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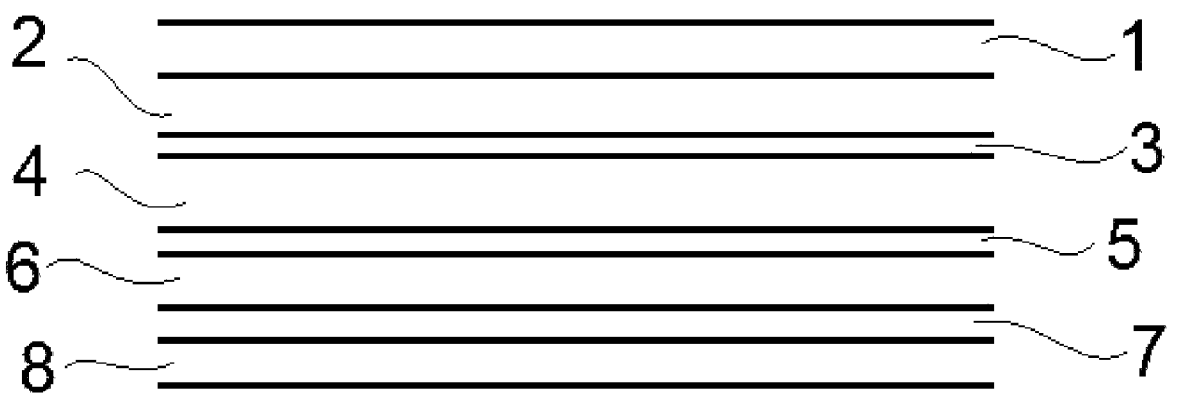
(54) Titre : MATERIAU COMPOSITE CONCU POUR PRODUIRE DES FLANS ET FLANS PRODUITS A PARTIR DE CE MATERIAU COMPOSITE

(54) Title: COMPOSITE MATERIAL FOR THE PRODUCTION OF SEALING FOILS AND SEALING FOILS MADE THEREFROM



(57) Abrégé/Abstract:
The invention relates to a composite material for producing plates for closing containers, comprising at least two plies, which in turn are, independently of each other, single-layer or multi-layer, wherein the one ply, the inner ply, which faces the container during sealing, has at least one closed weakening line, and wherein the outer ply can be peeled off the inner ply while the region delimited by the closed weakening line remains on the outer ply so that a hole is produced in the inner ply when the outer ply is peeled off. In order to reliably retain even regions of small area on the outer ply, the layer (6) that is in contact with the outer ply consists of semicrystalline ethylene-propylene copolymers, which are substantially free of dienes, and the layer of the outer ply that is in contact therewith is a lacquer (5).

Summary:

Composite material for the production of sealing foils and sealing foils made therefrom

The invention relates to a composite material for the production of sealing foils for container sealing consisting of at least two layers, which in turn, independently of one another, are single or multi-layered, wherein the inner layer, which faces the container during sealing has a self-contained weakening line, and the outer layer can be peeled off from the inner layer
and the area delimited by the closed weakening line remains on the outer layer, so that a hole is created in the inner layer when the outer layer is peeled off.

In order to reliably hold even small areas on the outer layer, it is provided that the layer (6), which is in contact with the outer layer, consists of semicrystalline ethylene-propylene copolymers which are essentially free of dienes and the outer layer that is in contact with it is a lacquer (5).

Composite material for the production of sealing foils and sealing foils made therefrom

The invention relates to a composite material for producing sealing foils (lids) for container sealing, according to the preamble of claim 1, sealing foils produced therefrom according to the preamble of claim 5 and EP 2 040 915 of the applicant.

This document exposes a composite material for the production of sealing foils, comprising of two layers, which in turn, independently of one another, can have one or more layers, whereby the inner layer, which faces the item or the container during sealing has a self-contained weakening line (in many cases also referred to as figure, area, part). This weakening line, preferably produced by a laser, ideally extends from the side facing the material, almost, but not all the way through the inner layer. Furthermore, the outer layer can be peeled off from the inner layer, whereby during peeling the area of the inner layer, which is delimited by the closed weakening line, remains on the outer layer, so that a hole is created in the inner layer when the outer layer is peeled off, through which the contents of the container are accessible. If several such weakening lines are provided, this applies mutatis mutandis to each figure, area, part.

Similar materials, respectively sealing foils (lids) are known from WO2008/006 123 A1 by the applicant and EP 2 327 635 A1 by the applicant. The PCT publication aims at the material itself and suggests the use of substances of different polarity in the border area of the layers to be separated. The European application is special in that the weakening line lies in the seal area, so that when the seal is opened, the seal is not broken, but rather the two layers separate in the area of the seal seam. This makes it possible to seal "hard" and still maintain the ability to reliably open.

The outer layer usually has an aluminum foil as a barrier layer, which is provided on its side facing the inner layer with a lacquer to protect the aluminum and optionally as an adhesion promoter. The inner layer of at least one polymer is then applied, preferably by coextrusion, which is so strongly or so weakly bonded to the lacquer that on the one hand peeling off is reliably possible, on the other hand the desired part of the inner layer when peeling off from the inner layer is loosened and adheres to the outer layer. The separation of the two layers during peeling thus takes place between the lacquer and the polymer layer

adjacent to the lacquer.

According to the cited document, this strength of adhesion is achieved by various combinations of polar and non-polar substances at the boundary of the layers, the contact surface, and has essentially proven itself. However, areas of application for such multilayer films have recently been opened up in which the self-contained weakening lines of the inner layer only enclose a very small area, so that there is a large length of weakening line per unit area of these areas, which in various cases leads the area to be actually removed to either stick to the lower layer or, what is even more undesirable, be peeled off along the weakening line, but due to the bending of the upper layer when peeling off, it does not stick to it, but falls into the container with the product. Since food is almost always in question, this is unpleasant and undesirable.

Basically, the problem is that both the quality of the weakening line, which is usually produced by a laser, despite all efforts has a certain range of fluctuation, and that the films used almost inevitably deviate from their global, average properties in small areas, and that the mentioned problems occur in the case of an unfavorable overlapping of these tolerances.

There is therefore a need for a connection between the two layers that reliably avoids these problems and, even in the case of very small-area parts of the inner layer to be removed, this reliably holds without making it difficult to peel off the outer (upper) layer. "Small areas" are circles with a diameter of less than 12 mm, more notably circles with a maximum diameter of 8 mm, most notably with a diameter of 4 mm and even less. For non-circular areas, the equivalent diameter (= diameter of a circle of the same area) is decisive.

It is the aim and object of the invention to provide a solution here.

According to the invention, this solution is achieved by a composite material which has the features specified in the characterizing part of claim 1 and by a sealing foil which has the features specified in the characterizing part of claim 4. In other words, at least the outermost layer of the inner layer is produced from a material as described in US 2004/0236042, or WO 2007/081491, or WO 2007/115816. Such materials are commercially available for example under the name Vistamaxx^{TM}, sold by Exxon Mobil

Chemical. The PP compositions known from EP 2 738 216 can also be used according to the invention.

These materials, as described in the literature, are semicrystalline ethylene-propylene copolymers that are substantially free of dienes. The intramolecular differences in tacticity are also statistically insignificant.

The contents of US 2004/0236042, WO 2007/081491, WO 2007/115816, EP 2 738 216 and US 2009/311475, corresponding to EP 2 040 915 mentioned at the beginning, are used, for the jurisdictions in which this is possible, as content of the present description, respectively application.

The innermost layer of the outer layer is the lacquer layer, which may serve as an adhesion promoter and / or protective layer (corrosion, mechanical damage) for the aluminum and which adheres firmly to the aluminum. This lacquer can be any of the lacquers used in the state of the art for such a purpose, for example

The material used according to the invention for the outermost layer of the inner layer has a density of $\leq$ 900 kg/m³, preferably of 879 ± 5 kg/m³, and, independently of one another, the following properties:

- The viscosity at 190 ° C is around 1200 mPas;

- The hardness (Shore C) is about 53;
- The tensile strength at break is about 6.2 MPa;
- The tensile strength at 100% at about 4 MPa;
- The elongation at break at about 1250%;
- The glass transition temperature at -22 ° C ± 3°C and
- The melting temperature at 97°C ± 3°C.

The upper limit of the density, according to previous tests, must be of exactly 900 kg/m³, the "approximate" values in this list mean a range of ± 5%; the ranges for densities and temperatures is given there.

A sealing foil according to the invention has, for example, from the outside (top) to the

inside (bottom), in the **single figure** the following structure, presented purely schematically, whereby the nomenclature "layers-folds" given at the beginning cannot be adhered to here because of the designation as "layer(s)" which is common in the state of the art:

1. Print protection layer 1 (facing the surroundings)
2. Print layer 2 (possibly including print base layer)
3. Adhesion promoter 3
4. Barrier layer 4, mostly aluminum foil
5. Lacquer 5 (adhesion promoter and / or protective layer for the aluminum)
6. layer 6 containing a material according to the invention
7. Inner sealing layer made of PP 7
8. Outer sealing layer 8 (facing the goods, sealed onto the container)

Further layers can be provided; layers 4, 6 and 8 are to be regarded as essential layers (again thusly called here in accordance with the nomenclature).

The material 6 used according to the invention is coextruded with PP in a proportion of 15-65% by weight, preferably 20-60% by weight. If an inner sealing layer 7 (the term "inner" refers here to the layer within the composite material) made of PP is present, the same PP is advantageously also used for the layer 6. The greater the proportion of the material used according to the invention, the thinner the layer 6 can be made, which is beneficial for processability, so that, despite the higher proportion in costs, no more of the more expensive material has to be used. With higher proportions, the toughness increases and thus the tear behavior is better, even if the layer thickness is minimized.

The PP 7 can be a PP homopolymer, to which about 30 wt.% LDPE or, alternatively, about 20 wt.% PP-HMS, or, again, alternatively, 10-30 wt. -% PP random polymer is added. These percentages relate to the sum of the PP homopolymer and the additive (still without the material according to the invention). This, simply referred to as "PP" for layer 6, is then mixed with the material used according to the invention.

Some of these layers can be omitted or replaced by others, essential is layer 6, which has direct contact with the outer layer (barrier 4 or lacquer 5), and that layer 7 contacting this

layer 6, if present, is made of PP.

The material of the barrier layer 4 can, in addition to the currently most popular aluminum, in the form of a film from the group of polyesters, such as polyethylene terephthalate (PET), the polyester film with an additional surface treatment in the form of a metallization or another inorganic layer, for example made of SiOx or AlOx or an adhesion-promoting layer (primer) can be provided for applying a sealing layer; of polyamides, such as PA 6 or PA 12, or other materials from this group; of polyolefins, such as polyethylene (PE), ethylene copolymers (EVA, EMA, etc.) or mixtures of these, of polypropylene (PP), PP copolymers or other thermoplastic polyolefins; of biopolymers based on renewable raw materials, such as from starch polymers, from polylactic acid (PLA), from lignin-based polymers, from polyhydroxyalkanoates (PHAs), from corresponding mixtures or compounds, from biodegradable / compostable raw materials such as special bio-polyesters; or combinations thereof; and the lamination adhesive is selected from wet lamination adhesives, dispersion adhesives, dry lamination adhesives, solvent-free adhesive systems, cold seal adhesives or extrusion-coated lamination.

As per the state of the art, the thickness of the layers 6 and 7 is important for the mechanical properties, whereby the use of the material used according to the invention under otherwise identical conditions improves the mechanical properties, so that a reduction over the two layers together is possible without impairment of the properties.

Regarding lacquer 5, which is almost without exception necessary as a barrier layer 4 for aluminum, provided that the surface of the aluminum is not prepared in a complex manner, but can be omitted for many of the other barrier layers mentioned, it should only be briefly stated that a solvent lacquer with an acrylate binder is appropriate, as by adding different amounts of mineral filler, in particular talc, the bond strength achieved can easily be brought to a narrow range, the bond strength decreasing while the filler content increases.

The acrylic varnish that can be appropriately used can be a commercially available "combination heat-sealing lacquer", which means combination lacquer systems which - when used in the state of the art for sealing foils, for example for yoghurt cups, seal against both polystyrene and PP cups so that they can be peeled off (e.g. ACTEseal® from ACTEGA, also available in a water-based version, or ODASeal from Hans Jung GmbH &

Co.KG).

In the state of the art there are also other so-called combination lacquer systems that can be used, which contain, for example, styrene-butadiene copolymers or polyester resins. The lacquer of DE 10 2011 086 327 A, likewise with filler to regulate the adhesion, should also be mentioned in this context. Furthermore, those that contain binders based on vinyl chloride polymers should also be mentioned (e.g. those under the brand VINNOL® available from Wacker Polymers); However, due to the frequent customer requests for PVC-free materials, these are not always employable, even if they could be used technically.

It thus comprises the outer layer of layers 1-5, the inner layer of layers 6-8; peeling occurs thusly between layers 5 and 6. The formation of the weakening lines, which for reasons of strength is only carried out after the merging of layers 1-8, mostly by means of a laser, should cover layers 7-8, but not layer 6. Even if this is mostly achieved, there is also a thermal influence on layer 6, which, when using the material according to the invention, however, unlike in the state of the art, does not lead to a noticeable reduction or even at least a change in the adhesion between layers 5 and 6.

While strongly fluctuating bond strengths of only 0.25 to 0.5 N/100 mm (measured in accordance with DIN 55543-5 to determine bond strength) and often slightly below that, are achieved in the state of the art, the films according to the invention can reliably achieve values of at least 0.8 N/100 mm and without great effort of 1.0 N/100 mm and, if desired, even more. These values ensure both reliable adhesion of the separated areas, even if these are very small, to the outer layer and also peeling off without the risk of tearing in or tearing off.

The invention is not confined to the exemplary embodiments described, but can be modified in various ways. Since it relates to peeling, in particular the layers that are not involved can be changed without problems and adapted to the respective use case, which is easily achievable for the packaging films field specialist with knowledge of the invention. This also applies to aluminum foil, because even if aluminum is an excellent barrier material, there has been for a number of years a strong tendency to manage without the use of aluminum. Any other material can then be used as the barrier layer, provided that it can

either be provided with the lacquer 5, such as aluminum, or inherently has properties such as the lacquer in relation to the adhesion of the layer 6 according to the invention.

In the description and the claims, the terms “front”, “rear”, “top”, “bottom” and so on are used in their usual form and with reference to the object in its usual position of use. This means that the muzzle of the barrel of a weapon is "in front", that the bolt or slide is moved "backwards" by the explosion gases, etc. In the case of vehicles, the usual direction of movement is “in front”. In the case of packaging, the container is “below” and the sealing foil is “above”; the underside of the sealing foil faces the good, the outside towards the surroundings.

It should also be pointed out that for terms in the description and the claims like e.g. such as "lower part" of a suspension, reactor, filter, structure, or a device or an object in general, is intended as the lower half - and particularly the lower quarter - of the total height, "lowest area" as the lowest quarter (particularly any fraction smaller than this); while "middle area" as the middle third of the total height (width – length). All this information has its common meaning, applied to the intended position of the object under consideration.

In the description and claims, "essentially", unless otherwise stated on the spot, means a deviation of up to 10% of the specified value, if this is physically possible, both downwards and upwards, or otherwise only in the sensible direction; for degrees (angles and temperature), this means ± 10°.

All quantities and proportions, particularly those delimiting the invention, unless they relate to the specific examples, are to be understood with a tolerance of ±10%, for example: 11% means: from 9.9% to 12.1%. For terms such as “a solvent”, the word “a” not to be seen as a numerical word, but as an indefinite article or as a pronoun, unless the context indicates otherwise.

The term: “combination” or “combinations”, unless otherwise stated, describes all types of combinations, starting from two of the constituents in question up to a large number or all

of such constituents; the term "containing" also means "consisting of".

The features and variants specified in the individual configurations and examples can, unless otherwise stated, be freely combined with those of the other examples and configurations, and can particularly be used to characterize the invention in the claims without necessarily including the other details of the respective configuration or the respective example.

Reference symbols list:

1	Pressure protection lacquer	5	Lacquer
2	Pressure layer	6	Material according to the
3	Adhesion promoter	7	Inner sealing layer made of
4	Barrier layer	8	Outer sealing layer

Patent claims:

1. Composite material for the production of sealing foils for container sealing, comprising of at least two layers, which in turn, independently of one another, are single or multi-layer, wherein the inner layer, which faces the container during sealing has a self-contained weakening line, and the outer layer can be peeled off from the inner layer, with the area of the inner layer delimited by the closed weakening line remaining on the outer layer, which preferably has a barrier layer (4), during peeling, so that when peeling off the outer layer a hole is created in the inner layer, characterized in that the layer (6), which is in contact with the outer layer, consists of semicrystalline ethylene-propylene copolymers which are essentially free of dienes and the outer layer which is connected to this layer (6), is the barrier layer (4) or a lacquer (5).
2. Composite material according to Claim 1, characterized in that the ethylene-propylene copolymer of the layer (6) has a density of less than 900 kg / m^3, preferably of 879 kg / m^3.
3. Composite material according to Claim 1 or 2, characterized in that the ethylene-propylene copolymer of the layer (6) has at least one of the following properties:
   - The viscosity at 190 ° C is around 1200 mPa ± 5%;
   - The hardness (Shore C) is around 53 ± 5%;
   - The tensile strength at break is about 6.2 MPa ± 5%;
   - The tensile strength at 100% is around 4 MPa ± 5%;
   - The elongation at break is around 1250% ± 5%;
   - The glass transition temperature is -22°C ± 3°C and
   - The melting temperature is 97°C ± 3°C.
4. Composite material according to one of Claims 1 to 3, characterized in that the barrier layer (4) is made of aluminum and that a lacquer (5) is provided.
5. Composite material according to one of Claims 1 to 4, characterized in that the lacquer (5) is a solvent lacquer with an acrylate binder and preferably with a mineral filler, in particular talc.
6. Composite material according to one of Claims 1 to 4, characterized in that the lacquer (5) is a so-called combination lacquer system, preferably containing styrene-butadiene copolymers or polyester resins and containing mineral filler, in particular talc.
7. Sealing foil for container sealing, consisting of a composite material, comprising of

at least two layers, which in turn, independently of one another, are single or multi-layer, wherein the inner layer, which faces the container during sealing has a self-contained weakening line, and the outer layer can be peeled off from the inner layer, with the area of the inner layer delimited by the closed weakening line remaining on the outer layer during peeling, so that a hole is created in the inner layer when the outer layer is peeled off, characterized in that the layer (6) of the inner layer, which is in contact with the outer layer, comprises semicrystalline ethylene-propylene copolymers which are essentially free of dienes, and the outer layer which is connected to this layer (6), is the barrier layer (4) or a lacquer (5).

8. Sealing foil according to Claim 7, characterized in that the ethylene-propylene copolymer has a density of less than 900 kg / m^3, preferably 879 kg / m^3.

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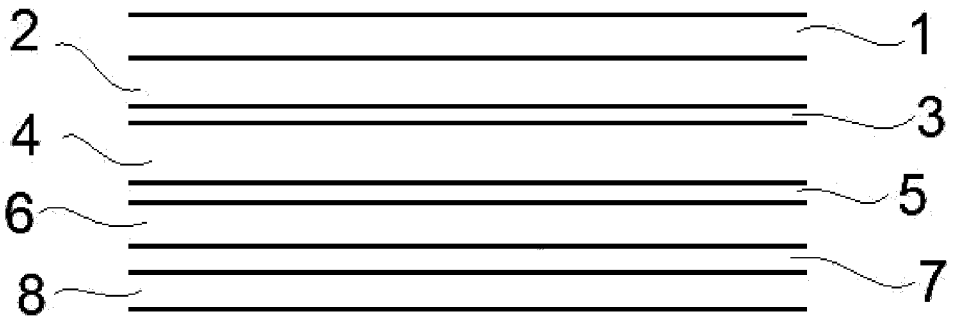

Fig.

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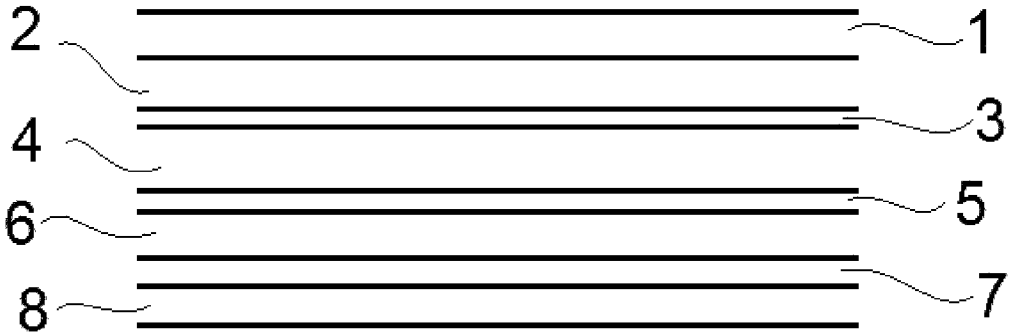
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