of the invention is to utilize the oxygen barrier property of polyamide in a sandwich-structured packaging material. Surprisingly, it has now been observed that the amount of oxygen permeated by the oxygen barrier, which is formed jointly by at least two layers of the same polymer, but different grades, and different polyamides herein, is especially low, but that it is not sensitive to humidity. The co-operative action between the layers is especially advantageous. The interface that is formed between these polyamide layers also plays a significant role in the effect of the oxygen barrier. When two superimposed polyamide layers are used, one such interface is formed in the structure; with three polyamides being located directly against each other, there are two interfaces in the sandwich structure, etc. The said polyamide layers of such a structure adhere to each other and to the base layer made of board without an added tie layer, which also results in a thinner total structure. Instead, between the oxygen barrier layer and the possible polyolefin layer providing the innermost moisture barrier, a tie layer is needed to ensure sufficient adherence. barrier layer comprises at least two polyamide-containing layers with different barrier properties.

The fibre-based heat-sealable packaging material according to the invention is characterized in comprising a base layer of fibrous material, at least one polymeric heat-sealable layer, and at least one polymeric barrier layer that forms the oxygen barrier and comprises at least two polyamide-containing layers with different barrier properties. According to a preferred embodiment, these layers are in contact with each other, i.e., they adhere to each other directly, forming an interface(s). In other words, the polyamide layers are located against each other without an adhesive or other layer between them. Without being bound to any theory, a discontinuity, a differentiation in crystallinity or orientation is believed to form on the interface of the polyamides with different barrier properties, having an advantageous effect on the prevention of oxygen permeation.

The sealed package according to the invention, which is formed from such a packaging material, is characterized in comprising a layer of fibrous material, at least two layers containing different polyamides in the barrier layer inside the same, their barrier properties being different, and an innermost polymeric heat-sealable layer. When needed, the sandwich structure may also comprise other layers.

The use of the heat-sealable packaging material according to the invention is characterized in that the said packaging material contains at least one polymeric barrier layer that constitutes the oxygen barrier and comprises at least two layers containing polyamide, their barrier properties being different.

In the following, the packaging materials according to the invention are described in detail by means of examples and with reference to the appended drawings.

Figs. 1 and 11 are simplified illustrations of possible packages that are moulded from packaging material blanks. Figs. 2 to 10 and 12 to 15, related thereto, are schematic cross-sectional views of the polymer-coated packaging boards according to the various embodiments of the invention. Figs. 16 and 17 show the results of the measurements of the different oxygen permeability properties of various polymer grades, which measurements can be used when selecting two or more polyamides for the structure according to the invention.

Fig. 1 shows an example of a liquid package manufactured from the material according to the invention. Cross section A-A illustrates the meaning of the inside and the outside of the package, and how the layers are located with respect to the same to provide the package with functionally advantageous properties. In the manufacture of such a liquid package, it is preferable to use liquid packaging board provided with a heat-sealable layer on both sides thereof.

The polyamide has an oxygen barrier property in the sandwich-structured packaging material. The oxygen barrier formed jointly by the layers containing different polyamides is better than what could be expected on the basis of the properties of single layers. The layers can each consist completely of one selected polyamide. Alternatively, blends containing polyamide can be used either so that both components of the blend are polyamides, or that some other appropriate polymer is blended with the polyamide. The invention also includes the use of polyamides that are enriched by adding ingredients that improve the properties.

If the oxygen barrier is formed from exactly two layers of different polyamides, they can be located in an optional order in the structure. However, it is more advantageous to place the polyamides so that the polyamide with the higher crystallinity is located closer to the fibre layer, protecting the structure against wetting. Such a structure is preferable when packing products that must be stored dry and protected against gases, e.g., dry foodstuff, especially if the moisture outside the package is high. According to another embodiment, the polyamide layer with the higher crystallinity is located closer to the heat-sealable layer, which, in the package, comes in contact with the product that is packed. Such a structure is preferable in liquid packages, wherein the moisture adverse to the gas barrier penetrates the material from inside the package.

Polyamide in this application refers to polyamides and copolyamides, i.e., polymers that contain amide bonds (-CONH-) in the direction of the molecular chain. The polyamides that form fibres, and their immediate chemical derivatives and copolymers are often also called nylons. Aromatic polyamides are also of a special interest within the invention. Usable polyamides include, e.g., nylon 6, nylon 11, nylon 66, nylon 610, nylon 612, nylon 6/66, amorphous polyamide, or the like. Various polyamides with optimal properties are commercially available, e.g., the polyamides of the Grivory® series, those of the Grilon® series, those of the Grilamid® series from the manufacturer EMS, Switzerland; MXD-6 polyamide and its derivatives from the manufacturer Mitsubishi, Japan, etc.

In connection with this invention, "the amorphous polyamide" refers to polyamides that exhibit no endothermic crystalline melting peak, when determined by the differential calorimetry (DSC). Examples of such polyamides include the amorphous polyamides manufactured form the following diamines: hexamethylenediamine, 2-methylpentamethyledediamine, 2,2,4-trimethylhexamethylenediamine, 2,2,4-trimethylhexamethylenediamine, bis(4-aminocyclohexyl)methane, 2,2-bis(4-aminocyclohexyl)isopropylidene, 1,4-diaminocyclohexane, 1,3-diaminocyclohexane, methaxylylene diamine, 1,5-diaminopentane, 1,4-diaminobutane, 1,3-diaminopropane, 2-ethyldiaminobutane, 1,4-diaminomethyl-cyclohexane, p-xylylenediamine, m-phenylenediamine, p-phenylenediamine, alkyl-substituted m-phenylenediamine and p-phenylenediamine. Examples of usable polyamides include amorphous polymers that are manufactured from the following dicarboxylic acids: isophthalic acid, terephthalic acid, alkyl-substituted isophthalic and terephthalic acids, adipic acid, sebacic acid, butanedicarboxylic acid and the like. The diamines and diacids mentioned above can be combined as desired, provided that the resulting polyamide is amorphous. Typically, an aliphatic diamine can be combined with an aromatic diacid, or an aromatic diamine can be combined with an aliphatic diacid to obtain a suitable amorphous polyamide. Advantageous amorphous polyamides include those, wherein either the diamine or the diacid is aromatic and the other portion is aliphatic. These aliphatic groups contain a chain of

4 to 12 carbons or a cyclic ring of 15 carbons at the most. The aromatic rings of the polyamides are preferably monocyclic or bicyclic and they can have substituents that contain 6 carbon atoms at the most.

In this context, "semi-crystalline polyamide" refers to polyamides, the crystalline melting point of which can be determined by a standard method in certain conditions. Such polyamides can also have amorphous regions and glass transition temperatures (Tg) that can be measured. Preferable semi-crystalline polyamides include nylon 6, nylon 11, nylon 12, nylon 66, nylon 69, nylon 610, nylon 612, MXD6, nylon 6/66, nylon 6/12, nylon 6/66 copolymer, nylon 66/610 copolymer, nylon 6/69 copolymer, and blends of the above. Alternatively, the abbreviation PA also refers to many polyamides, e.g., PA6.

It is appreciated that in the applications typical in the field, it is sometimes preferable to blend additives that improve the properties. The term "polyamide-containing layer" refers to a layer, wherein the main component comprises any polymer(s) that is (are) classified as polyamide in the manner defined above. Those skilled in the art know a group of various admixtures or additives, which are conventionally blended with polyamides: thermal stabilizers, light stabilizers, softeners, lubricants, reinforcing fillers, pigments, biocides, nucleating agents, and fire retardants. According to an embodiment, the layer may consist of one polyamide or a blend of several polyamides. When a layer consists "essentially of polyamide", it consists of polyamide and an additive mixed therewith, the amount of the additive being relatively considerably smaller than that of the polymer. Typical additives usable in the solutions according to the invention, which are well-known to those skilled in the art, include, without limiting thereto, nanoparticles, oxygen interceptors, normal pigments, etc. Correspondingly, it is appreciated that the essentially semi-crystalline polyamide refers to a layer of mainly semi-crystalline polyamide, and the essentially amorphous polyamide to a layer of mainly amorphous polyamide, both of which can contain another admixture(s) typical in the field, blended in the manner described above.

"Layers with different barrier properties", as expressed within the invention, refers to the materials used in the layers, which differ from one another in terms of their gas and/or moisture barrier properties. Generally, the oxygen and/or moisture barrier properties are essential in packaging applications. These properties have a certain relationship to the structure of polyamides, but as the properties are a function of several factors, they cannot unambiguously be determined by the structural features alone. For example, the moisture barrier properties typically improve with the growth of crystallinity, but no direct determination can be made as the crystallinity of the different grades may vary according to the crystallizing conditions. The properties essential to the invention, the moisture, gas, and especially oxygen barrier properties, cannot be unambiguously expressed by means of the technical features; therefore, a functional determination is used within the invention. The other factors that may have an effect on the barrier properties include, among others, the chemical nature of the polyamides used (length of the carbon chain, aliphaticity/aromaticity, side chains, substituents, etc.), the processing conditions and the admixtures. Methods of determining the barrier properties and, especially, comparing the barrier properties of two or more different materials are well-known to those skilled in the art. In the following, a determination used in the field for each most essential barrier property is incorporated herein by reference.

An evaluation method of the oxygen barrier typical in the field is to measure the oxygen permeability of a material in a time unit. The determinations are made in standard temperature and humidity conditions. The usual determination conditions comprise a temperature of 23°C / relative humidity of 0%, a temperature of 23°C / relative humidity of 60%, and a temperature of 23°C / relative humidity of 85%. Equipment designed for the purpose, e.g., Ox-Tran 2/20 (Oxygen Transmission Rate Measurement Rate Measurement System), Mocon, Minneapolis, USA, is used to measure the oxygen flowing through a sample from one chamber to another, and it is given in a unit of cm^3/m^2.d.b. Detailed information of the determination is given, e.g., by the American National Standards Institute by means of the standard method ASTM D 3985. Accordingly, polyamides that have different oxygen barrier properties, as intended by the invention, are those that, in similar conditions, yield considerably different oxygen permeability values by the method referred to above, for example.

An evaluation method of the moisture barrier properties typical in the field is, e.g., the determination according to the method "Water vapour permeability (electrolysis method) DIN 53122-2 / DIN 533122-2-A". For example, the Permatran W 3/31 device (Water Vapour Permeability) from Mocon, Minneapolis, USA, can be used for the measurement. In the measurement, the water vapour permeated by the sample in the measuring time is determined and the result is given in a unit of g/m^2.d. On the basis of this or an equivalent measurement, those skilled in the art are capable of selecting polyamides with different moisture barrier properties.

In the sandwich structure according to the invention, the combined polyamide layer similar to the one described above is located between the fibre layer and the inner heat-sealable layer so that it is not in contact with the packaged product.

In the packaging material according to the invention, the coating can be omitted from one side of the fibre base, when so desired. However, the fibre base is most preferably provided with a polymeric heat-sealable layer on both sides thereof but, certainly, other functional layers can lie between or on top of them. In that case, the same polymer is preferably used in all the heat-sealable layers.

When manufacturing the sandwich structure, the layers can be added to the structure one by one or by first combining certain layers to one another and incorporating them into the coated or uncoated fibre layer. There are numerous different combinations and those skilled in the art can deduce them on the basis of the properties of the layers that are combined. Some or all polymer layers are preferably joined to the paper or board base layer by coextrusion.

In the structure according to the invention, the aim is a total thickness of the barrier layer of typically 1 to 20 micrometers (µm), preferably 2 to 12µm, and most preferably 6 to 12µm. In that case, the thickness of each single polyamide layer, of which there are thus two or more in the layer, is about 1 to 10 micrometers (µm), preferably 1 to 7µm, and more preferably 2 to 6µm. The layer thicknesses shown in the appended drawings are not to scale, and not even referentially in proportion to each other.

A sealed package can be formed from the packaging material described above, comprising a layer of fibrous material, at least two layers of different polyamides with different barrier properties inside the same, and an innermost polymeric heat-sealable layer. In addition to the inner surface, the polymeric heat-sealable layer can also be provided on the outer surface of the package that is moulded from the material according to the invention. By heat sealing the blank that is cut and shaped from the material described above, a package container or carton of the polymer-coated packaging board is provided. One preferred embodiment comprises a food package sealed in an oxygen-tight manner. The packaging material described is preferable in liquid packages, in particular.

The liquid tightness of the package is obtained by a sufficiently thick heat-sealable layer. Typically, polyolefins, such as different grades of polyethylene PE or polypropylene PP, are used herein. Correspondingly, other heat-sealable polymers can be applied, e.g., a heat-sealable PET grade.

Another aspect of the invention comprises the use of two different polyamide layers with different barrier properties in the fibre-based packaging material as polymer layers that form the oxygen barrier. The use is especially advantageous in a package consisting of polymer-coated packaging board, which is exposed to moisture both on the inside and/or the outside.

Table 1 shows different layer combinations according to the invention.

Table 1. Different polyamide layer combinations and a reference to the figure that illustrates the structure.

PB/barrier layer/tie layer/PO, wherein PB is the base layer

PO/PB/barrier layer/tie layer/PO, wherein PO is polyolefin

PO/PB/barrier layer/tie layer/PO^P/PO, wherein PO^P is polyolefin with pigment

PO/PO^P/PB/barrier layer/tie layer/PO^P/PO, wherein PO^P is polyolefin with pigment

Barrier layer:	PA1/PA2	Figs. 2, 3, 7, 12
	PA1/PA2/ PA1	Fig. 4
	PA1/PA2/ PA3	Fig. 5
	PA1/PA2/PA1/PA2	Fig. 6
	PA1/PA2/PA3/PA1	Fig. 8
	PA1/PA2/PA3/PA4	Fig. 9
	PA1/PA2/PA3/PA2	Fig. 10

Wherein PA refers to polyamide and the numbering is used to referentially indicate the mutual uniformity or difference of the layers so that PA1 and PA1 on one line are mutually the same polyamide, but different from PA2. Instead, symbol PA1 between the different lines is not bound to a certain type of polyamide but it may refer, for example, to nylon 6 on the first line and MXD6 on the second one, etc. It is appreciated that the polyamide grades can be freely selected to be the most appropriate at each time, and the order from right to left has no significance in that case. As described earlier, the layer may consist of exactly one polyamide, a blend of two or more polyamides, a polyamide, with which some additives have been blended, or a blend containing additives. For example, in an oxygen barrier layer consisting of two polyamides, the layers could be selected so that one layer comprises PA6 and the other layer PA6, with which nanoparticles have been blended.

Fig. 2 shows a packaging board according to the invention, which is provided with an oxygen barrier, and provided with a heat-sealable polymer coating on both sides thereof. The structure is otherwise similar to that in patent EP 0630745, but instead of one oxygen barrier layer described therein, the oxygen barrier layer in the structure according to the invention is divided, i.e., it includes two polyamide layers. Starting from the outside of the package, the figure shows, first, a heat-sealable layer 12 combined directly with a base layer 11. The heat-sealable layer 12 consists of heat-sealable polyolefin and the base layer consists of paper or board. On the other side thereof, i.e., on the inside of the package, there are oxygen barrier layers 1b and 1a. On the inner side of the oxygen barrier layer 1a, there is a tie layer 13 that joins the heat-sealable layer 12 to the structure. Typically, the heat-sealable layers also have moisture barrier properties. If no heat-sealable layer is to be provided on the outer surface of the package, a structure according to Fig. 12 is obtained, the base layer 11 constituting the outermost layer of the package.

In Fig. 2, the heat-sealable layers 12 are preferably selected so that they are sealable not only to themselves but also to each other. This is simply implemented so that they consist of the same heat-sealable polymer, typically, polyolefin, e.g., low density polyethylene (LD-PE). They can also be different polyolefins, for example, so that the sealing layer on the outside comprises low density polyethylene and the heat-sealable layer on the inside is linear low density polyethylene (LLD-PE). In certain applications, polypropylene is used. The strength of the heat-sealable layers can be less than $20g/m^2$ for dry packages, for example, and over $20g/m^2$ for liquid packaging materials. For example, the tie layer 13 can consist of acid-treated linear low density polyethylene with a strength of 1 to $6g/m^2$. The weight of the board of the base layer is at least about $170g/m^2$ and, generally, in the order of $225g/m^2$ or higher. If paper is used as the base structure, its weight is less than $170g/m^2$. The total thickness of the oxygen barrier layers may vary from 2 to $20g/m^2$ so that the layers can either be mutually of the same thickness or of a different thickness. The most conventional thicknesses of a single polyamide layer range from 3 to $8g/m^2$. In this example, e.g., types PA 6 and MXD6 can be selected as the polyamides.

Compared with Fig. 2, Fig. 3 shows otherwise the same layers but the heat-sealable layer inside the package is divided into a transparent layer 12 and a pigmented layer 14. Alternatively, it could be conceived that, between the heat-sealable layer and the tie layer, a pigmented layer made of the same polymer (typically PE) as the material of the heat-sealable layer is added, which can also participate in the formation of the seam. Such a structure is described in detail in patent application WO2004007195. Depending on the use, the said pigmented layer 14 can contain a black pigment only, and a black (e.g., carbon black) and a white (e.g., titanium oxide) pigment, mixed in a suitable proportion, whereby the inner surface of the finished product looks as if having a layer of aluminium foil. The light-shielding properties of such a layer are comparable to using a metal layer. When such a structure is used in liquid packages, the oxygen barrier layer can be manufactured from two or more polyamides, according to the invention. The structure according to Fig. 3 can also be implemented without the outermost heat-sealable layer so that the base layer 11 of board comprises the outermost layer of the structure.

Fig. 5 shows a structure that otherwise corresponds to the sandwich structure of Fig. 2, except that the oxygen barrier layer consists of a film comprising three different polyamides, or it could be conceived that the oxygen barrier layer is divided into three parts, each of them thus being a different polyamide. According to this embodiment, a polymer film structure can be applied to the packaging material structure according to the present invention, wherein amorphous polyamide is layered on a symmetrical structure between two semi-crystalline polyamides. Thus, the structure comprises three layers of polyamide, which are located so that one amorphous polyamide layer is joined, on both sides, to the layers of semi-crystalline polyamide. Such a structure is described in Fig. 5.

According to the invention, a sandwich structure can also be arranged, comprising three polyamides so that the said polyamides are semi-crystalline. The layers can either be arranged so that all three semi-crystalline polyamides are different polyamides or that two semi-crystalline polyamides are used, being arranged so that on both sides of the middlemost polyamide, there is a layer of the same polyamide. When using three different semi-crystalline polyamides, their mutual order can be selected freely according to Fig. 5, for example. However, the most preferable embodiment is the semi-crystalline/amorphous/semi-crystalline one, which according to the reference numbers in Fig. 5 means that layers 1a and 1c represent the semi-crystalline polyamide and 1b the amorphous one. Thus, the layers of the semi-crystalline polyamide may either be mutually the same or a different polyamide.

They are preferably mutually the same polyamide, according to Fig. 4. Fig. 4 thus includes three directly parallel polyamide layers, but the polyamide layer (1b) in this structure is between two layers of the same polyamide. Naturally, by combining several types of polyamides, several combinations are provided in the structures according to Fig. 4 or 5. In Figs. 4 and 5, the innermost heat-sealable layer 12 is marked with a footnote (14), implying that the three-layer polyamide can also be applied to applications containing pigmented polymers.

In Fig. 6, the barrier layer structure is divided into four parts so that two different polyamides are used. In other words, the structure can be described so that each polyamide is divided into two and the layers are extruded alternatively. One layer of each grade remains surrounded by the second grade on both sides thereof, and one layer of the first grade is in contact with the base layer on one side thereof, and with the second polyamide grade on the other side, and one layer of the second grade is in contact with the first grade and the tie layer. If the heat-sealable layer in such a structure is divided into two so that the "half" remaining inside the sandwich structure is pigmented, the structure according to Fig. 13 is obtained.

An additional feature in the structure of Fig. 7 is the symmetry, which is an advantage when forming the coating layers by coextrusion. It comprises, first, polyamide layers 1b on both sides of the substrate or base layer 11 consisting of board and, next, polyamide layers 1a, which are joined to the heat-sealable layers 12 by tie layers 13.

Fig. 8 shows a special packaging board, which is suitable for food packages that suitable for processing in an autoclave, in particular, its material comprising transparent heat-sealable layers 12a, 12c of polypropylene that lie on the outer surface of the package, polyamide layers 15 inside the fibre base 11, oxygen barrier layers 1a, 1b of polyamide, and the tie layer 13, which adheres the oxygen barrier surrounded by the polyamide to the pigment layer 14a, the material of the tie layer being, e.g., a polymer by the name of Admer marketed by Mitsui Chemicals. The package formed from the material is thus protected against the yellowing of the fibre base 11 in the autoclave by the pigmented layers, of which 12b is polypropylene provided with a white pigment, and 14a is polypropylene pigmented black; and the oxygen-shielding layers 15, 1a, 1b and the light-shielding layer 14a inside the package protect the packaged product, lengthening its preservability and useful selling period. Within the invention, the layers 12b and/or 14a may optionally contain a white or black pigment or a blend thereof, producing a grey layer with a layer strength of 5 to 50g/m^2. As the layers 14a and 12b can be seamed together, the transparent heat-sealable layers 12a and 12c can optionally be omitted from such a structure. The material can be folded and heat sealed into a sealed package so that the superimposed, pigmented polymer layers 12c and 12b lie on the outer surface of the package, i.e., outside the fibre base 11, and the grey light-shielding layer 14a and the transparent heat-sealable layer 12a on the inner surface of the package, i.e., inside the fibre base 11, the oxygen barrier layers 1b, 1a, and the tie layer 13. The external superimposed pigmented layers 12c, 12b of the package give the package a light, almost white tint, which does not change when the package is heat-treated in the autoclave, for example.

The structure according to Fig. 8 can also be implemented without the polyamide layers 15, which is illustrated in Fig. 15. Another alternative way of implementing the structure of Fig. 8 is to use, as the heat-sealable layers 12c and 12b, polypropylene that is pigmented white and black, respectively. When using two polyamides as layers 1a and 1b, one preferable selection as the barrier layers is, for example, PA6 from Honeywell, USA and Grivory G21® from EMS, Switzerland.

In the packaging materials according to Fig. 8, the fibre base 11 can consist of a packaging board containing bleached sulphate pulp, its weight being 130 to 500g/m^2, preferably 170 to 300g/m^2. If the fibre base alternatively consists of bleached paper, its weight can be 20 to 120g/m^2. The weight of each polyamide barrier layer 15, 1a, and 1b can be 3 to 15g/m^2, preferably 3 to 8g/m^2. The weight of the transparent heat-sealable layers 12a, 12c can be 3 to 30g/m^2, preferably 7 to 20g/m^2. The weight of the external pigmented layer 12b of the fibre base 11 can be 20 to 50g/m^2 and that of the other pigment-containing layer 14a 3 to 10g/m^2. The weight of the internal light-shielding layer 14a of the fibre base 11, which is pigmented grey, can be 5 to 50g/m^2, preferably 25 to 40g/m^2. The content of titanium dioxide in the coating layer 12b dyed white can be 5 to 25%, preferably 7 to 12%. The content of carbon black in the inner coating layer 3 can be 0.05 to 0.5%, preferably 0.06 to 0.15%. If the layer 14a also comprises titanium dioxide, its content can be 5 to 25%, preferably 7 to 15%. The content of carbon black in the light-shielding layer 14a pigmented grey can be 0.05 to 0.5%, preferably 0.12 to 0.15%, and the content of titanium dioxide, correspondingly, 5 to 25%, preferably 7 to 12%. The weight of the Admer tie layers 13 can be 3 to 15g/m^2, preferably 5 to 10g/m^2.

Figs. 9 and 10 show further layer alternatives, the packaging material containing a four-layer barrier layer. All the layers in Fig. 9 are polyamides with different barrier properties. In the structure of Fig. 10, there are three different polyamides so that one of the layers is surrounded by two layers of the second polyamide on both sides thereof, the third polyamide being joined to one of the two. When a corresponding structure is implemented so that the heat-sealable layer of the inner surface of the package is divided into two, a pigmented and a conventional heat-sealable layer, the structure according to Fig. 14 is obtained.

Fig. 11 shows a sealed package with the shape of a rectangular prism, which is manufactured by folding and heat sealing from a blank consisting of the packaging material according to Fig. 12. The package is suitable to packing dry products and designed to protect the packaged product against moisture and gases coming from the outside. The figure includes section B-B from the wall of the package. This sandwich structure is shown in Fig. 12.

EXAMPLE

Determining the different oxygen barrier properties

The Ox-Tran 2/20 equipment (Oxygen Transmission Rate Measurement Rate Measurement System) was used in the determination.

Cut-to-size pieces with a sample size of $50cm^2$, which were suitable for the equipment, were cut from the materials that were to be measured.

Suitable parameters were selected for the equipment and the temperature was set at 23°C. Other parameters included, e.g.,

Method: OTR, Oxygen transmission rate 2/20 MH

Sample size 50cm2

N_2 flow 10 ml

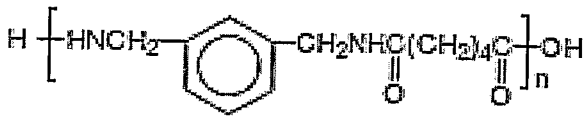
O_2 flow 20 ml

100 % O_2

60% RH

23°C

MXD6 is a product of Mitsubishi Gas Chemical Co, its chemical formula being:



Nylon-MXD6

B73TP is a PA6 grade of Honeywell.

The results are shown in Table 2.

Table 2. Measured oxygen barrier properties of two oxygen barrier materials.

O_2TR (60 % RH, 23 °C, after stabilization

Sample	Before autoclaving		1 day after autoclaving
MXD-6	1.5	1.5	11.9
B73TP	1.4	1.3	25.3

In autoclaving, the PA layer becomes moist, which is why PA6 loses more barrier than MXD6.

Another way of illustrating the comparison of the properties of the barrier layer comprises indicators. The graphs of the barrier properties shown in Figs. 15 and 16 are found in literature, for example.

According to the obtained results, samples PA6 and MXD6 yield different values to the barrier properties; herein, the oxygen barrier properties in a board coating, and in terms of the invention, they are different polyamides, i.e., by combining them as adjacent layers in the board sandwich structure, for example, the product according to the invention would be implemented.

The reference numbers used in the drawings

1a Layer of a polyamide (PA1)

1b A layer of a second polyamide (PA2)

1c A layer of a third polyamide (PA3)

1d A layer of a fourth polyamide (PA4)

11 Base layer, fibrous, generally consisting of board

12 Heat-sealable layer

12a The innermost heat-sealable layer of the package, consisting of polypropylene (PP)

12b Pigmented heat-sealable layer of polypropylene (PP)

12c The outermost heat-sealable layer of the package, consisting of polypropylene (PP)

13 Tie layer

14 Heat-sealable layer with pigment

14a Pigmented black or grey heat-sealable layer of polypropylene (PP)

15 The polyamide layer (PA) of an application example

CLAIMS:

1. A polymer-coated heat-sealable packaging material, comprising a base layer of fibrous material, at least one polymeric barrier layer that forms an oxygen barrier, and at least one polymeric heat-sealable layer, **characterized** in that the barrier layer comprises at least two polyamide-containing layers with different barrier properties.

2. Packaging material according to Claim 1, **characterized** in that the said polyamide-containing layers consist essentially of polyamide.

3. Packaging material according to Claim 1 or 2, **characterized** in that the at least two polyamide-containing layers are in contact with each other.

4. Packaging material according to Claim 1, **characterized** in being provided, on at least one side thereof, with an outermost polymeric heat-sealable layer.

5. Packaging material according to any of the preceding claims, **characterized** in being provided, on both sides thereof, with an outermost polymeric heat-sealable layer.

6. Packaging material according to any of the preceding claims, **characterized** in that the polyamide in at least one of the layers contains semi-crystalline polyamide.

7. Packaging material according to any of the preceding claims, **characterized** in that at least one of the polyamides contains amorphous polyamide.

8. A sealed package that is formed from the packaging material according to any of the preceding claims, **characterized** in comprising a layer of fibrous material, at least two layers of polyamide (PA) with different barrier properties inside the same, and an innermost polymeric heat-sealable layer.

9. A package according to Claim 8, **characterized** in being provided with an outermost polymeric heat-sealable layer.

10. A package according to Claim 8 or 9, **characterized** in being a package container or carton consisting of polymer-coated packaging board.

11. A package according to any of Claims 8 to 10, **characterized** in being a food package that is sealed in an oxygen-tight manner.

12. The use of at least two different polyamides (PA) with different barrier properties in the fibre-based packaging material in the polymer layer that constitutes the oxygen barrier.

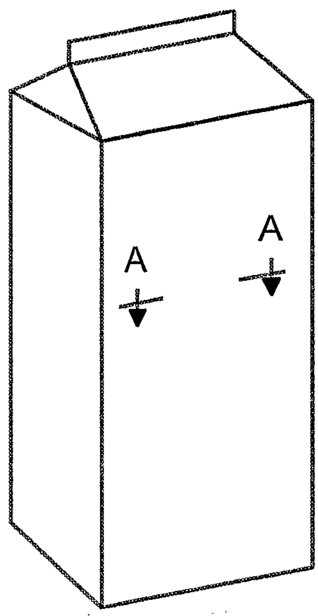


Fig. 1

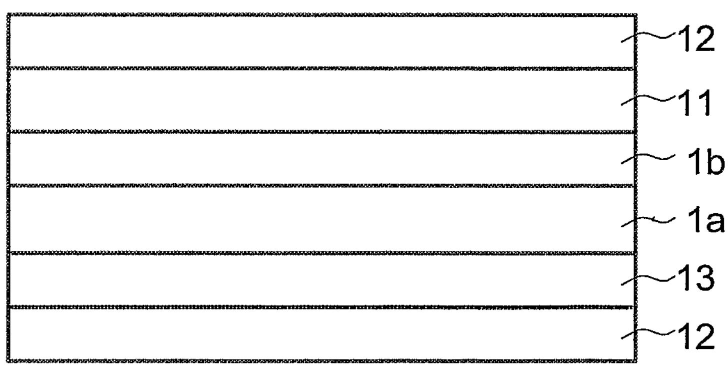


Fig. 2

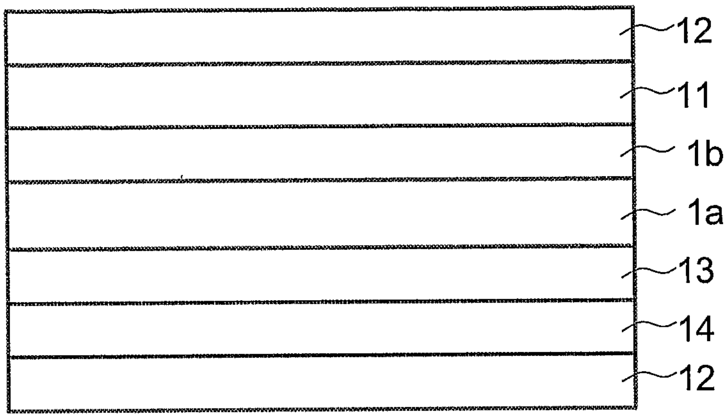


Fig. 3

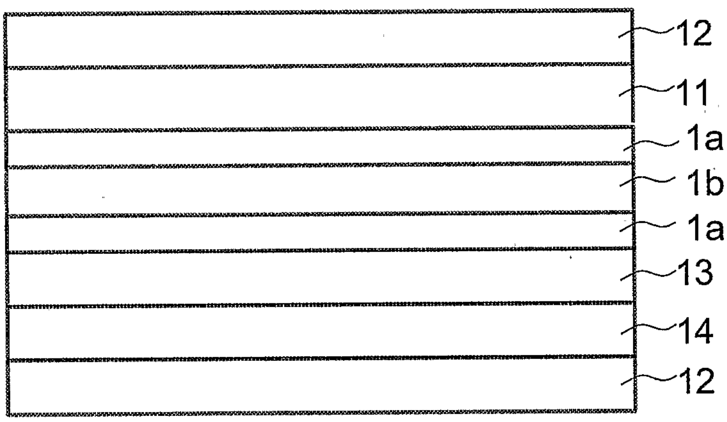


Fig. 4

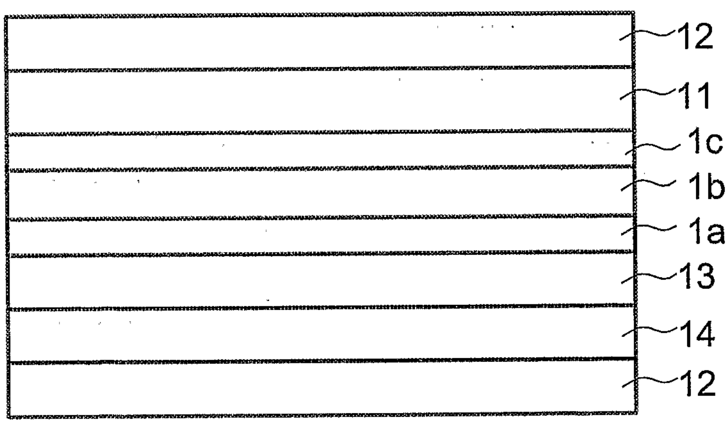


Fig. 5

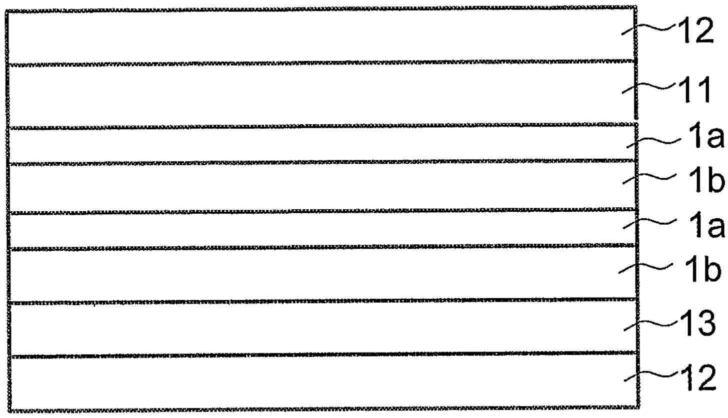


Fig. 6

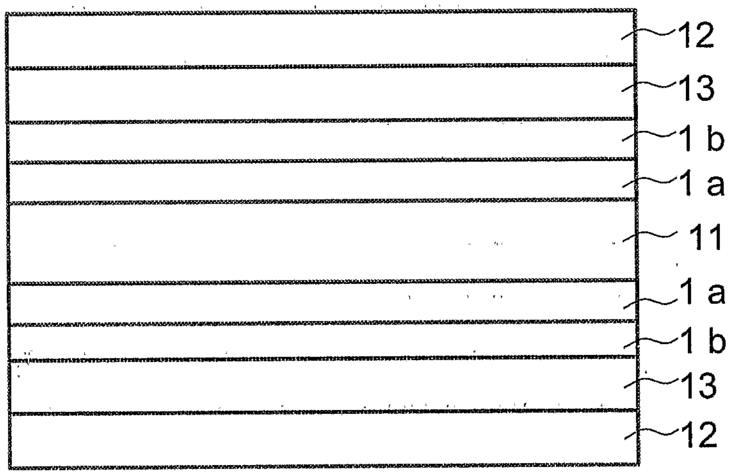


Fig. 7

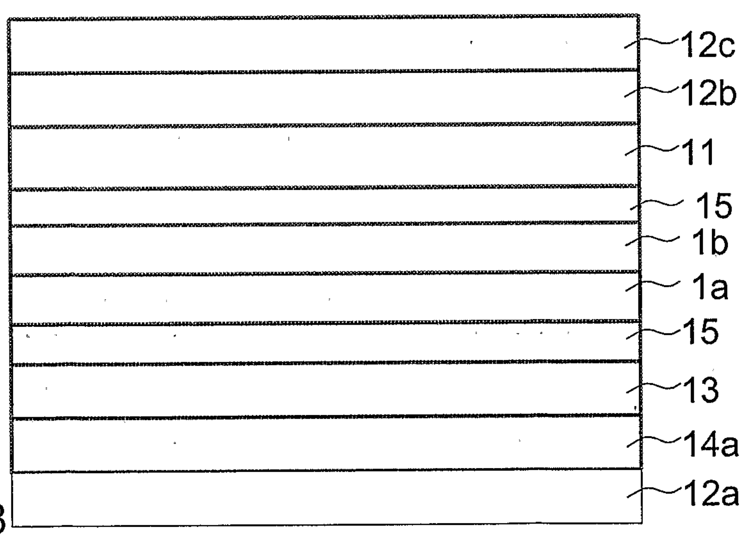


Fig. 8

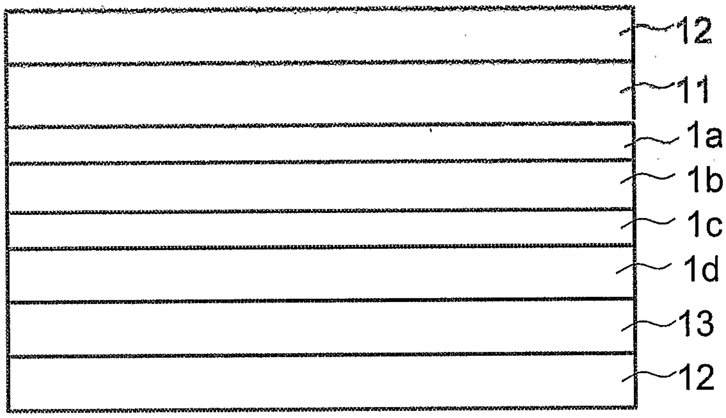


Fig. 9

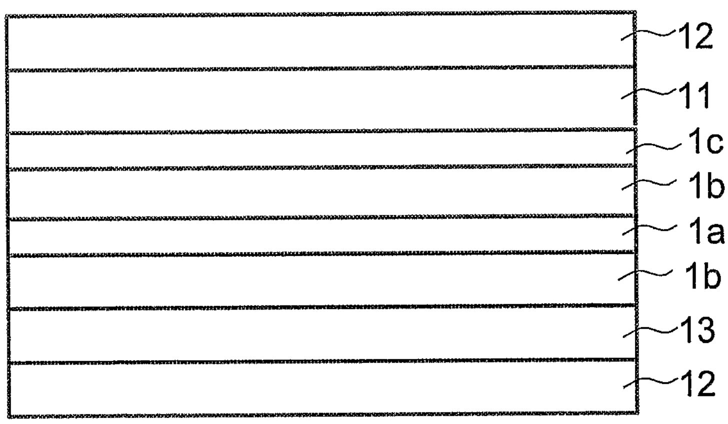


Fig. 10

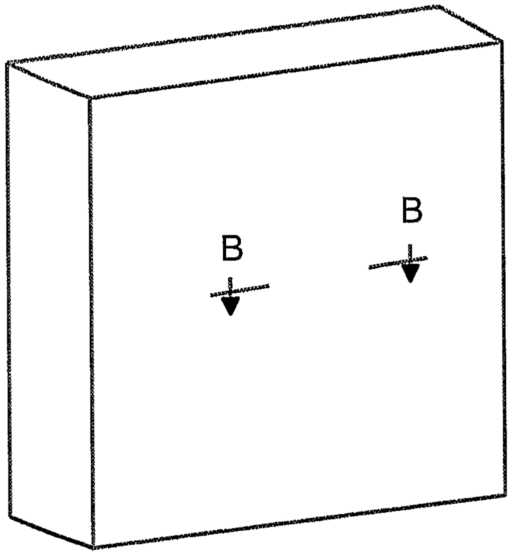


Fig. 11.

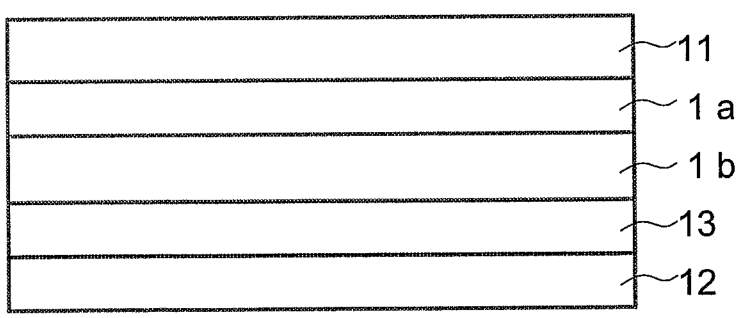


Fig. 12

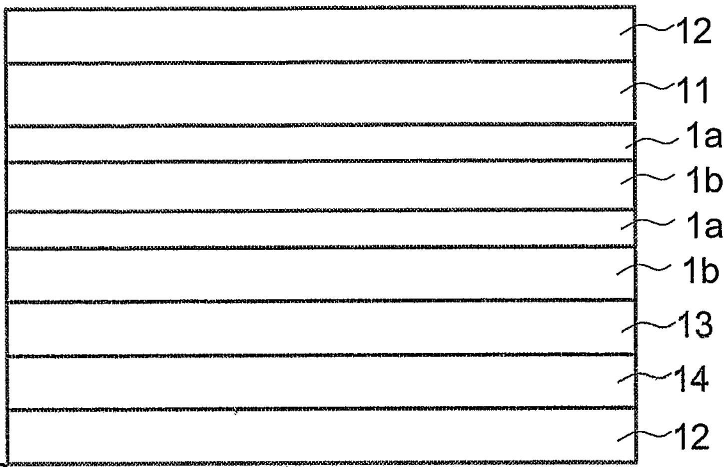


Fig. 13

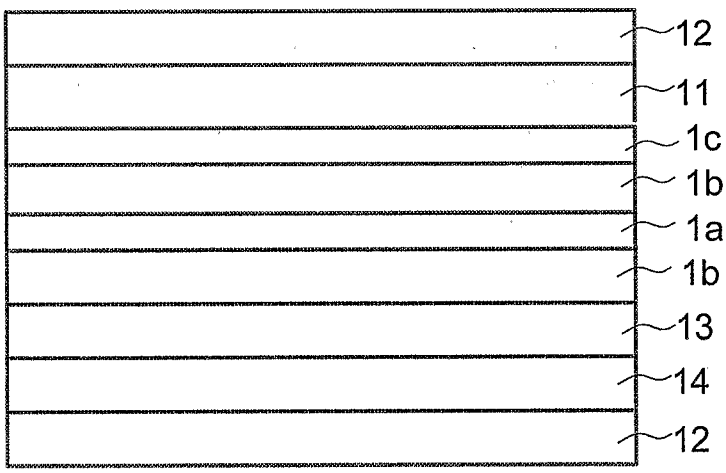


Fig. 14

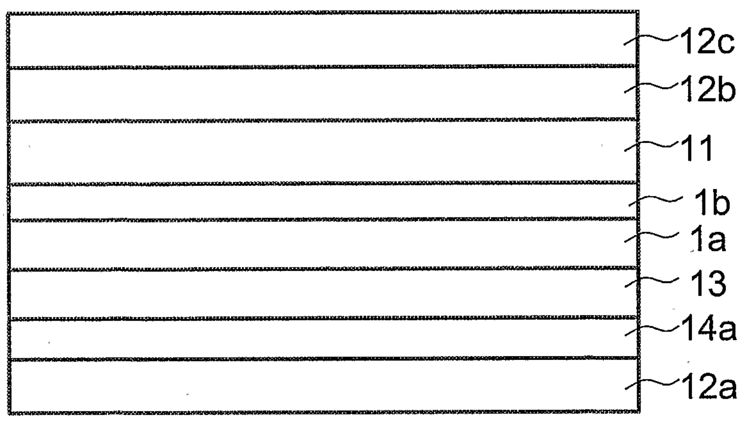


Fig. 15

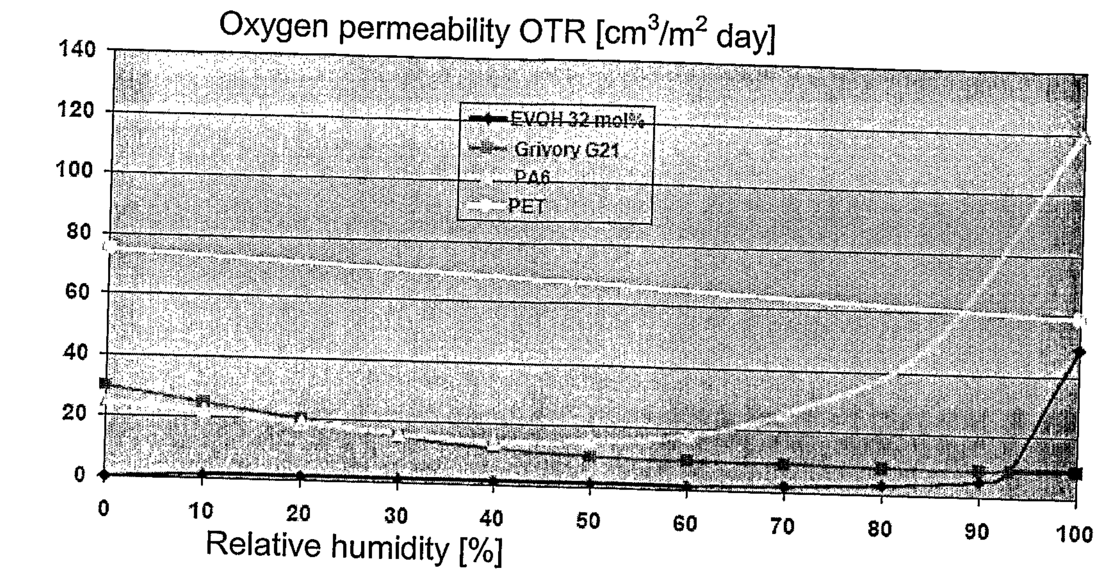

Oxygen permeability OTR [cm3/m2 day]
140
120
100
80
60
40
20
0
EVOH 32 mol%
Grivory G21
PA6
PET
0
10
20
30
40
50
60
70
80
90
100
Relative humidity [%]

Fig. 16

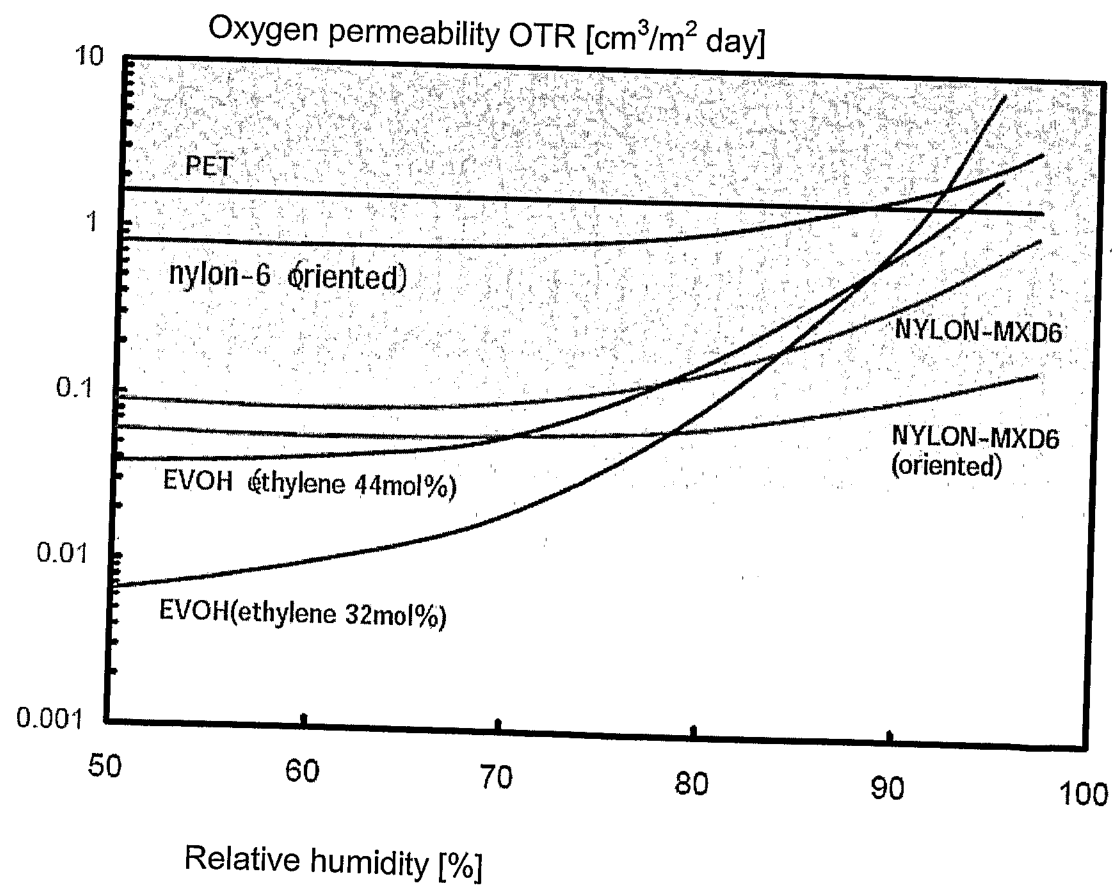

Oxygen permeability OTR [cm3/m2 day]
10
1
0.1
0.01
0.001
PET
nylon-6 (oriented)
NYLON-MXD6
NYLON-MXD6
(oriented)
EVOH (ethylene 44mol%)
EVOH(ethylene 32mol%)
50
60
70
80
90
100
Relative humidity [%]

Fig. 17

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2007/000194

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet
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: B32B, B65D

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

SE,DK,FI,NO classes as above

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

EPO-INTERNAL, WPI DATA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2004074785 A, DAINIPPON PRINTING CO LTD, 2004-03-11: (abstract) Retrieved from: WPI database, WEEK 200441, AN 2004-433306 claim 1; paragraph (0008), (0015), (0016) --	1-12
X	JP 6305086 A, MITSUBISHI KASEI CORP, 1994-11-01: (abstract) Retrieved from: WPI database, WEEK 199503, AN 1995-018828, page 1 and 7 --	1-12
X	US 5418068 A (CALUORI, HANS-JÖRG ET AL), 23 May 1995 (23.05.1995), column 3, line 14 - line 29, abstract, examples --	1-12

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
16 November 2007	20 -11- 2007

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2007/000194

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 20010010846 A1 (HOFMEISTER, FRANK ET AL), 2 August 2001 (02.08.2001), abstract --	1-12
A	JP 2001278330 A, NIPPON TETRAPAK KK, 2001-10-04: (abstract) Retrieved from: WPI database, WEEK 200208, AN 2002-061832 --	1-12
A	WO 9912735 A1 (E.I. DU PONT DE NEMOURS AND COMPANY), 18 March 1999 (18.03.1999), claim 1 --	1-12
A	US 6436547 B1 (TOFT, NILS ET AL), 20 August 2002 (20.08.2002), abstract, claim --	1-12
A	US 6872459 B1 (FRISK, PETER ET AL), 29 March 2005 (29.03.2005), column 3, line 41 - line 53 -- --------	1-12

International patent classification (IPC)

B65D 65/40 (2006.01)
B32B 27/34 (2006.01)
B65D 81/24 (2006.01)

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Cited literature, if any, will be enclosed in paper form.

INTERNATIONAL SEARCH REPORT
Information on patent family members

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PCT/FI2007/000194

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				WO	9950066	A	07/10/1999
				SE	9900514	D	00/00/0000
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				AU	5651499	A	17/04/2001
				CN	1290698	C	20/12/2006
				CN	1379714	A	13/11/2002
				DE	69936005	D	00/00/0000
				EP	1232856	A,B	21/08/2002
				WO	0119611	A	22/03/2001