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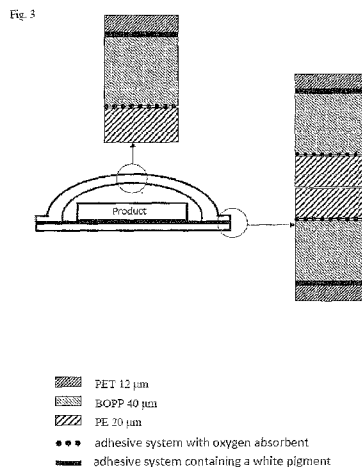
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- (54) **Title:** LAYERED LAMINATES WITH OXYGEN-ABSORBING, WHITENING OR OXYGEN-ABSORBING AND WHITENING ADHESIVE LAYERS, METHODS OF THEIR PREPARATION AND APPLICATION



- (57) **Abstract:** The invention relates to a method of making a layered laminate with an oxygen-absorbing adhesive layer, which consists in that in the first step the oxygen sorbent is introduced into the adhesive polyurethane system, to form an adhesive system absorbing oxygen, which is then applied to the surface of ribbon-bed layer and later dried, and in the second step a coating layer of thermoplastic material is applied on a layer of the adhesive system absorbing oxygen by a method of extrusion coating. The invention further provides a method of making a layered laminate with a whitening adhesive layer applied on it, and it also relates to an oxygen-absorbing layer laminate, bleached layered laminate, layered bleached laminate absorbing oxygen, and also to the use of the laminates for the manufacture of packaging in the food industry.



**LAYERED LAMINATES WITH OXYGEN-ABSORBING, WHITENING OR OXYGEN-ABSORBING
AND WHITENING ADHESIVE LAYERS, METHODS OF THEIR PREPARATION AND
APPLICATION**

The present invention relates to a method of making a layered laminate with an oxygen-absorbing adhesive layer, a method of making a layered laminate with the bleached adhesive layer, oxygen-absorbing layer laminate, layered whitened laminate, layered oxygen-absorbing bleached laminate, packaging and use of these laminates.

5 Currently in the packaging industry oxygen absorbers are placed mostly in the form of sachets and labels. Examples of commercially available products are sachets of the following companies: Mitsubishi Gas Chemical Co., Toppan Printing Co., Ltd, Nippon Soda Co., Ltd., Finetec C, labels of companies: Multisorb Technologies Inc., Standa Industries. Both sachets and labels containing oxygen absorbing substances pose a risk associated with the use of food
10 products due to their ability to be swallowed.

 There are also solutions consisting in the incorporation of sinks directly in the packaging material so that they can be an integral part of the package. In these embodiments sinks are in the form of a flexible film or a multilayer laminate involving plastics such as eg. Polyolefins, polyesters, polystyrene, ethylene and vinyl acetate). Examples are the products Cryovac®
15 OS200™, wherein the oxygen absorber is introduced into the packaging film during the extrusion process and Amosorb® - a mixture of copolyester and polybutadiene containing oxygen absorber.

 Regardless of the form of presence of oxygen scavengers, the most commonly used substances absorbing oxygen are iron and its compounds, ascorbic acid and derivatives thereof,
20 sulfites and derivatives thereof, boron compounds, unsaturated fatty acids and unsaturated hydrocarbons, enzymes, easily oxidizable polymers, alcohols such as ethylene glycol, propylene glycol, glycerin, sorbitol, xylitol, mannitol.

 Unfortunately, the oxygen-absorbing agents often bring their own color (usually brown), which results in unaesthetic appearance of such a package. Moreover, this color packaging
25 material prevents the correct color reproduction of printed trademarks and other information usually placed on the packaging.

 At the same time, there is a need to place the color information on packages, mapping carefully colors of colorful packaging elements, such as e.g. trademarks, logos, etc. in order to properly present the product to the customer and to ensure the aesthetic presentation of the

product and to increase the attractiveness of the appearance of the packaging.

In the patent literature there are many solutions based on the integration of the substance absorbing oxygen to the packaging material.

Publication WO 2012/091587 A1 discloses compounds absorbing oxygen based on nanoiron, capable of absorbing oxygen in the presence of both water and in an anhydrous environment. These compounds - nanoiron and iron at zero oxidation of boron may be placed in a container in the form of sachets or in another form, to prevent contact with food. Furthermore, these compounds may be incorporated in the mass of certain materials, such as silicone rubber, polyamide and polyethylene.

Nanoiron can also be introduced into polyvinyl alcohol by mixing nanoiron with PVA dissolved in acetone and pouring a thin film with the Cast method, and then subjected to UV radiation. Iron at zero oxidation containing boron can be added to the modified cellulose acetate butyrate. Oxygen absorbers can appear in the form of nanocomposites allowing to keep them in a pack or as part of the packaging or in the form of: a film for packaging, containers, trays, bottles, pins, caps, gaskets, labels and inserts.

Both nanoiron and iron at zero oxidation of boron have a good ability to absorb oxygen. The carbon dioxide content does not affect the ability to absorb oxygen. In the case of iron at zero oxidation boron absorption of 100% oxygen followed by after 1 day in an anhydrous atmosphere, and after 1 hour at presence of water. The carbon dioxide content also did not affect the ability to absorb oxygen. However, the introduction of packaging for foods containing oxygen absorbers such as nanoiron-based compounds may be difficult. Nano molecules exhibit chemical and physical properties that significantly differ from those at a larger scale, which may lead to different toxicological properties. Therefore, before the application of absorbers based on nanoiron for food products one must evaluate them in relation to the risk posed. Such an assessment, according to Commission Regulation (EC) nr10 / 2011 should be done by an appropriate agency.

Publication EP 1270206 A1 discloses a multilayer oxygen-absorbing structure consisting of an outer layer consisting thermoplastic resin, an adhesive layer consisting of epoxy resin, oxygen-absorbing layer consisting of a thermoplastic resin and built-in iron, and the heat-weldable film, which made by oxygen-friendly thermoplastic resin. An adhesive layer is prepared by applying a solution of epoxy resin on the external surface of the multilayer structure absorbing oxygen-containing thermoplastic resin. This structure is used in materials for food packaging, pharmaceuticals, and others. The disadvantage of the described solution is a very complicated preparation used for coating, as well as the complex process of preparing substances

absorbing oxygen. The complicated process of obtaining individual components may not provide adequate reproducibility for the final laminate.

U.S. Publication 19935274024 A describes a resin composition consisting of olefin resin and a water-absorbing polymer selected from modified polyethylene oxide, acrylic acid-vinyl alcohol copolymers, sodium poly(acrylate), vinyl polymer alcohol. In this composition, the resin can be thermoformed and modified by oxide polyethylene or a copolymer of acrylic acid and vinyl alcohol. The binder of the oxygen is made of the reduced iron and a compound which promotes the oxidation reaction, wherein the content value of copper is less than 150 ppm of sulfur and less than 500 ppm. The resin composition is intended for production (extrusion process), the caps and containers used for products liquid, e.g., drinks.

In the literature there are also known methods for obtaining a white color of the packaging film. These methods mainly include extrusion of films doped with mineral fillers down, as titanium oxide, calcium carbonate, talc, etc.. These methods are associated with high costs of the use of machines (high costs are generated as a result of having to clean reactor parts using materials with low melt flow index, so-called MFI).

Example on how to obtain a laminate comprising a packaging film obtained by extrusion, bleached by the addition of the inflator shown in US 25 5 449 552 describes the production of multilayer laminates comprising a layer external (which is a multilayer biaxially-oriented polypropylene film (BOPP), that is rendered white in color by the addition of inorganic fillers, ie. CaCO_3 and TiO_2), a two-component polyurethane adhesive gas-barrier layer, a two-component polyurethane adhesive and an inner layer consisting of a copolymer of ethylene and vinyl acetate. It is worth noting that this solution is a bleached film, which is not always is easy to use in manufacturing environments with different requirements than the fixed ones.

Similarly, the co-extrusion method for the preparation of multilayer films looking like a paper, colored white while welding is described in US 5 446 520. The described multilayer films comprise isotactic polypropylene, linear low-density ethylene modified with rubber and anhydride maleic random copolymer of propylene and ethylene, and an inorganic filler. The publication does not specify the use of the multilayer-drawn film thus there is no certainty as to the possibility of using this product as packaging in the food industry. In addition, the described disadvantage of the invention is the use of the method for manufacturing the same extrusion. This method is not flexible to change of parameters, which makes it difficult to apply it at the production of different product range. This is due to the need for large amounts of raw materials and a time-consuming process parameter selection, leading to large losses of raw materials during the first production run.

A bleached, biaxially-oriented polyester film was also obtained by co-extrusion method, as described in US 7 329 453 B2. Such a film layer comprises a sealable outer layer comprising a polyester and an inorganic or organic filler and an inner layer consisting of bleached, white inorganic pigment and/or a polymer incompatible with polyester. The film described in the above publication is intended for closing the trays used to hold the ready food products. It is the only described application which limits the range of products. Additionally, a disadvantage of the multi-layer drawn polyester film is associated with the use of co-extrusion methods for its production. As mentioned earlier, this co-extrusion method of the invention requires significant resources, which is troublesome during a time-consuming modification of technological parameters.

Another way to obtain a white film used for the production of packaging is bleaching typical polymeric films prior to printing the package. This makes it difficult, however, to conduct a continuous production of such a package and increases the time of manufacture for such a package.

Each of the prior solutions has some disadvantages. In all the described embodiments, both the oxygen consumption and bleaching of packaging film uses the increased temperature and extrusion or co-extrusion. With the modification of parameters the final product is difficult to determine the conditions with a minimal consumption of materials for technological tests.

There was, therefore, a need for a simple and rapid method for the preparation of universal and safe use of an oxygen absorbent in the food package for easy application of the color information, color and imaging shape trademarks, company logo, etc.

The invention relates to a method of making a layered laminate with a coated adhesive absorbing oxygen, wherein in the first stage of introduction, the oxygen-absorbing agent is introduced to the polyurethane adhesive system to form an oxygen sorbent, which is then applied to the surface of the ribbon substrate layer and dried, and in the second step, to the adhesive layer of the oxygen absorbent the coating layer of thermoplastic material is applied by extrusion coating.

Preferred is a method, wherein the oxygen-absorbing adhesive system is applied to the ribbon surface layer by roll coating shaft or rotogravure method.

Preferred is a method, wherein the oxygen-absorbing agent is a mixture of monohydrate iron hydroxide $\text{FeO}(\text{OH})\cdot\text{H}_2\text{O}$ and ascorbic acid in a weight ratio of from 1:2 to 2:1, most preferably 1:1 or of iron oxide (III) Fe_2O_3 and ascorbic acid in a weight ratio from 1:2 to 2:1, most preferably 1:1.

Preferred is a method, wherein to the oxygen absorber is introduced additionally

carboxylic acid, preferably mono- or dicarboxylic acid, most preferably acetic acid, tartaric acid, malonic acid and/or oxalic acid.

Preferred is a method, wherein the ratio of the carboxylic acid to the hydroxide monohydrate iron $\text{FeO}(\text{OH}) \cdot \text{H}_2\text{O}$ oxide or iron (III) Fe_2O_3 is 1:1.

5 Preferred is the process, wherein the layer laminate bearing the adhesive oxygen system absorbing heat is sealed under the conditions of temperature of sealing 113-132°C.

Preferred is a method, wherein a ribbon surface layer the form of materials is selected from a plastic film, preferably of polyethylene (ethylene terephthalate), poly(vinyl chloride), polyethylene or polypropylene, aluminum foil, and combinations thereof.

10 Preferred is a method, wherein the coating layer of thermoplastic material with the adhesion-ability of the ribbon to the backing layer, is preferably selected from the group consisting of polyethylene, including LDPE, LLDPE, and HDPE, polypropylene, ethylene and vinyl acetate copolymers, ethylene and acrylic acid copolymers, ethyl methacrylate and mixtures thereof.

15 The invention also relates to a method of making a layered laminate applied with a whitening adhesive layer, wherein in the first step the white pigment is introduced into polyurethane adhesive system, to obtain a whitening of the adhesive system, which is then applied to the surface of the ribbon substrate layer and dried, and in the second stage bleaching layer of the adhesive coating is coated by extrusion with a layer of thermoplastic material.

20 Preferred is a method, wherein the white pigment is titanium dioxide, white zinc, and/or white lithopone.

Preferred is a method, wherein the bleaching adhesive system is applied by a coating roller shaft or a rotogravure method to the ribbon surface layer.

25 Preferred is a method, wherein the concentration of white pigment in a polyurethane adhesive system is in the range of 10-20% by weight.

Preferred is a method, in which a layered laminate of the coated bleaching CYM system adhesive printing the printing inks, preferably using flexographic or rotogravure printing.

30 Preferred is a method, wherein a ribbon surface layer in the form of stripe materials is selected from a plastic film, preferably polyethylene (ethylene terephthalate), poly(vinyl chloride), polyethylene or polypropylene, aluminum foil, and combinations thereof.

Preferred is a method, wherein the coating layer of thermoplastic material of the adhesion-ability to the ribbon surface layer, is preferably selected from the group consisting of polyethylene, including LDPE, LLDPE, and HDPE, polypropylene, ethylene and vinyl acetate copolymers, ethylene and acrylic acid copolymers, ethyl methacrylate and mixtures thereof.

Preferred is a process, wherein the layer laminate and the bleaching adhesive system are sealed on conditions: sealing temperature 113-132°C.

Preferred is a method, wherein in the first step the oxygen absorbent is added to the polyurethane adhesive system to form an adhesive system absorbing oxygen, which is then applied to the surface of the ribbon substrate layer and dried, and in the second step to the adhesive layer of the oxygen absorbent a ribbon surface layer is applied by extrusion coating, bearing the bleached adhesive system, and then in the third step further it is coated by extrusion coating with a coating layer of a thermoplastic material to form a layered bleached laminate absorbing oxygen.

Preferred is a method, in which the layer laminate is sealed under conditions of temperature welding 130-225°C.

Preferred is a method, in which on a layered laminate conducted is printing by printing inks, preferably by rotogravure or flexographic printing.

The invention further relates to an oxygen-absorbing layer laminate, which comprises of:

- a ribbon backing layer, with a weight of 5 to 300 g/m²;
- a layer of an oxygen absorbing adhesive system consisting of an oxygen sorbent introduced into the polyurethane adhesive system; and
- coating layer of a thermoplastic material having a thickness of from 5 to 200 microns, applied by extrusion coating on the ribbon surface layer with the previously applied oxygen absorbent adhesive system layer.

A preferred laminate is a layer, in which an oxygen absorbing agent is a mixture of iron hydroxide monohydrate $\text{FeO(OH)} \cdot \text{H}_2\text{O}$ and ascorbic acid in a weight ratio of from 1:2 to 2:1, most preferably 1:1 or of iron oxide (III) Fe_2O_3 and ascorbic acid weight ratio of from 1:2 to 2:1, preferably 1:1.

A preferred laminate is a layer, in which oxygen absorbing agent further comprises carboxylic acid, preferably mono- or dicarboxylic acid, most preferably acetic acid, tartaric acid, malonic acid and/or oxalic acid.

Preferred is a layered laminate, wherein the carboxylic acid to monohydrate iron hydroxide $\text{FeO(OH)} \cdot \text{H}_2\text{O}$ oxide or iron (III) Fe_2O_3 is 1:1.

Preferred is a layered laminate, wherein the ribbon surface layers is made of materials selected from a plastic film, preferably of polyethylene (ethylene terephthalate), poly(chloride of vinyl), polyethylene or polypropylene films and mixtures thereof.

Preferred is a layered laminate wherein the layer of coating material indicates the ability of the thermoplastic adhesion to the ribbon substrate layer, it is preferably selected from the

group consisting of polyethylene, including LDPE, LLDPE, and HDPE, polypropylene, ethylene and vinyl acetate copolymers, ethylene and acrylic acid copolymers, ethyl methacrylate and mixtures thereof.

The invention also relates to a bleached layer laminate, which comprises of

- 5 - a ribbon backing layer, with a weight of 5 to 300 g/m²;
- a bleaching adhesive layer consisting of a white pigment introduced to a polyurethane adhesive system; and
- a coating layer of a thermoplastic material having a thickness of from 5 to 200 μm, applied by extrusion coating on the ribbon substrate layer of the previously applied whitening layer of the adhesive system.

10 Preferred is a bleached, layered laminate, wherein the white pigment is titanium dioxide, white zinc and/or white lithopone.

Preferred is a bleached, layered laminate, wherein the concentration of white pigment in the polyurethane adhesive system is in the range of 10-20% by weight.

- 15 Preferred is a bleached, layered laminate, wherein the laminate layer is whitened and additionally printed with inks, preferably by flexographic printing or rotogravure method.

Preferred is a bleached, layered laminate, wherein the ribbon surface layer is made of materials selected from a plastic film, preferably made of polyethylene (ethylene terephthalate), poly (vinyl chloride), polyethylene or polypropylene, aluminum foil, and combinations thereof.

- 20 Preferred is a bleached, layered laminate, wherein the coating layer of a material shows the ability of the thermoplastic adhesion to the ribbon surface layer, and it preferably is selected from the group consisting of polyethylene, including LDPE, LLDPE, and HDPE, polypropylene, ethylene and vinyl acetate copolymers, ethylene and acrylic acid copolymers, ethyl methacrylate and mixtures thereof.

25 The invention further relates to a layered bleached laminate, absorbing oxygen, which comprises of:

- a ribbon surface layer, with a weight of 5 to 300 g/m²;
- a layer of an oxygen absorbing adhesive system consisting of an oxygen absorbent introduced into the polyurethane adhesive system;
- 30 - a layer of a bleaching adhesive system, consisting of a white pigment incorporated into a polyurethane adhesive system; and
- a coating layer of a thermoplastic material having a thickness of from 5 to 200 μm, applied by extrusion coating on the ribbon surface layer of the previously applied whitening layer of the adhesive system.

Preferred is a bleached layered absorbing oxygen laminate, wherein the oxygen sorbent is a mixture of iron hydroxide monohydrate $\text{FeO}(\text{OH})\cdot\text{H}_2\text{O}$ and ascorbic acid in a weight ratio of from 1:2 to 2:1, preferably 1:1 or of iron oxide (III) and Fe_2O_3 ascorbic acid in a weight ratio of from 1:2 to 2:1, preferably 1:1.

5 Preferred is a bleached, layered laminate, absorbing oxygen, wherein the oxygen absorbent is further comprised of a carboxylic acid, preferably mono- or dicarboxylic acid preferably acetic acid, tartaric acid, malonic acid and/or oxalic acid.

Preferred is a bleached, layered, oxygen- absorbing laminate, wherein the ratio of carboxylic acid iron hydroxide monohydrate $\text{FeO}(\text{OH})\cdot\text{H}_2\text{O}$ or iron oxide (III) Fe_2O_3 is 1:1.

10 Preferred is a bleached, layered, oxygen-absorbing laminate, wherein the ribbon-surface layer of material selected from the ribbon of plastic film, preferably poly(ethylene terephthalate), poly(vinyl chloride), polyethylene or polypropylene film aluminum and combinations thereof.

Preferred is a bleached layered oxygen-absorbing laminate, wherein the coating layer of the thermoplastic material has the ability to adhere to the layer of the ribbon-acetate fibers, preferably selected from the group consisting of polyethylene, including LDPE, LLDPE and HDPE, polypropylene, ethylene and vinyl acetate copolymers, ethylene and acrylic acid copolymers, ethyl methacrylate and mixtures thereof.

Preferred is a bleached, layered, oxygen-absorbing laminate, wherein the white pigment is titanium dioxide, zinc white and/or white lithopone.

20 Preferred is a bleached, layered, oxygen-absorbing laminate, wherein the concentration of white pigments in a polyurethane adhesive system is in the range of 10-20% by weight.

Preferred is a bleached, layered, oxygen-absorbing laminate, which is additionally printed with inks, preferably by flexographic printing or rotogravure method.

25 Preferred is a bleached layered oxygen-absorbing laminate, wherein the ribbon surface layer of material is selected from the ribbon of plastic film, preferably poly (ethylene terephthalate), poly(vinyl chloride), polyethylene or polypropylene film aluminum, and combinations thereof.

30 Preferred is a bleached, layered, oxygen-absorbing laminate, wherein the coating layer of thermoplastic material has the ability to adhere to the layer of the ribbon acetate fibers, preferably selected from the group consisting of polyethylene, including LDPE, LLDPE and HDPE, polypropylene, ethylene and vinyl acetate copolymers, ethylene and acrylic acid copolymers, ethyl methacrylate, and mixtures thereof.

The invention also relates to a package particularly for the food industry, which consists of an oxygen-absorbing layer laminate as defined above, a layered bleached laminate as defined

above, or a layered bleached laminate absorbing oxygen as defined above.

The invention also relates to the use of an oxygen-absorbing layer laminate as defined above, a bleached layered laminate as defined above, or a layered bleached oxygen-absorbing laminate as defined above for the preparation of packaging in the food industry.

5 The invention described represents a new technological solution. An important advantage of the present invention is the use of ingredients approved for food contact according to Commission Regulation (EC) No 10/2011 on materials and articles of plastic materials intended for contact with food, and easy availability, low price and uncomplicated chemical structure of the substances used.

10 The present invention has also a simple method for preparing modified adhesive systems, since all the mixture components are pre-mixed, whereby the process for producing a packaging film boils down only to the operation of coating, laminating and printing. by using white pigment it obtains a white background; it is excellent for further printing including various dyes, yielding a packaging film accurately reproducing the colors of the print in demand (e.g. company logo,
15 trademark, etc.). In contrast to the described in the state-of-the-art solutions, the present invention is the only one suitable to specific applications, i.e. printing on packaging films by a gravure method.

Embodiments of the present invention have been described in the accompanying figures.

Fig. 1 shows a schematic cross-section of the packaging material and laminate built from
20 the packaging film of PET/PE with a layer of polyurethane adhesive system containing oxygen consuming substances.

Figure 2 shows a schematic cross-section of the packaging material and laminate built from the packaging film BOPP/PE layer of a polyurethane adhesive system of any addition of white pigment.

25 Figure 3 shows a schematic cross-section of the packaging material and laminate built from the packaging film of PET/BOPP/PE layer of a polyurethane adhesive system with the addition of oxygen-absorbing layer and the polyurethane adhesive system with the addition of white pigment.

In the present invention, oxygen absorbents are mixtures of hydroxide monohydrate iron
30 $\text{FeO}(\text{OH}) \cdot \text{H}_2\text{O}$ and ascorbic acid in a weight ratio of from 1:2 to 2:1, most preferably 1:1 or of iron oxide (III) Fe_2O_3 and ascorbic acid in a weight ratio of 1:2 to 2:1, preferably 1:1. To initiate the process of oxygen absorption by the said oxygen absorbents presence of water is necessary. Therefore, the oxygen absorbents described herein are intended for containers of flexible plastic, e.g., polyethylene terephthalate (PET) and polyethylene (PE) for the packaging of products

containing water, for example meat, dairy. Moreover, under Commission Regulation (EC) no 10/2011 on materials and plastic products intended for contact with food, all substances used in the present invention are used as an additive or auxiliary substance in the manufacture of polymers.

5 In the case of products with low water content it is possible to generate a small quantities of water by the introduction of carboxylic acids with oxygen absorbers into a polyurethane adhesive system. In this embodiment, the water formed in the polycondensation reaction of carboxylic acid component with the hydroxyl groups of the adhesive. Carboxylic and boxylic acids used in the described embodiment are the mono- and dicarboxylic acids, for example,
10 acetic acid, tartaric acid, malonic acid, oxalic acid. These acids are introduced in a weight ratio 1:1 to use oxygen absorbents.

As used in accordance with the invention, a polyurethane adhesive system is obtained by combining isocyanate resin and hardener which is a mixture of polyester and polyether in a suitable weight ratio of 12.5:0,7-37,5:2.10, preferably CYM 25:1.39. An adhesive composition
15 as well as oxygen absorbents contain components released for direct contact with food – to meet the requirements of Commission Regulation (EC) No 10/2011 on materials and plastic products intended for contact with food.

The invention further relates to a process for the preparation of layered laminate applied an adhesive layer containing a white pigment which is a modification of the polyurethane
20 adhesive system with white pigments and applying it to the packaging film by coating with a shaft roller or by rotogravure method.

Surprisingly, it was found that the method for obtaining a layered laminate with an adhesive layer applied, containing a white pigment of the present invention is much simpler compared to existing methods of whitening a film packaging. In addition, the finished product,
25 i.e. the package with a certain degree of whitening may be used for packaging all kinds of food products, and printing any prints.

Preferred is a three-fold laminate.

As the white pigments in the present invention are titanium dioxide, zinc oxide and white lithopone. These pigments are added in amounts of 5-30% by weight to the polyurethane
30 adhesive system with an organic solvent, e.g. ethyl acetate. The polyurethane adhesive system is obtained, as already described above, by the combination of the isocyanate resin and a hardener being a mixture of polyester and polyether in a suitable weight ratio of 12.5:0,7-37,5:2.10 preferred ratio of 25:1.39.

Components of polyurethane adhesive and white pigments are safe and approved for

indirect contact with food – they meet the requirements of Commission Regulation (EC) No 10/2011 on materials and plastic products intended for contact with food.

The invention further provides a method of making a layered laminate bearing polyurethane adhesive system containing an oxygen absorbing agent, and a polyurethane adhesive system modified with a white pigment. Absorbing oxygen agents, white pigments and polyurethane adhesive system are those used for the preparation of three-layer laminates absorbing oxygen and three-layer laminates with high degree of whiteness described in this invention. The laminate may in a preferred embodiment consist of the following layers:

- PET film with a thickness of 12 microns,
- 10 - polyurethane adhesive system with the addition of white pigments, the thickness of 4-10 microns,
- BOPP film with a thickness of 40 microns,
- polyurethane adhesive system with the addition of absorbing oxygen, the thickness of 4-10 microns,
- 15 - PE foil with a thickness of 20 microns.

Preferred is a layered laminate of five layers.

The diagram of a preferred five-layer laminate is shown in FIG. 3.

A process for preparing a layered laminate of the present invention combines the advantages of the above three-fold laminate according to the invention. As a result of this method is obtained a laminate which has excellent oxygen absorption and at the same time gives way to printing any prints. Such a finished product can be used for different kinds of packaging of food products.

Layered laminates favorably weld in the following conditions: 0,4-4,0 kN clamping force, time pressure 0.5-4 s.

25 The present invention is described in the following examples.

Example 1 - method of preparing a three layer laminate with the adhesion layer absorbing oxygen

30 A slurry of ferrous hydroxide monohydrate $\text{FeO}(\text{OH})\cdot\text{H}_2\text{O}$ (Roh Europe) and ascorbic acid (Chempur) is made in a weight ratio of 1:1 ethyl acetate (JarbuR). The suspension is vigorously stirred by a magnetic stirrer for 30 mins, after which the resin is incorporated into Liofol UR 3720 (Henkel) and hardener Liofol UR 6055 (Henkel) and stirring is continued for 15 mins. The concentration of both oxygen absorbents on the total the adhesive is 10% by weight. The system is coated on the shaft roller with a PET film of a thickness of 12 μm , which is dried for 1 h at 75°C. The thickness of the layer is 4-10 microns. After drying, the formed laminate of

a polyethylene film (PE) with a thickness microns using the Cast method is conditioned in a climatic chamber at preset weight under conditions of temperature 23°C and 50% RH for 2 to 4 days. Laminates are used in the manufacture of packaging with dimensions: 9 x 13 cm of food by heat-sealing conditions: temperature of sealing 113°C, 0.41 kN clamping force, holding time of 0.5 s. Fig. 1 shows a cross-section of packaging marked with various layers.

Table 1. Results of measuring the composition of the atmosphere inside packages made of the laminates PET/PE bearing adhesive system containing an oxygen-absorbing agent: monohydrate of iron hydroxide and ascorbic acid. The containers bear agar as a model product.

dimensions of package [cm]	amount of an oxygen absorbent [g]	conditioning time [days]	composition of the atmosphere [vol.%]	6th day of measurement
9x13	0.275	2	O ₂	11.8
			CO ₂	7.9
			N ₂	80.3
9x13	0.476	4	O ₂	14.9
			CO ₂	5.3
			N ₂	79.8

Example 2 – a method of preparing a three-layer laminate with an adhesive, oxygen-absorbing layer applied

A slurry of iron oxide (III) Fe₂O₃ (ROHA Europe) and ascorbic acid (Chempur) is made in a weight ratio of 1:1 and malonic acid (Alfa Cesar) at 1:1 ratio of iron oxide (III) in ethyl acetate (JarbuR). The solution is intense by stirring with a magnetic stirrer for 30 min, then the resin is incorporated into Liofol UR 3720 (Henkel) and a hardening agent Liofol UR 6055 (Henkel) and stirring is continued for 15 mins. The concentration of oxygen absorbent of the entire adhesive system is 5 wt.%, and malonic acid is 2.5% by weight. The system is coated on the roller shaft with a thick PET film of 12 microns, which is dried for 1 h at 75°C. The thickness of the layer is 4-10 microns. After drying, the laminate is formed of a polyethylene film (PE) with a thickness of 20 µm by the Cast method and conditioned in a climatic chamber at preset conditions at 23°C and 50% RH for one day. Laminates are used to produce containers of dimensions: 18 × 26 cm of food by heat-sealing in modified atmosphere conditions: sealing temperature 113°C, 0.41 kN clamping force, holding time of 0.5 s. Fig. 1 shows cross-section of the package with the selected individual layers.

Table 2. The results of measurements of the composition of the atmosphere inside the

packaging made with laminates PET/PE bearing adhesive system containing an oxygen absorbing agent: iron oxide (III), ascorbic acid and malonic acid. The packaging agar is provided as a model product.

dimensions of package [cm]	amount of an oxygen absorbent [g]	conditioning time [days]	composition of the atmosphere [vol.%]	5th day of measurement
18x26	0.307	1	O ₂	15.6
			CO ₂	5.1
			N ₂	79.3
				7th day of measurement
18x26	0.057	1	O ₂	13.8
			CO ₂	6.7
			N ₂	79.5

5 Example 3 - a process for preparing a three-layer laminate with an adhesive oxygen-absorbing layer applied

A slurry of ferrous hydroxide monohydrate FeO(OH)·H₂O (Roh Europe) and ascorbic acid (Chempur) in a weight ratio of 1:1 is formed and malonic acid in an amount of 1:1 in relation to the iron oxide hydroxide monohydrate in ethyl acetate (JarbuR). The slurry is subjected to intensive mixing by magnetic stirring for 30 min, the resin is incorporated into
 10 Liofol UR 3720 (Henkel) and hardener Liofol UR 6055 (Henkel) and stirring is continued for 15 min. The concentration of both oxygen absorbents on the total adhesive system is 5 wt.% malonic acid and 2.5% by weight. The system is coated with a shaft roller on a PET film having a thickness of 12 microns, which is dried for 1 h at 75°C. The thickness of the applied layer is 4-10 microns. After drying, the laminate is formed with a polyethylene film (PE) with a thickness
 15 of 20 microns using the Cast method and conditioned in a climatic chamber with the preset conditions of temperature 23°C and 50% RH for one day. Laminates are used for manufacturing the package size: 18 × 26 cm for the food sealing in modified atmosphere conditions: sealing temperature 113°C, downforce of 0.41 kN, the pressing time of 0.5 s. Fig. 1 shows a cross-sectional view the package with the selected individual layers.

20 Table 3. The results of measurements of the composition of the atmosphere inside packages made of the PET V PE laminates, bearing adhesive system containing an oxygen-

absorbing agent: iron oxide hydroxide monohydrate, ascorbic acid and malonic acid. Agar was placed as a product model in the packaging

dimensions of package [cm]	amount of an oxygen absorbent [g]	conditioning time [days]	composition of the atmosphere [vol.%]	5th day of measurement
18x26	0.277	1	O ₂	14.0
			CO ₂	6.0
			N ₂	80.1
				7th day of measurement
18x26	0.618	1	O ₂	8.6
			CO ₂	8.0
			N ₂	83.4

Example 4 – a method for producing a three-layer laminate with a whitening adhesive layer

5 A 19.6% by weight suspension of titanium dioxide (Chemical Plant POLICE SA) in ethyl acetate (JarbuR) is made, which is obtained by mixing a magnetic stirrer NYM at room temperature for 0.5 h period with a high degree of agitation. To the suspensions there are applied resin Liofol UR 3720 (Henkel) and hardener Liofol UR 6055 (Henkel). The mixture is stirred for about 15 mins. The concentration of titanium dioxide (Chemical Plant POLICE) of the resulting
 10 adhesive system is 10.0% by weight. The system is coated with a shaft on a biaxially oriented polypropylene film (BOPP) having a thickness 10 40 Pm, which is then subjected to drying for 1 h at 75°C. The thickness of the layer is 4-10 microns. After drying, the formed laminate of a polyethylene film (PE) with a thickness of microns using the Cast method. Laminates are subjected to conditioning in a temperature of 23°C with 50% humidity for a period 1-5 days.
 15 This laminate can be used to form a package with dimensions of 9 × 13 cm or 18 × 26 cm for food by welding PE film under the following conditions: welding temperature 113°C, downforce of 0.41 kN time pressure of 0.5 s. Fig. 2 shows a cross-section of the package with the selected individual layers.

20 Example 5 - a process for preparing a three layer laminate applied to a bleaching adhesive layer

The process is carried out analogously to Example 4, wherein the pigment concentration, i.e. titanium dioxide (Chemical Plant POLICE SA) system adhesive is 15% by weight.

Example 6 - a method of producing three-layer laminate with a whitening adhesive layer applied

The process is carried out analogously to Example 4, wherein the pigment concentration, i.e. titanium dioxide (Chemical Plant POLICE SA) system adhesive is 20% by weight.

5 Example 7 - a method for producing three-layer laminate with an adhesive whitening layer applied

The process is carried out analogously to Example 4, wherein the pigment concentration, i.e. titanium dioxide (Chemical Plant POLICE SA) system adhesive is 30% by weight.

Example 8 - process for preparing a three layer laminate applied to the bleaching adhesive layer

10 The process is carried out analogously to Example 4, wherein the pigment there is a white zinc (Chempur) and its concentration in the adhesive system is 20% by weight.

Example 9 - a process for preparing a three layer laminate applied to the bleaching adhesive layer

15 The process is carried out analogously to Example 4, wherein the pigment is a white lithopone (P. P. H. STANLAB Sp. J.), and its concentration in the system the adhesive is 20% by weight.

The results of the degree of whiteness laminates described in Examples 4 - 9 shows Table 4.

Table 4. Results of the degree of bleaching of laminates PET/PE with added polyurethane adhesive systems, containing white pigments

example no.	pigment type	pigment concentration in the adhesive system [% wt.]	laminate bleaching degree [%]*
1	titanium dioxide	10	48.9
2	titanium dioxide	15	59.7
3	titanium dioxide	20	68.8
4	titanium dioxide	30	78.8
5	white zinc	20	34.8
6	lithopone bleaching	20	25.2
*measured on opacitometer EEL 12M			

Example 10 - process for preparing a five-layer oxygen-absorbing bleached laminate

20 A slurry of ferrous hydroxide monohydrate $\text{FeO}(\text{OH}) \cdot \text{H}_2\text{O}$ (Roh Europe) and ascorbic acid (Chempur) is made in a weight ratio of 1:1 ethyl acetate (JarbuR). The suspension is vigorously stirred by a magnetic stirrer for 30 min. after which the resin is incorporated into Liofol UR 3720 (Henkel) and hardener Liofol UR 6055 (Henkel) and stirring continued for 15

mins. The concentration of both oxygen scavengers on the total the adhesive is 10% by weight. The system is coated on a biaxial roller shaft with a polypropylene film (BOPP) oriented on it, having a thickness of 40 microns, which is dried by 1 h at 75°C. The thickness of the applied layer is 4-10 microns.

5 One needs to prepare 19.6% by weight a suspension of titanium dioxide (Chemical Plant POLICE SA) in ethyl acetate. The system is stirred with a magnetic stirrer at room temperature for a time of 0.5 h, with a high degree of intensity. Into the solution resin of 10 Liofol UR 3720 (Henkel) and hardener Liofol UR 6055 (Henkel) are introduced. The mixture is stirred for about 15 min. The concentration of titanium dioxide in the obtained adhesive system is 10.0%. This
10 system is coated on the shaft with a PET film having a thickness of 12 microns, which is then treated is dried for 1 h at 75 °C. The thickness of the applied layer is 4-10 microns.

After drying, the laminate is formed into a PET film of the adhesive system with the addition of di titanium oxide is laminated BOPP film coated with the adhesive system of the oxygen absorbers, which is then laminated with a PE film having a thickness of 20 µm by the
15 Cast method and conditioned in programmed climatic chamber conditions at 23°C and 50% RH for 1 day.

This laminate can be used to form a package with the dimensions 9 x 13 cm for food by welding PE film under the following conditions: temperature welding 131°C, 0.41 kN clamping force, holding time of 0.5 s.

20 A laminate according to Example 10, as schematically shown in FIG. 3 comprises of the following layers:

- a PET film with a thickness of 12 microns,
- a polyurethane adhesive system with the addition of white pigments, the thickness of 4-10 microns,
- 25 - a BOPP film with a thickness of 40 microns,
- a polyurethane adhesive system with the addition of absorbing oxygen, the thickness of 4-10 microns,
- a PE foil with a thickness of 20 microns.

The results of the degree of whiteness for the laminate of Example is 10 shown in Table
30 5.

Table 5. Results of the degree of bleaching and atmosphere contents inside the packaging made laminates of PET/BOPP/PE with added polyurethane adhesive systems containing white pigments and oxygen absorbing agents - iron monohydrate hydroxide $\text{FeO}(\text{OH})\cdot\text{H}_2\text{O}$ and ascorbic acid

dimensions of package [cm]	degree of bleaching a laminate [%] *	amount of an oxygen absorbent [G]	composition of the atmosphere [vol.%]	20th day of measurement
9x13	82.9	0.054	O ₂	15.5
			CO ₂	2.2
			N ₂	82.3
* measured on opacitometer EEL 12M				

The laminates of the present invention show good oxygen absorption, allowing them to be used in the food industry. Additionally, through the use of white pigment, a white background is obtained, ideally suitable for further printing of other dyes. The method of the invention is simple, fast and can easily be adapted to other requirements of relevant parameters of the derived end products.

Claims

1. A method of making a layered laminate with oxygen-absorbing adhesive layer, **characterized in that** in the first stage, the oxygen-absorbing agent is introduced into a polyurethane adhesive system to form an adhesive system absorbing oxygen, which is then applied to the surface of the ribbon surface layer and dried, and in the second step to the adhesive, oxygen-absorbing layer, a layer of thermoplastic material is applied by extrusion coating.
2. A method of claim 1, **characterized in that** the oxygen-absorbing adhesive is applied to the ribbon surface layer by a corrugating roller coating method or a rotogravure method.
3. A method of claims 1 or 2, **characterized in that** the oxygen-absorbing agent is a mixture of iron hydroxide monohydrate $\text{FeO}(\text{OH}) \cdot \text{H}_2\text{O}$ and ascorbic acid in the weight ratio of 1: 2 to 2:1, preferably 1:1 or of iron oxide (III) Fe_2O_3 and ascorbic acid in the weight ratio of from 1: 2 to 2:1, preferably 1:1.
4. A method of claims 1 - 3, **characterized in that** carboxylic acid is introduced to the oxygen absorber, preferably mono- or dicarboxylic acid, most preferably acetic acid, tartaric acid, malonic acid and/or oxalic acid.
5. A method of claims 1 - 4, **characterized in that** the ratio of carboxylic acid monohydrate iron hydroxide $\text{FeO}(\text{OH}) \cdot \text{H}_2\text{O}$ oxide or iron (III) Fe_2O_3 is 1:1.
6. A method of claims 1 - 5, **characterized in that** the layer laminate with the oxygen-absorbing adhesive system is sealed under conditions of sealing temperature 113-132°C.
7. A method of claims 1 - 6, **characterized in that** a ribbon surface layer is used in the form of ribbon materials selected from a plastic film, more preferably poly(ethylene terephthalate), poly(vinyl chloride), polyethylene or polypropylene, film aluminum and combinations thereof.
8. A method of claims 1 - 7, **characterized in that** the coating layer of a thermoplastic adhesion-ability material is applied to the ribbon surface layer, preferably selected from the group consisting of polyethylene, including LDPE, LLDPE, and HDPE, polypropylene, copolymers of ethylene and acetate of vinyl, ethylene-acrylic acid copolymers, ethyl methacrylate and mixtures thereof.
9. A method of making a layered laminate with an adhesive whitening layer applied, **characterized in that** in the first step the white pigment is introduced into the polyurethane adhesive system, to give a whitening of the adhesive system, which is then applied to the surface of the ribbon surface layer and dried, and in the second stage the bleaching layer of the adhesive

system undergoes coating by extrusion with a coating layer of thermoplastic material.

10. The method of claim 9, **characterized in that** the white pigment is titanium dioxide, white zinc and/or white lithopone.

11. The method of claim 9 or 10, **characterized in that** the bleaching adhesive system is applied by corrugating roll coating or rotogravure on the ribbon surface layer.

12. A method of claims 9 - 11, **characterized in that** the concentration of white pigment in a polyurethane adhesive system is in the range of 10-20% by weight.

13. The method of claims 9 - 12, **characterized in that** the bearing of the layered laminate whitening system adhesive printing is conducted with the printing inks, preferably by rotogravure or flexographic printing.

14. The method of claims 9 - 13, **characterized in that** it uses a ribbon surface layer in the form of ribbon materials selected from plastic film, preferably poly(ethylene terephthalate), poly(vinyl chloride), polyethylene or polypropylene, aluminum film, and combinations thereof.

15. The method of claims 9 - 14, **characterized in that** the layer of coating thermoplastic material with the adhesion-ability of the ribbon surface layer, is preferably selected from the group consisting of polyethylene, including LDPE, LLDPE, and HDPE, polypropylene, ethylene and acetate vinyl copolymers, ethylene-acrylic acid copolymers, ethyl methacrylate and mixtures thereof.

16. A method of claims 9 - 15, **characterized in that** the layer laminate with the whitening system is sealed with the adhesive system at the conditions of seal temperature 113-132°C.

17. The method of claims 1 - 16, **characterized in that** in the first step the oxygen absorbent is introduced into the polyurethane adhesive system, with creating an adhesive system absorbing oxygen, which is then applied to the surface of the ribbon layer and the substrate is dried, and in the second step the adhesive layer of the oxygen absorbent is covered by extrusion coating with a ribbon surface layer bearing an adhesive bleaching system, and then in the third step it is further coated by extrusion coating with a coating layer of thermoplastic material, to give it a bleached layered laminate absorbing oxygen.

18. The method of claim 17, **characterized in that** the laminate layer is welded to the conditions: welding temperature 130-225°C.

19. A method of claims 17 or 18, **characterized in that** a layered laminate contains printing inks, preferably by a flexographic, graphic or rotogravure printing method.

20. An oxygen-absorbing overlay laminate, **characterized in that** it comprises of:
- a ribbon surface layer, with a weight of 5 to 300 g/m²;

- a layer of an oxygen getter adhesive system consisting of an oxygen absorbent, introduced into an polyurethane adhesive system; and

- a coating layer of a thermoplastic material having a thickness of from 5 to 200 μm , applied by extrusion coating on the ribbon surface layer of the previously applied layer of an oxygen-absorbing adhesive system.

21. A layered laminate of claim 20, **characterized in that** the oxygen-absorbing agent is a mixture of iron hydroxide monohydrate $\text{FeO}(\text{OH})\cdot\text{H}_2\text{O}$ and ascorbic acid weight ratio of from 1: 2 to 2:1, preferably 1:1 or of iron oxide (III) acid and Fe_2O_3 ascorbic acid in a weight ratio of from 1: 2 to 2:1, preferably 1:1.

22. A layered laminate of claims 20 or 21, **characterized in that** the oxygen absorbent consists of a carboxylic acid, preferably mono- or dicarboxylic acid, most preferably acetic acid, tartaric acid, malonic acid and/or oxalic acid.

23. A layered laminate of claims 20 - 22, **characterized in that** the ratio of the carboxylic acid and monohydrate of iron hydroxide $\text{FeO}(\text{OH})\cdot\text{H}_2\text{O}$ or iron oxide (III) Fe_2O_3 is 1:1.

24. A layered laminate of claims 20 - 23, **characterized in that** the ribbon surface layer material is selected from the ribbon of plastic film, preferably out of poly(ethylene terephthalate), poly (vinyl chloride), polyethylene or polypropylene, aluminum foil and combinations thereof.

25. A layered laminate of claims 20 - 24, **characterized in that** the coating layer of the thermoplastic material has the ability to adhere to the ribbon surface layer, preferably it is selected from a group consisting of polyethylene, including LDPE, LLDPE, and HDPE, polypropylene, ethylene acetate vinyl copolymers, ethylene and acrylic acid copolymers, ethyl methacrylate, acetate, and mixtures thereof.

26. The layered whitened laminate, **characterized in that** it comprises of:

- a ribbon surface layer, with a weight of 5 to 300 g/m^2 ;
- bleaching layer of the adhesive system, consisting of a white pigment introduced by a polyurethane adhesive system; and
- coating layer of a thermoplastic material having a thickness of from 5 to 200 μm , applied by the method of extrusion coating on the ribbon surface layer of the previously applied layer of the whitening adhesive system.

27. A layered bleached laminate of claim 26, **characterized in that** the white pigment is titanium dioxide, white zinc and/or white lithopone.

28. A layered bleached laminate of claims 26 or 27, **characterized in that** the

concentration of a white pigment in the polyurethane adhesive system is in the range of 10-20% by weight.

29. A layered bleached laminate of claims 26 - 28, **characterized in that** the layered bleached laminate is additionally printed with inks, preferably by a flexographic or rotogravure printing method.

30. A layered bleached laminate of claims 26 - 29, **characterized in that** the ribbon surface layer makes the material selected from the ribbon of plastic film, preferably poly(ethylene terephthalate), poly(vinyl chloride), polyethylene or polypropylene, film aluminum, and combinations thereof.

31. A layered bleached laminate of claims 26 - 30, **characterized in that** the coating layer of the thermoplastic material has the ability to adhere to the ribbon surface layer is preferably selected from the group consisting of polyethylene, including LDPE, LLDPE, and HDPE, polypropylene, ethylene and acetate vinyl copolymers, ethylene and acrylic acid copolymers, ethyl methacrylate and mixtures thereof.

32. A layered, oxygen absorbing bleached laminate, **characterized in that** it comprises

- a ribbon surface layer, with a weight of 5 to 300 g/m²;
- a layer of an oxygen-absorbing adhesive system consisting of an oxygen sorbent introduced into the polyurethane adhesive system;
- a layer of adhesive bleaching system consisting of a white pigment incorporated into a polyurethane adhesive system; and
- a coating layer of a thermoplastic material having a thickness of from 5 to 200 μm, applied by extrusion coating on the ribbon-surface layer of the previously applied layer of the bleaching adhesive system.

33. A layered, oxygen-absorbing bleached laminate of claim 32, **characterized in that** the oxygen absorbing agent is a mixture of monohydrate of iron hydroxide FeO(OH)·H₂O and ascorbic acid in a weight ratio of from 1: 2 to 2:1, preferably 1:1 or iron oxide (III) Fe₂O₃ and ascorbic acid in a weight ratio of from 1: 2 to 2:1, preferably 1:1.

34. A layered, oxygen-absorbing bleached laminate of claims 32 or 33, **characterized in that** the oxygen-absorbing agent further contains a carboxylic acid, preferably mono or dicarboxylic acid, most preferably acetic acid, tartaric acid, malonic acid and/or oxalic acid.

35. A layered, oxygen-absorbing bleached laminate of claims 32 - 34, **characterized in that** the ratio of carboxylic acid to monohydrate hydroxide of iron FeO(OH)·H₂O or iron oxide (III) Fe₂O₃ is 1:1.

36. A layered, oxygen-absorbing bleached laminate of claims 32 - 35, **characterized in**

that the ribbon surface layer makes the material selected from the ribbon material of plastic film, preferably a poly(ethylene terephthalate), poly(vinyl chloride), polyethylene, or polypropylene, aluminum foil, and combinations thereof.

37. A layered, oxygen-absorbing bleached laminate of claims 32 - 36, **characterized in**
5 **that** the surface layer of the thermoplastic material has the ability to adhere to the ribbon substrate layer and it is preferably selected from the group consisting of polyethylene, including LDPE, LLDPE and HDPE, polypropylene, ethylene and vinyl acetate copolymers, ethylene and acrylic acid copolymers, ethyl methacrylate and mixtures thereof.

38. A layered, oxygen-absorbing bleached laminate of claims 32 - 37, **characterized in**
10 **that** the white pigment is titanium dioxide, zinc white, and/or white lithopone.

39. A layered, oxygen-absorbing bleached laminate of claims 32 - 38, **characterized in**
that the concentration of white pigment in a polyurethane adhesive system is in the range of 10-20% by weight.

40. A layered absorbing oxygen bleached laminate of claim. 32 - 39, **characterized in**
15 **that** the bleached layered laminate is additionally printed with inks, preferably using flexographic or rotogravure printing.

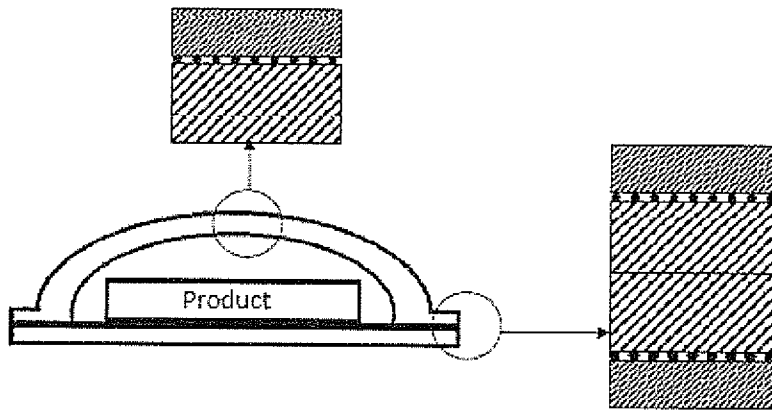
41. A layered, oxygen-absorbing bleached laminate of claims 32 - 40, **characterized in**
that the ribbon surface system layer makes the material selected from a foil of an artificial material, preferably poly(ethylene terephthalate), poly(vinyl chloride), polyethylene, or
20 polypropylene, aluminum foil, and combinations thereof.


42. A layered oxygen-absorbing bleached laminate of claims 32 - 40, **characterized in**
that the coating layer made of thermoplastic material has the ability to adhere to, it is preferably selected from the group consisting of polyethylene, including the LD 30 PE, LLDPE, and HDPE, polypropylene, ethylene and vinyl acetate copolymers, ethylene and acrylic acid copolymers,
25 ethyl methacrylate and mixtures thereof.


43. Package in particular for the food industry, **characterized in that** it consists of an oxygen-absorbing layer laminate as defined in the claims 20 - 25, a layered bleached laminate as defined in the claims 26 - 31, or a layered bleached oxygen-absorbing laminate as defined in the claims 32 - 42.

30 44. The use of an oxygen-absorbing layer laminate as defined in the claims 20 - 25, a bleached oxygen-absorbing layered laminate as defined in the claims 26 - 31, or a layered bleached oxygen-absorbing laminate as defined in the claims 32 - 42 for the preparation of packaging in the food industry.

Fig 1



 PET 12 μm

 PE 20 μm


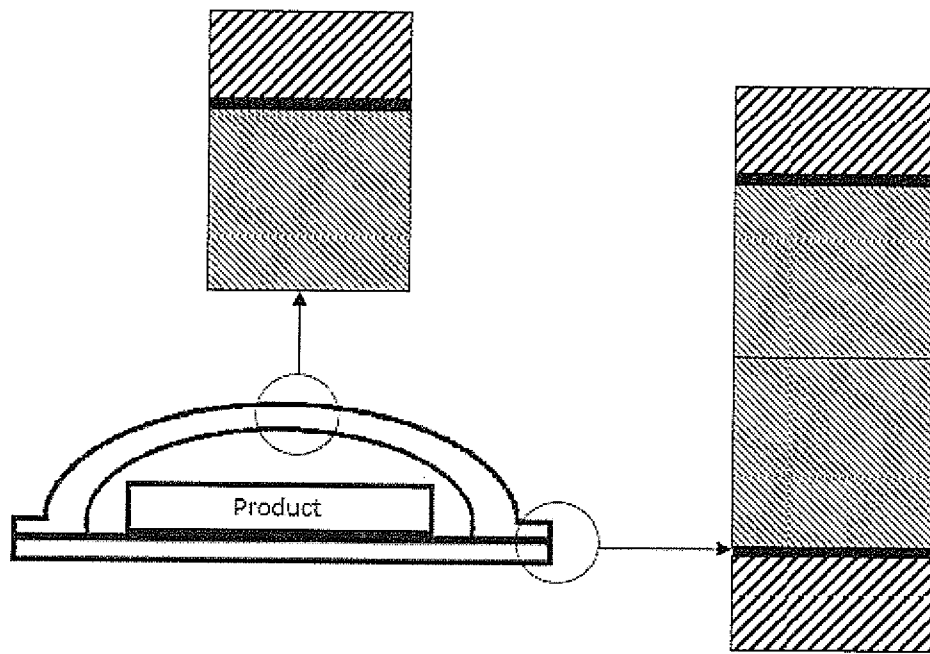
 adhesive system with oxygen absorbent

Fig. 2






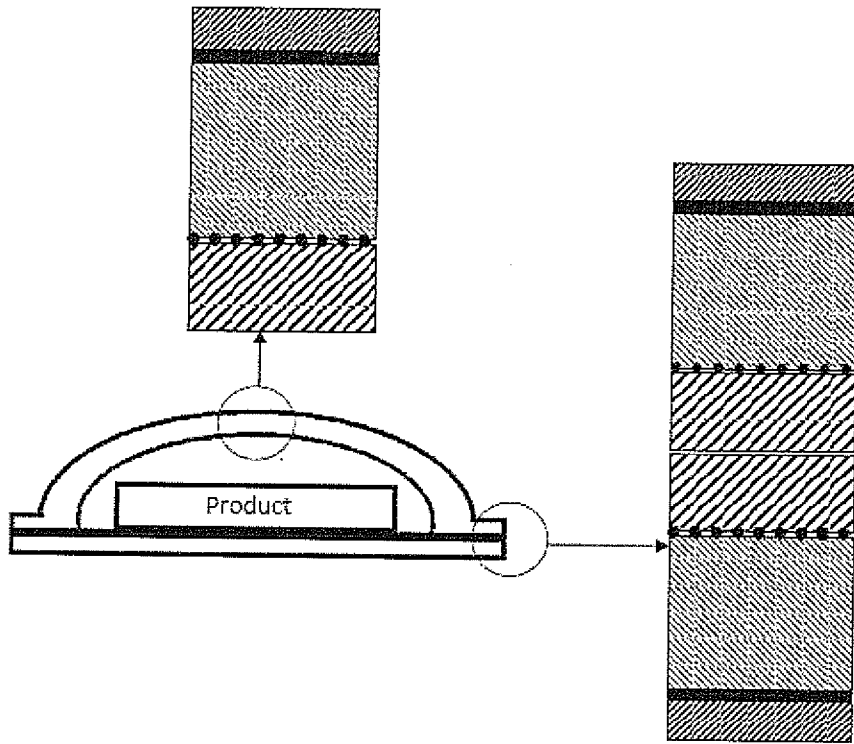





-  BOPP 40 μm
-  PE 20 μm
-  adhesive system containing a white pigment

Fig. 3



-  PET 12 μm
-  BOPP 40 μm
-  PE 20 μm
-  adhesive system with oxygen absorbent
-  adhesive system containing a white pigment

INTERNATIONAL SEARCH REPORT

International application No.

PCT/PL2017/050001

A. CLASSIFICATION OF SUBJECT MATTER B32B 27/18 (2006.01), B32B27/40 (2006.01), B32B33/00 (2006.01)		
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) B32B27, B32B33		
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) Epodoc, WPI, Databases of the Polish Patent Office		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2008308625 A (MITSUI MINING & SMELTING CO., JP), 2008-12-25 abstract, the whole document	1, 2, 6-8, 20, 24, 25, 43, 44
A		3-5, 21-23
Y	US 6391407 B1 (MITSUBISHI GAS CHEMICAL CO., JP), 2002-05-21 abstract, columns 2-6, claims, Fig. 1	32, 36-44
A		17-19, 33-35
Y	JP 2006224399 A (DAINIPPON PRINTING CO LTD, JP), 2006-08-31 abstract, the whole document	32, 36-44
A		17-19, 33-35
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> 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	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search 23 May 2017		Date of mailing of the international search report 25 May 2017
Name and mailing address of the ISA/ Visegrad Patent Institute/Branch office PL Al. Niepodległości 188, 00-950 Warsaw, Poland Facsimile No. +48225790001		Authorized officer Wioleta Świerczyńska Telephone No. +48 22 579 00 87

INTERNATIONAL SEARCH REPORT

International application No.

PCT/PL2017/050001

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.:
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:

- 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) The first invention: claims 1-8, 17-25, 32-42, 43-44 (in part)
- 2) The second invention: claims 9-16, 26-31, 43-44 (in part)

- 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 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.:

1-8, 17-25, 32-42, 43-44 (in part)

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.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/PL2017/050001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2008308625 A -----	2008-12-25 -----	None -----	
US 6391407 B1 -----	2002-05-21 -----	EP 0884173 A2 EP 0884173 A3 EP 0884173 B1 DE 69817262 T2 AU 7004498 A AU 728300 B2 -----	1998-12-16 1999-07-28 2003-08-20 2004-06-17 1998-12-17 2001-01-04 -----
JP 2006224399 A -----	2006-08-31 -----	None -----	