

Acrylic foils with improved UV-protection properties

- 5 The present invention relates to a multi-layer PMMA-based foil comprising at least two distinct layers each of the layers comprising at least one UV-absorber. Typically, the foil of the present invention is a co-extruded foil. The foil has a particularly high UV-resistance, a high weathering resistance and excellent mechanical properties. Therefore, the foil of the present invention is highly suitable for outdoor applications such as surface-protection of materials such as polyvinyl chloride (PVC) and for use in high-pressure laminates (HPLs).

HPLs are typically produced by laminating melamine- and phenol-resin-impregnated papers to one another under high pressure of at least 3 MPa (spec.), at temperatures above 120 °C with a cycle time that is generally from 30 to 100 min. The resultant composite material is equipped with a decorative outer layer to realize visual effects such as wood imitations or single-colour decorative effects. These decorative high-pressure laminates are used in various applications including but not limited to table tops, doors, furniture, kitchen worktops, and also sheets for cladding of walls, of balconies or of facades. Indoor applications normally require no particular protection from UV radiation, but a melamine resin surface must be equipped with an additional protective layer for outdoor use, where unprotected melamine resin surfaces would exhibit a significant degradation even after a relatively short time.

Prior art

- 25 Polymethyl methacrylate (PMMA) has an excellent weathering resistance and is therefore particularly suitable for any of the applications in outdoor areas subject to weathering. For this reason, PMMA-based foils have become established in the market for use as surface-protection foils for coloured polyvinyl chloride (PVC) window profiles. There is a rising demand for surface-protection foils which markedly exceed the existing requirements for weathering resistance of the surface-protection foils. The foils obtainable on the market typically use benzotriazole type UV absorbers for stabilization with respect to UV radiation (wavelengths from 300 to 400 nm). These UV absorbers are known to lose their activity to a significant extent over a period of about 15 years. The weathering-protection foils modified therewith first become matt, and then microcracks form, followed by cracks. However, these UV absorbers also have advantageous properties: they are colour-neutral (no yellowness index), non-volatile (important for extrusion of the foils) and inexpensive.

WO 2007/0074138 A1 describes a PMMA-based foil which, in terms of weathering resistance, is superior to the foils available hitherto on the market and provides an improved weathering stability

over more than 10 years. The foil typically uses a combination of a benzotriazole type UV absorber, a triazine type UV absorber and a sterically hindered amine (HALS, hindered amine light stabilizer). These components are employed as a mixture during manufacturing of said foil.

- 5 US 2008/0311406 A1 teaches a three-layer film composed of: an external PVDF layer, an intermediate layer composed of a PVDF-PMMA blend which comprises a UV absorber e.g. Tinuvin® 234, and an adhesion-promoter layer which comprises *inter alia* an anhydride of methacrylic acid. A particular advantage of the film is that it exhibits no white discoloration when tested in water for 2 h at 100 °C, and moreover exhibits good adhesion to melamine-resin-
10 impregnated papers. However, the film has only a moderate long-term weathering resistance.

- WO 2015/180995 A1 discloses a UV-protective film suitable for lamination on high-pressure laminates (HPLs). The film has, from the outside to the inside, the following layers bonded to one another: a layer A comprising a fluoropolymer, a PMMA layer B comprising at least one UV
15 stabilizer and/or UV absorber, and a layer C comprising at least one adhesion promoter and at least one poly(meth)acrylate, where the layer C can be laminated with a resin-impregnated paper to give an HPL and the layers B and/or C comprise at least one impact modifier. This film has an excellent long-term weathering resistance, exhibits no delamination, no blue sheen, and has advantageous optical properties, in particular a low haze value.

- 20 In recent years HPLs found an increasing use in architectural applications in countries having a relatively warm and humid climate and higher average sunshine duration. Additionally, due to ongoing global warming and destruction of the ozone layer HPLs used for such applications are exposed to higher temperatures and increasingly stronger solar UV-radiation. This poses even
25 more stringent requirements on PMMA-based foils for use in these countries.

- For instance, unplasticized poly(vinyl chloride) (PVC-U) window profiles and doors with laminated decorative foils need to comply with the norm RAL-GZ 716 (Climate M, total radiant exposure of 30 GJ/m²). Manufacturers of PVC windows profiles and doors with laminated decorative foils
30 continuously develop products with an increasingly high long-term weathering resistance. Hence, decorative PVC foils with protective acrylic films for such applications are expected to resist to weathering over a period of about 30 years in Central Europe.

Object

- 35 There is an ongoing demand for PMMA-based foils which, in terms of weathering resistance, are superior to the foils hitherto available on the market, and, in particular, provide an improved outdoor stability over a prolonged period (over 15 years), even in areas having a warm and humid climate and higher average sunshine duration. Such foils should provide an improved intrinsic stability of

the foil with respect to UV effects and weathering effects and improved stability of its UV-protective action (discernible from the stability of the colour locus of a colour layer covered with the protective foil). Furthermore, it is desired, that the foil is substantially colour-neutral, has good mechanical properties and is substantially free from stress-whitening.

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The term "*stability*" as used herein refers not only to the intrinsic stability of the foil with respect to weathering effects and mechanical damages but also to sustainability of its protective action.

Summary of the invention

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The present invention is based on a surprising finding that the long-term weathering stability of the foil described in WO 2007/0074138 A1 can be even further improved, if the UV-absorbers employed in WO 2007/0074138 A1 are placed in at least two separate layers. In particular, it showed to be advantageous, that the layer exposed to the outdoor solar radiation comprises at least one triazine type UV-absorber, whereas the layer beneath comprises at least one benzotriazole type UV absorber. Despite in the foil of the present invention the UV absorbers of WO 2007/0074138 A1 are located in separate layers, the synergistic effect resulting from their presence is even enhanced. Additionally, the inventors found that triazine type UV-absorbers can be replaced by inorganic UV absorbers such as titanium dioxide, tin dioxide or glass in form of glass beads or glass powder without affecting the long-term stability of the resulting foil.

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Hence, the foil of the present invention successfully solves the technical problems defined above.

Additionally, the foil of the present invention provides the following advantages:

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- It can be employed for lamination of various substrates at varying temperatures and upon using different lamination equipment. The appearance of the resulting laminated product is highly uniform and substantially independent on the processing conditions such as lamination temperature or material of the lamination rolls.
- It has an excellent weathering resistance and a very good chemicals resistance, for example with respect to commercially available cleaning compositions.
- It retains an appealing uniform appearance over a prolonged period.
- It can be manufactured in an extrusion plant in a cost-effective manner.

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As will be readily appreciated by a skilled person, the term "*foil*" as used herein, refers to a sheet having a thickness below 5 mm, more preferably, below 1 mm. Although the foil of the present invention can be advantageously used as a protective coating, the term "*foil*" as used in the present application should be generally distinguished from the term "*coating*". A coating is typically a top layer of a multi-layer substrate and cannot be handled separately from said substrate. In contrast to

a coating, the foil of the present invention is not necessarily a layer of a multi-layer article *i.e.* is not necessarily attached to any substrate and can therefore be separately handled and used for a variety of different purposes.

- 5 In its first aspect, the present invention is directed to a multi-layer foil comprising at least a layer A and a layer B, wherein the layer A comprises, based on the total weight of the layer A:

- from 0.0 to 99.9 wt.-% of a polymethyl(meth)acrylate;
- from 0.0 to 95.0 wt.-% of one or several impact modifiers;
- from 0.0 to 30.0 wt.-% of a fluoropolymer;
- 10 from 0.1 to 5.0 wt.-% of a first UV-absorber;
- from 0.0 to 5.0 wt.-% of one or several UV-stabilizers;

- wherein the cumulative content of the polymethyl(meth)acrylate and of one or several impact modifiers in the layer A is at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least
- 15 70 wt.-%, yet even more preferably at least 80 wt.-%, still more preferably at least 90 wt.-%, particularly preferably at least 95 wt.-% and not more than 99.9 wt.-%, based on the weight of the layer A; and wherein the spectral transmittance of the layer A at any wavelength λ_A is not more than 10%; wherein $270 \text{ nm} \leq \lambda_A \leq 360 \text{ nm}$; and

- 20 the layer B comprises, based on the total weight of the layer B:

- from 0.0 to 99.9 wt.-% of a polymethyl(meth)acrylate;
- from 0.0 to 85.0 wt.-% of one or several impact modifiers;
- from 0.1 to 5.0 wt.-% of a second UV-absorber, which is distinct from the first UV-absorber;
- 25 from 0.0 to 5.0 wt.-% of one or several UV-stabilizers; and
- from 0.0 to 20.0 wt.-% of an adhesion-promoting copolymer comprising
 - (i) from 70.0 to 95.0 wt.-% methyl methacrylate;
 - (ii) from 0.5 to 15.0 wt.-% maleic anhydride; and
 - (iii) from 0.0 to 25.0 wt.-% of other vinyl-copolymerizable monomers having no
- 30 functional groups other than the vinyl function, based on the weight of the adhesion-promoting copolymer; and

- wherein the cumulative content of the polymethyl(meth)acrylate and of one or several impact modifiers in the layer B is at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least
- 35 70 wt.-%, yet even more preferably at least 80 wt.-%, still more preferably at least 90 wt.-%, particularly preferably at least 95 wt.-% and not more than 99.9 wt.-%, based on the weight of the layer B, and wherein the spectral transmittance of the layer B at any wavelength λ_B is not more than 10%; wherein $270 \text{ nm} \leq \lambda_B \leq 370 \text{ nm}$.

Furthermore, the layer A comprises not more than 0.1 wt.-%, preferably not more than 0.05 wt.-% of the second UV absorber and the layer B comprises not more than 0.1 wt.-%, preferably not more than 0.05 wt.-% of the first UV absorber.

5 According to the present invention, the first UV absorber is distinct from the second UV absorber.

According to the present invention, the foil is applied on a substrate in such a way, that the layer A is directed towards the environment and the layer B is directed towards the surface of the substrate.

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In this embodiment, the first UV-absorber is typically an organic UV-absorber such as a triazine type UV-absorber. In a particularly preferred embodiment, the layer A comprises a triazine type compound as a first UV absorber and the layer B comprises a benzotriazole type compound as a second UV absorber.

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The spectral transmittance of the layers A and B can be measured using an extruded monolayer foil of a given thickness with a suitable instrument such as Cary 5000 spectrophotometer, available from former Varian Inc. (Palo Alto, California, United States). For this purpose, the thickness of the monolayer foil used for the measurement corresponds to the thickness of the corresponding layer of the multilayer foil of the present invention. Alternatively, in particular if thickness of said layer is lower than 10 μm , the spectral transmittance of said layer can be determined by applying a monolayer coating onto a quartz glass (fused silica) plate and measuring the spectral transmittance of the coating. The way of applying said coating is not particularly limited and includes e.g. extrusion onto the quartz glass plate, lamination, application of a solution of the material of said layer, followed by evaporation of the solvent etc. For instance, the monolayer can be advantageously applied using spin coating of a solution/dispersion of the material of said layer in acetone.

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Alternatively, for the sake of determining the spectral transmittance, the layer in question can be co-extruded with a polymeric thermoplastic material having a particularly low spectral transmittance at the wavelengths of interest. For instance, the layer in question can be co-extruded with a 40 μm thick layer of Plexiglas® 7H, available from Röhm GmbH (Darmstadt, Germany).

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The spectral transmittance of the layers A and B is measured as a function of wavelength according to ISO 13468-2:1999. In addition, the instrument must have an extended wavelength range, such that it is capable of measuring in the UV spectral region. The measurement is carried out at a temperature of 23 ± 2 °C and relative humidity of 50 ± 5 %.

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In yet a further aspect, the present invention is directed to a multi-layer foil comprising at least a layer A and a layer B, wherein the layer A comprises, based on the total weight of the layer A:

- from 0.0 to 99.0 wt.-% of a polymethyl(meth)acrylate;
- 5 from 0.0 to 95.0 wt.-% of one or several impact modifiers;
- from 0.0 to 30.0 wt.-% of a fluoropolymer;
- from 1.0 to 30.0 wt.-% of a first UV-absorber, wherein the first UV-absorber is an inorganic particulate material, which is preferably selected from zinc oxide, titanium dioxide, cerium dioxide, tin dioxide, silica and glass;
- 10 from 0.0 to 5.0 wt.-% of one or several UV-stabilizers;

wherein the cumulative content of the polymethyl(meth)acrylate and of one or several impact modifiers in the layer A is at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least 70 wt.-%, yet even more preferably at least 80 wt.-%, still more preferably at least 90 wt.-%, particularly preferably at least 95 wt.-% and not more than 97.0 wt.-%, based on the weight of the layer A and wherein the spectral transmittance of the layer A at any wavelength λ_A is not more than 20%; wherein $270 \text{ nm} \leq \lambda_A \leq 310 \text{ nm}$; and

the layer B comprises, based on the total weight of the layer B:

- 20 from 0.0 to 99.9 wt.-% of a polymethyl(meth)acrylate;
- from 0.0 to 85.0 wt.-% of one or several impact modifiers;
- from 0.1 to 5.0 wt.-% of a second UV-absorber, which is distinct from the first UV-absorber;
- from 0.0 to 5.0 wt.-% of one or several UV-stabilizers; and
- 25 from 0.0 to 20.0 wt.-% of an adhesion-promoting copolymer comprising
 - (i) from 70.0 to 95.0 wt.-% methyl methacrylate;
 - (ii) from 0.5 to 15.0 wt.-% maleic anhydride; and
 - (iii) from 0.0 to 25.0 wt.-% of other vinyl-copolymerizable monomers having no functional groups other than the vinyl function, based on the weight of the
- 30 adhesion-promoting copolymer; and

wherein the cumulative content of the polymethyl(meth)acrylate and of one or several impact modifiers in the layer B is at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least 70 wt.-%, yet even more preferably at least 80 wt.-%, still more preferably at least 90 wt.-%, particularly preferably at least 95 wt.-% and not more than 99.9 wt.-%, based on the weight of the layer B, and wherein the spectral transmittance of the layer B at any wavelength λ_B is not more than 10%; wherein $270 \text{ nm} \leq \lambda_B \leq 370 \text{ nm}$.

Still, in a further aspect of the present invention the multi-layer foil comprises at least a layer A and a layer B, wherein the layer A comprises, based on the total weight of the layer A:

- 5 from 0.0 to 97.0 wt.-% of a polymethyl(meth)acrylate;
- from 0.0 to 95.0 wt.-% of one or several impact modifiers;
- from 0.0 to 30.0 wt.-% of a fluoropolymer;
- from 3.0 to 30.0 wt.-% of a first UV-absorber, wherein the first UV-absorber is an inorganic particulate material, which is preferably selected from zinc oxide, titanium dioxide, cerium dioxide, tin dioxide, silica and glass; and
- 10 from 0.0 to 5.0 wt.-% of one or several UV-stabilizers;

- wherein the cumulative content of the polymethyl(meth)acrylate and of one or several impact modifiers in the layer A is at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least 70 wt.-%, yet even more preferably at least 80 wt.-%, still more preferably at least 90 wt.-%,
- 15 particularly preferably at least 95 wt.-% and not more than 97.0 wt.-%, based on the weight of the layer A; and wherein
- the spectral transmittance of the layer A at any wavelength λ_A is not more than 10%; wherein
- $270 \text{ nm} \leq \lambda_A \leq 310 \text{ nm}$; and

- 20 the layer B comprises, based on the total weight of the layer B:

- from 0.0 to 99.9 wt.-% of a polymethyl(meth)acrylate;
- from 0.0 to 85.0 wt.-% of one or several impact modifiers;
- from 0.1 to 5.0 wt.-% of a second UV-absorber, which is distinct from the first UV-absorber;
- 25 from 0.0 to 5.0 wt.-% of one or several UV-stabilizers; and
- from 0.0 to 20.0 wt.-% of an adhesion-promoting copolymer comprising
 - (i) from 70.0 to 95.0 wt.-% methyl methacrylate;
 - (ii) from 0.5 to 15.0 wt.-% maleic anhydride; and
 - (iii) from 0.0 to 25.0 wt.-% of other vinyl-copolymerizable monomers having no
- 30 functional groups other than the vinyl function, based on the weight of the adhesion-promoting copolymer; and

- wherein the cumulative content of the polymethyl(meth)acrylate and of one or several impact modifiers in the layer B is at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least 70 wt.-%, yet even more preferably at least 80 wt.-%, still more preferably at least 90 wt.-%,
- 35 particularly preferably at least 95 wt.-% and not more than 99.9 wt.-%, based on the weight of the layer B, and wherein
- the spectral transmittance of the layer B at any wavelength λ_B is not more than 10%; wherein
- $270 \text{ nm} \leq \lambda_B \leq 370 \text{ nm}$; and

the layer A comprises not more than 0.1 wt.-%, preferably not more than 0.05 wt.-% of the second UV absorber and

the layer B comprises not more than 0.1 wt.-%, preferably not more than 0.05 wt.-% of the first UV absorber.

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Again, the layer A comprises not more than 0.1 wt.-%, preferably not more than 0.05 wt.-% of the second UV absorber and the layer B comprises not more than 0.1 wt.-%, preferably not more than 0.05 wt.-% of the first UV absorber.

10 In this embodiment, it is preferred that the inorganic particulate material acting as the first UV-absorber is substantially uniformly dispersed in the material of the layer A. The term "*uniform*" as used herein means that the concentration of the particulate material within the foil is substantially constant.

15 A further aspect of the present invention relates to a coated article comprising the foil of the present invention on its surface. Said coated article comprises a substrate which is at least partially covered by the foil, so that the layers of the foil are arranged in the following order:

20 the layer D, if present, forms an outer surface of the coated article;
the layer A is located between the layer D and the substrate;
the layer E, if present, is located between the layer A and the layer B
the layer B is located between the layer A and the substrate; and
the layer C, if present, is located between the layer B and the substrate.

25 Finally, a further aspect of the present invention relates to use of a foil as defined above for coating of a substrate, preferably by a process selected from co-extrusion, lamination or extrusion lamination.

Brief description of the drawings

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Figure 1 is a schematic illustration of lamination process in Production Examples 7-16

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1. Steel plate
 2. Rubber plate
 3. Separation paper
 4. Monolayer foil 1
 5. Monolayer foil 2

Detailed description of preferred embodiments

The multilayer foil of the present invention comprises at least the layers A and B. Preferably, the foil of the present invention is a co-extruded foil.

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According to the present invention, the layer B has the following composition:

- from 0.0 to 99.9 wt.-% of a polymethyl(meth)acrylate;
- from 0.0 to 85.0 wt.-% of one or several impact modifiers;
- 10 from 0.1 to 5.0 wt.-% of a second UV-absorber, which is distinct from the first UV-absorber of the layer A;
- from 0.0 to 5.0 wt.-% of one or several UV-stabilizers; and
- from 0.0 to 20.0 wt.-% of an adhesion-promoting copolymer;
- 15 wherein the layer B comprises not more than 0.1 wt.-%, preferably not more than 0.05 wt.-% of the first UV absorber.

Adhesion-promoting copolymers are known in the prior art and are commonly employed in acrylic foils in order to improve their adhesion to a substrate. The adhesion-promoting copolymer in the layer B, if present, comprises:

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- (i) from 70.0 to 95.0 wt.-% methyl methacrylate;
- (ii) from 0.5 to 15.0 wt.-% maleic anhydride; and
- (iii) from 0.0 to 25.0 wt.-% of other vinyl-copolymerizable monomers having no
- 25 functional groups other than the vinyl function, based on the weight of the adhesion-promoting copolymer.

The cumulative content of the polymethyl(meth)acrylate and of one or several impact modifiers in the layer B is at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least 70 wt.-%, yet

30 even more preferably at least 80 wt.-%, still more preferably at least 90 wt.-%, particularly preferably at least 95 wt.-% and not more than 99.9 wt.-%, based on the weight of the layer B. The content of the one or several impact modifiers in the layer B can be readily adjusted by a skilled person depending on the intended application. For instance, in applications in which a highly flexible soft foil is required relatively high contents of impact modifiers up to 85 wt.-% can be

35 employed. On the other hand, for applications requiring relatively brittle hard foils the layer B may have a lower content of impact modifiers or even be substantially free of impact modifiers.

In order to ensure an adequate protection of the substrate material located beneath the multilayer foil, the spectral transmittance of the layer B at any wavelength λ_B is not more than 10%; wherein

$270\text{ nm} \leq \lambda_B \leq 370\text{ nm}$. In addition, the optical transmittance of the layer B at the wavelength of 370 nm is preferably chosen to be not more than 10%.

The exact composition of the layer A depends on the nature of the first UV absorber employed therein. In one aspect of the present invention, the layer A comprises:

- from 0.0 to 99.9 wt.-% of a polymethyl(meth)acrylate;
- from 0.0 to 95.0 wt.-% of one or several impact modifiers;
- from 0.0 to 30.0 wt.-% of a fluoropolymer;
- from 0.1 to 5.0 wt.-% of a first UV-absorber;
- from 0.0 to 5.0 wt.-% of one or several UV-stabilizers;

wherein the layer A comprises not more than 0.1 wt.-%, preferably not more than 0.05 wt.-% of the second UV absorber.

The cumulative content of the polymethyl(meth)acrylate and of one or several impact modifiers in the layer A is at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least 70 wt.-%, yet even more preferably at least 80 wt.-%, still more preferably at least 90 wt.-%, particularly preferably at least 95 wt.-% and not more than 99.9 wt.-%, based on the weight of the layer A.

Again, the content of the one or several impact modifiers in the layer A can be readily adjusted by a skilled person depending on the intended applications as described above.

Without wishing to be bound by theory, the inventors surprisingly found that in order to achieve an excellent long-term weathering stability in this embodiment it is important that the spectral transmittance of the layer A at any wavelength λ_A is not more than 10%; wherein $270\text{ nm} \leq \lambda_A \leq 360\text{ nm}$.

In yet a further embodiment of the present invention, the layer A has the following composition:

- from 0.0 to 99.0 wt.-% of a polymethyl(meth)acrylate;
- from 0.0 to 95.0 wt.-% of one or several impact modifiers;
- from 0.0 to 30.0 wt.-% of a fluoropolymer;
- from 1.0 to 30.0 wt.-% of a first UV-absorber, wherein the first UV-absorber is an inorganic particulate material, which is preferably selected from zinc oxide, titanium dioxide, cerium dioxide, tin dioxide, silica and glass;
- from 0.0 to 5.0 wt.-% of one or several UV-stabilizers;

wherein the layer A comprises not more than 0.1 wt.-%, preferably not more than 0.05 wt.-% of the second UV absorber.

The cumulative content of the polymethyl(meth)acrylate and of one or several impact modifiers in the layer A is at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least 70 wt.-%, yet even more preferably at least 80 wt.-%, still more preferably at least 90 wt.-%, particularly preferably at least 95 wt.-% and not more than 97.0 wt.-%, based on the weight of the layer A.

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In this particular embodiment, the spectral transmittance of the layer A at any wavelength λ_A is not more than 20%; wherein $270 \text{ nm} \leq \lambda_A \leq 310 \text{ nm}$.

10 In addition to the layers A and B described above, the multilayer foil of the present invention may further comprise an adhesion-promoting layer C. The layer C additionally improves adhesion of the foil of the present invention on a substrate and is particularly advantageous for the manufacturing of HPLs. Typically, the layer C comprises, based on the total weight of the layer C:

15 from 0.0 to 95.0 wt.-% of a polymethyl(meth)acrylate;
from 0.0 to 75.0 wt.-% of one or several impact modifiers;
from 0.0 to 5.0 wt.-% of a UV-absorber, which is preferably the second UV-absorber;
from 0.0 to 5.0 wt.-% of one or several UV-stabilizers; and
from 5.0 to 80.0 wt.-% of an adhesion-promoting copolymer as specified above.

20 The cumulative content of the polymethyl(meth)acrylate and of one or several impact modifiers in the layer C is at least 20.0 wt.-%, preferably at least 30.0 wt.-%, more preferably at least 40.0 wt.-% and not more than 95.0 wt.-%, based on the weight of the layer C. Furthermore, in order to ensure a good adhesion between the foil of the present invention and the substrate, the adhesion promoting layer C comprises at least 5 wt.-%, preferably at least 10 wt.-% of one or several impact
25 modifiers.

It further proved to be advantageous in terms of mechanical properties of the foil, if the total content of one or several impact modifiers in the adhesion-promoting layer C is lower than in the layer B and the total content of one or several impact modifiers in the layer B is lower than in the layer A.

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If the adhesion-promoting layer C is present, the layer B comprises less than 3.0 wt.-%, preferably less than 1.0 wt.-%, based on the weight of the layer B, of the adhesion-promoting copolymer.

35 If desired, the multi-layer foil of the present invention can be optionally rendered particularly weathering-resistant by providing it with a fluoropolymer-based layer D, which is located on top and adjacent to the layer A. The layer D may comprise, based on the total weight of the layer D:

from 40.0 to 100.0 wt.-% of at least one fluoropolymer;
from 0.0 to 60.0 wt.-% of a polymethyl(meth)acrylate; and

from 0.0 to 30.0 wt.-% of substantially spherical glass beads.

The structure and the composition of the layer D are described in detail in the patent application WO 2018/104293 A1 the entire disclosure of which is incorporated herein by reference.

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The fluoropolymer in the layer D may be selected from polyvinylidene fluoride (PVDF), polyvinylfluoride (PVF), polytetrafluoroethylene (PTFE), polyethylenetetrafluoroethylene (ETFE), fluorinated ethylene-propylene (FEP) or a mixture or copolymers thereof.

10 Furthermore, in some embodiments, the foil may further comprise a layer E, which is located between the layer A and the layer B and comprises a combination of the first UV absorber and the second UV absorber as described above. Typically, the layer E has the following composition:

from 0.0 to 99.9 wt.-% of a polymethyl(meth)acrylate;
 15 from 0.0 to 95.0 wt.-% of one or several impact modifiers;
 from 0.0 to 30.0 wt.-% of a fluoropolymer;
 from 0.0 to 20.0 wt.-% of an adhesion-promoting copolymer comprising
 (i) from 70.0 to 95.0 wt.-% methyl methacrylate;
 (ii) from 0.5 to 15.0 wt.-% maleic anhydride; and
 20 (iii) from 0.0 to 25.0 wt.-% of other vinyl-copolymerizable monomers having no
 functional groups other than the vinyl function, based on the weight of the
 adhesion-promoting copolymer; and
 from 0.1 to 5.0 wt.-% of a combination of the first UV-absorber with the second UV
 absorber;
 25 from 0.0 to 5.0 wt.-% of one or several UV-stabilizers;

wherein the cumulative content of the polymethyl(meth)acrylate and of one or several impact
 modifiers in the layer E is at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least
 70 wt.-%, yet even more preferably at least 80 wt.-%, still more preferably at least 90 wt.-%,
 30 particularly preferably at least 95 wt.-% and not more than 99.9 wt.-%, based on the weight of the
 layer E.

Advantageously, the layer E comprises, based on the total weight of the layer E:

35 from 0.0 to 99.9 wt.-% of a poly(methyl)methacrylate;
 from 0.0 to 95.0 wt.-% of one or several impact modifiers;
 from 0.1 to 5.0 wt.-% of a combination of the first UV-absorber with the second UV
 absorber;
 from 0.0 to 5.0 wt.-% of one or several UV-stabilizers.

wherein the cumulative content of the polymethyl(meth)acrylate and of one or several impact modifiers in the layer E is at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least 70 wt.-%, yet even more preferably at least 80 wt.-%, still more preferably at least 90 wt.-%, particularly preferably at least 95 wt.-% and not more than 99.9 wt.-%, based on the weight of the layer E.

Depending on the envisaged purpose, the foil of the present invention may have a total thickness between 1.0 μm and 300.0 μm , more preferably between 1.0 μm and 200.0 μm , yet even more preferably between 30.0 μm and 150.0 μm .

The PMMA-based layer A typically has a thickness from 10.0 μm to 100.0 μm , preferably from 15.0 μm to 50.0 μm , more preferably from 20.0 μm to 40.0 μm .

The PMMA-based layer B commonly has a thickness from 10.0 μm to 80.0 μm , preferably from 15.0 μm to 50.0 μm , more preferably from 20.0 μm to 40.0 μm .

The adhesion-promoting layer C, if present, has a thickness from 1.0 μm to 20.0 μm , preferably from 2.0 μm to 15.0 μm , more preferably from 3.0 μm to 10.0 μm .

The fluoropolymer-based layer D, if present, has a thickness from 1.0 μm to 40.0 μm , preferably from 2.0 μm to 30.0 μm , more preferably from 3.0 μm to 20.0 μm .

The PMMA-based layer E, if present, has a thickness from 10.0 μm to 80.0 μm , preferably from 15.0 μm to 50.0 μm , more preferably from 20.0 μm to 40.0 μm .

The thickness of the foil of the present invention and of its layers can be determined by mechanical scanning according to the norm ISO 4593-1993. Preferably however, the thickness of the foil of the present invention and of its individual layers is determined using photomicrographs obtained using a scanning electron microscope such as JEOL JSM-IT300 (commercially available from JEOL GmbH, Freising, Germany). For this purpose, the foil samples can be frozen in liquid nitrogen, mechanically broken and the freshly obtained surfaces are analysed. For example, the measurement can be carried out using the following parameters:

Current source:	variable flow of electrons from a tungsten filament (cathode)
Vacuum system:	rotary pump / oil diffusion pump
X-Y-Z-rotation-tilt:	totally motorized
Working distance (WD):	5 to 70 mm (common: 10 mm)
Sample rotation:	360°

Sample tilting:	- 5 to max. 90° (depending on WD)
Magnification:	10 x to 300 000 x
Maximum resolution:	~ 3 nm
Detectors:	Secondary Electrons (SE)
5	Back Scattered Electrons (BSE, 5 segments)
	Energy dispersive X-Ray Analysis (EDS)

In summary, the multilayer foil of the present invention has the following order of layers:

- 10 the fluoropolymer-based layer D, if present, is directly exposed to the environment;
the PMMA-based layer A is located beneath the layer D;
the PMMA-based layer E, if present, is located between the layer A and the layer B
the PMMA-based layer B is located beneath the layer A or, if the layer E is present, beneath the layer E; and
- 15 the adhesion-promoting layer C, if present, is located beneath the layer B.

The following embodiments of multilayer foils of the present invention showed particularly advantageous properties:

- 20 (1) • layer A comprising glass beads as a first UV absorber; and
• layer B comprising a benzotriazole type UV absorber which is preferably selected from 2,2'-methylene-bis[6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol], 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol or a mixture thereof.
- 25 (2) • layer A comprising inorganic particulate material selected from cerium oxide, titanium dioxide or zinc oxide as a first UV absorber; and
• layer B comprising a benzotriazole type UV absorber which is preferably selected from 2,2'-methylene-bis[6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol], 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol or a mixture thereof.
- 30 (3) • layer A comprising a triazine type UV absorber as a first UV absorber, which is preferably selected from 6-[4,6-bis(4-phenylphenyl)-1,2-dihydro-1,3,5-triazin-2-ylidene]-3-[(2-ethylhexyl)oxy]cyclohexa-2,4-dien-1-one, 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-((hexyl)oxy)phenol, 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]-5-(octyloxy)phenol or a combination of at least two of those; and
- 35 • layer B comprising a benzotriazole type UV absorber which is preferably selected from 2,2'-methylene-bis[6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol], 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol or a mixture thereof.

- (4) • layer D comprising glass beads dispersed in a fluoropolymer matrix;
- layer A comprising a triazine type UV absorber as a first UV absorber, which is preferably selected from 6-[4,6-bis(4-phenylphenyl)-1,2-dihydro-1,3,5-triazin-2-ylidene]-3-[(2-ethylhexyl)oxy]cyclohexa-2,4-dien-1-one, 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-((hexyl)oxy)phenol, 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]-5-(octyloxy)phenol or a combination of at least two of those; and
- layer B comprising a benzotriazole type UV absorber which is preferably selected from 2,2'-methylene-bis[6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol], 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol or a mixture thereof.
- (5) • fluoropolymer based layer D, preferably comprising at least 80 wt.%, preferably at least 90 wt.%, more preferably at least 95 wt.%, even more preferably at least 99 wt.-% PVDF, based on the weight of the layer D;
- layer A comprising a triazine type UV absorber as a first UV absorber, which is preferably selected from 6-[4,6-bis(4-phenylphenyl)-1,2-dihydro-1,3,5-triazin-2-ylidene]-3-[(2-ethylhexyl)oxy]cyclohexa-2,4-dien-1-one, 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-((hexyl)oxy)phenol, 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]-5-(octyloxy)phenol or a combination of at least two of those; and
- layer B comprising a benzotriazole type UV absorber which is preferably selected from 2,2'-methylene-bis[6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol], 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol or a mixture thereof.
- (6) • layer A comprising inorganic particulate material selected from cerium oxide, titanium dioxide or zinc oxide as a first UV absorber;
- layer E comprising a triazine type UV absorber as a first UV absorber, which is preferably selected from 6-[4,6-bis(4-phenylphenyl)-1,2-dihydro-1,3,5-triazin-2-ylidene]-3-[(2-ethylhexyl)oxy]cyclohexa-2,4-dien-1-one, 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-((hexyl)oxy)phenol, 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]-5-(octyloxy)phenol or a combination of at least two of those; and
- layer B comprising a benzotriazole type UV absorber which is preferably selected from 2,2'-methylene-bis[6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol], 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol or a mixture thereof.
- (7) • layer A comprising a triazine type UV absorber as a first UV absorber, which is preferably selected from 6-[4,6-bis(4-phenylphenyl)-1,2-dihydro-1,3,5-triazin-2-ylidene]-3-[(2-ethylhexyl)oxy]cyclohexa-2,4-dien-1-one, 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-((hexyl)oxy)phenol, 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]-5-(octyloxy)phenol or a combination of at least two of those;

- layer E comprising a triazine type UV absorber as a first UV absorber, which is preferably selected from 6-[4,6-bis(4-phenylphenyl)-1,2-dihydro-1,3,5-triazin-2-ylidene]-3-[(2-ethylhexyl)oxy]cyclohexa-2,4-dien-1-one, 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-((hexyl)oxy)phenol, 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]-5-(octyloxy)phenol or a combination thereof and a benzotriazole type UV absorber which is preferably selected from 2,2'-Methylene-bis[6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol], 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol or a mixture of at least two of those; and
- layer B comprising a benzotriazole type UV absorber which is preferably selected from 2,2'-methylene-bis[6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol], 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol or a mixture thereof.
- (8) • layer D comprising glass beads dispersed in a fluoropolymer matrix;

• layer A comprising a triazine type UV absorber as a first UV absorber, which is preferably selected from 6-[4,6-bis(4-phenylphenyl)-1,2-dihydro-1,3,5-triazin-2-ylidene]-3-[(2-ethylhexyl)oxy]cyclohexa-2,4-dien-1-one, 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-((hexyl)oxy)phenol, 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]-5-(octyloxy)phenol or a combination of at least two of those;

• layer B comprising a benzotriazole type UV absorber which is preferably selected from 2,2'-methylene-bis[6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol], 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol or a mixture thereof; and

• layer C.
- (9) • layer A comprising glass beads as a first UV absorber

• layer E comprising a triazine type UV absorber as a first UV absorber, which is preferably selected from 6-[4,6-bis(4-phenylphenyl)-1,2-dihydro-1,3,5-triazin-2-ylidene]-3-[(2-ethylhexyl)oxy]cyclohexa-2,4-dien-1-one, 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-((hexyl)oxy)phenol, 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]-5-(octyloxy)phenol or a combination of at least two of those and a benzotriazole type UV absorber which is preferably selected from 2,2'-methylene-bis[6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol], 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol or a mixture thereof; and

• layer B comprising a benzotriazole type UV absorber which is preferably selected from 2,2'-methylene-bis[6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol], 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol or a mixture thereof.
- (10) • layer A comprising glass beads as a first UV absorber

• layer E comprising a triazine type UV absorber as a first UV absorber, which is preferably selected from 6-[4,6-bis(4-phenylphenyl)-1,2-dihydro-1,3,5-triazin-2-ylidene]-3-

[(2-ethylhexyl)oxy]cyclohexa-2,4-dien-1-one, 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-((hexyl)oxy)phenol, 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]-5-(octyloxy)phenol or a combination of at least two of those; and

- layer B comprising a benzotriazole type UV absorber which is preferably selected from 2,2'-methylene-bis[6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol], 2-(2*H*-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol or a mixture thereof.

In the following, the individual components of the layers A, B, C, D and E will be described in a greater detail.

Polymethyl(meth)acrylate

As already mentioned above, the PMMA-based layers A and B may comprise up to 99.9 wt.-% polymethyl (meth)acrylate (PMMA). PMMA is generally obtained by free-radical polymerization of mixtures which comprise methyl methacrylate. These mixtures generally comprise at least 40 wt.-%, preferably at least 60 wt.-%, particularly preferably at least 80 wt.-%, and even more preferably at least 90 wt.-%, based on the weight of the monomers, of methyl methacrylate (MMA).

The mixtures for production of PMMA can also comprise other (meth)acrylates copolymerizable with methyl methacrylate. The term “(meth)acrylate” as used herein is meant to encompass methacrylates, acrylates and mixtures thereof. (Meth)acrylates may derive from saturated alcohols, e.g. methyl acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, *n*-butyl (meth)acrylate, *tert*-butyl (meth)acrylate, isobutyl (meth)acrylate, pentyl (meth)acrylate and 2-ethylhexyl (meth)acrylate; or from unsaturated alcohols, e.g. oleyl (meth)acrylate, 2-propynyl (meth)acrylate, allyl (meth)acrylate, vinyl (meth)acrylate; and also aryl (meth)acrylates, such as benzyl (meth)acrylate or phenyl (meth)acrylate, cycloalkyl (meth)acrylates, such as 3-vinylcyclohexyl (meth)acrylate, bornyl (meth)acrylate; hydroxyalkyl (meth)acrylates, such as 3-hydroxypropyl (meth)acrylate, 3,4-dihydroxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate; glycol di(meth)acrylates, such as 1,4-butanediol (meth)acrylate, (meth)acrylates of ether alcohols, e.g. tetrahydrofurfuryl (meth)acrylate, vinyloxyethoxyethyl (meth)acrylate; amides and nitriles of (meth)acrylic acid, e.g. *N*-(3-dimethylaminopropyl)(meth)acrylamide, *N*-(diethylphosphono)-(meth)acrylamide, 1-methacryloylamido-2-methyl-2-propanol; sulphur-containing methacrylates, such as ethylsulphinylethyl (meth)acrylate, 4-thiocyanatobutyl (meth)acrylate, ethylsulphonylethyl (meth)acrylate, thiocyanatomethyl (meth)acrylate, methylsulphinylmethyl (meth)acrylate, bis((meth)acryloyloxyethyl) sulphide; polyfunctional (meth)acrylates, such as trimethyloxypropane tri(meth)acrylate.

The polymerization reaction is generally initiated by known free-radical initiators. Among the preferred initiators are *inter alia* the azo initiators well known to persons skilled in the art, e.g. AIBN

and 1,1-azobiscyclohexanecarbonitrile, and peroxy compounds, such as methyl ethyl ketone peroxide, acetylacetone peroxide, dilauryl peroxide, *tert*-butyl 2-ethylperhexanoate, ketone peroxide, methyl isobutyl ketone peroxide, cyclohexanone peroxide, dibenzoyl peroxide, *tert*-butyl peroxybenzoate, *tert*-butylperoxy isopropyl carbonate, 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane, *tert*-butyl 2-ethylperoxyhexanoate, *tert*-butyl 3,5,5-trimethylperoxyhexanoate, dicumyl peroxide, 1,1-bis(*tert*-butylperoxy)cyclohexane, 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane, cumyl hydroperoxide, *tert*-butyl hydroperoxide, bis(4-*tert*-butylcyclohexyl) peroxydicarbonate, mixtures of two or more of the abovementioned compounds with one another and mixtures of the abovementioned compounds with compounds that have not been mentioned but which can likewise form free radicals.

The compositions to be polymerized can comprise not only the (meth)acrylates described above but also other unsaturated monomers which are copolymerizable with methyl methacrylate and with the abovementioned (meth)acrylates. Among these are *inter alia* 1-alkenes, such as 1-hexene, 1-heptene; branched alkenes, such as vinylcyclohexane, 3,3-dimethyl-1-propene, 3-methyl-1-diisobutylene, 4-methyl-1-pentene; acrylonitrile; vinyl esters, such as vinyl acetate; styrene, substituted styrenes having an alkyl substituent in the side chain, e.g. α -methylstyrene and α -ethylstyrene, substituted styrenes having an alkyl substituent on the ring, e.g. vinyltoluene and *p*-methylstyrene, halogenated styrenes, such as monochlorostyrenes, dichlorostyrenes, tribromostyrenes and tetrabromostyrenes; heterocyclic vinyl compounds, such as 2-vinylpyridine, 3-vinylpyridine, 2-methyl-5-vinylpyridine, 3-ethyl-4-vinylpyridine, 2,3-dimethyl-5-vinylpyridine, vinylpyrimidine, vinylpiperidine, 9-vinylcarbazole, 3-vinylcarbazole, 4-vinylcarbazole, 1-vinylimidazole, 2-methyl-1-vinylimidazole, *N*-vinylpyrrolidone, 2-vinylpyrrolidone, *N*-vinylpyrrolidine, 3-vinylpyrrolidine, *N*-vinylcaprolactam, *N*-vinylbutyrolactam, vinyloxolane, vinylfuran, vinylthiophene, vinylthiolane, vinylthiazoles and hydrogenated vinylthiazoles, vinyloxazoles and hydrogenated vinyloxazoles; vinyl ethers and isoprenyl ethers; maleic acid derivatives, such as maleic anhydride, methylmaleic anhydride, maleimide, methylmaleimide; and dienes, such as divinylbenzene.

The amount of these comonomers generally used is from 0.0 wt.-% to 60.0 wt.-%, preferably from 0.0 to 40.0 wt.-% and particularly preferably from 0.0 to 20.0 wt.-%, based on the weight of monomers, and the compounds here can be used individually or in the form of a mixture.

Further preference is given to PMMA which is obtainable by polymerization of a composition having, as polymerizable constituents:

- (a) from 50.0 to 99.9 wt.-%, preferably from 80.0 to 99.9 wt.-%, more preferably from 91.0 to 99.9 wt.-% of methyl methacrylate,

- (b) from 0.1 to 50.0 wt.-%, preferably from 0.1 to 20.0 wt.-%, more preferably from 0.1 to 9.0 wt.-% of an acrylic acid ester of a C1-C4 alcohol,
- (c) from 0.0 to 10.0 wt.-% of at least one further monomer copolymerizable with the monomers (a) and (b).

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Use of the component (c) in the range from 8.0 to 10.0 wt.-%, the component (c) being preferably *n*-butyl acrylate, raises the intrinsic stability of the foil. As the proportion of the component (c) increases, the stability of the foil increases. However, an increase beyond the limiting values is disadvantageous.

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In yet a further embodiment preference is given to PMMA composed of from 80.0 to 99.9 wt.-% of methyl methacrylate and from 0.1 to 20.0 wt.-% of methyl acrylate, the amounts here being based on 100 wt.-% of the polymerizable constituents. Particularly advantageous copolymers are those obtainable by copolymerization of from 95.0 to 99.9 wt.-% of methyl methacrylate and from 0.1 to 5.0 wt.-% of methyl acrylate, where the amounts are based on 100 wt.-% of the polymerizable constituents. For instance, the PMMA may comprise 96.0 wt.-% of methyl methacrylate and 4.0 wt.-% of methyl acrylate, 98.0 wt.-% of methyl methacrylate and 2.0 wt.-% of methyl acrylate or 99.0 wt.-% of methyl methacrylate and 1.0 wt.-% of methyl acrylate. The Vicat softening points VSP (ISO 306-B50) of said PMMA is typically at least 90 °C, preferably from 95 °C to 112 °C.

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The chain lengths of the PMMA polymers and its molecular weight can be adjusted by polymerization of the monomer mixture in the presence of molecular-weight regulators, particular examples being the mercaptans known for this purpose, *e.g.* *n*-butyl mercaptan, *n*-dodecyl mercaptan, 2-mercaptoethanol or 2-ethylhexyl thioglycolate, or pentaerythritol tetrathioglycolate; the amounts generally used of the molecular-weight regulators being from 0.05 to 5.0 wt.-%, based on the weight of the monomer mixture, preference being given to amounts of from 0.1 to 2.0 wt.-% and particular preference being given to amounts of from 0.2 to 1.0 wt.-%, based on the monomer mixture (*cf.* H. Rauch-Puntigam, Th. Völker, "Acryl- und Methacrylverbindungen" ["Acrylic and Methacrylic Compounds"], Springer, Heidelberg, 1967; Houben-Weyl, Methoden der organischen Chemie, [Methods of Organic Chemistry], Vol. XIV/1, page 66, Georg Thieme, Heidelberg, 1961, or Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 1, pages 296 et seq., J. Wiley, New York, 1978).

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The weight-average molar mass *M_w* of the PMMA employed is usually above 80 000 g/mol, determined by means of gel permeation chromatography (GPC with reference to PMMA as a calibration standard, as for all of the *M_w* determinations on the matrix PMMA), more preferably $\geq 120\,000$ g/mol. For the purposes of the invention, it is possible to achieve foils of even greater weathering resistance if the weight-average molar mass *M_w* of PMMA is above 140 000 g/mol. The weight-average molar mass *M_w* of the PMMA is generally in the range from 80 000 g/mol to

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220 000 g/mol. Particularly good weathering resistances are obtained from foils with PMMA having an average molar mass M_w in the range from 80 000 g/mol to 180 000 g/mol, preferably in the range from 100 000 g/mol to 180 000 g/mol, more preferably in the range from 120 000 g/mol to 180 000 g/mol, in each case determined by means of GPC against PMMA calibration standards.

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A particularly advantageous weathering stability and processability of the foil is observed if the polymethyl(meth)acrylate is PMMA having an average molar weight M_w of from 80 000 g/mol to 220 000 g/mol and is obtainable by polymerization of a composition whose polymerizable constituents comprise, based on the weight of the polymerisable composition:

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- (a) from 50.0 to 99.9 wt.-%, preferably from 80.0 to 99.9 wt.-%, more preferably from 91.0 to 99.9 wt.-% of methyl methacrylate,
- (b) from 0.1 to 50.0 wt.-%, preferably from 0.1 to 20.0 wt.-%, more preferably from 0.1 to 9.0 wt.-% of an acrylic acid ester of a C1-C4 alcohol,
- 15 (c) from 0.0 to 10.0 wt.-% of at least one further monomer copolymerizable with the monomers (a) and (b).

Typically, the PMMA is not cross-linked and it therefore suitable for thermoplastic processing. Nevertheless, in an alternative embodiment, a cross-linked PMMA may be employed in one or
20 several layers, for instance as a e-beam, UV or thermally cross-linkable PMMA coating.

Impact modifiers

Impact modifiers for use in the present invention *per se* are well known and may have different
25 chemical compositions and different polymer architectures. The impact modifiers may be crosslinked or thermoplastic. In addition, the impact modifiers may be in particulate form, as core-shell or as core-shell-shell particles. Typically, particulate impact modifiers have an average particle diameter between 20 and 400 nm, preferably between 50 and 300 nm, more preferably between 100 and 285 nm and most preferably between 150 and 270 nm. "*Particulate*" in this
30 context means crosslinked impact modifiers which generally have a core-shell or a core-shell-shell structure.

In the simplest case, the particulate impact modifiers are crosslinked particles obtained by means of emulsion polymerization whose average particle size is in the range from 10 to 150 nm,
35 preferably from 20 to 100 nm, in particular from 30 to 90 nm. These are generally composed of at least 40.0 wt.-%, preferably from 50.0 to 70.0 wt.-% of methyl methacrylate, from 20.0 to 40.0 wt.-%, preferably from 25.0 to 35.0 wt.-% of butyl acrylate, and from 0.1 to 2.0 wt.-%, preferably from 0.5 to 1.0 wt.-% of a crosslinking monomer, e.g. a polyfunctional (meth)acrylate, e.g. allyl methacrylate and, if appropriate, other monomers, e.g. from 0.0 to 10.0 wt.-%, preferably from 0.5

to 5.0 % wt.-%, of C₁-C₄-alkyl methacrylates, such as ethyl acrylate or butyl methacrylate, preferably methyl acrylate, or other vinylically polymerizable monomers, e.g. styrene.

Preferred impact modifiers are polymer particles which can have a two- or three-layer core-shell structure and are obtained by emulsion polymerization (see, for example, EP-A 0 113 924, EP-A 0 522 351, EP-A 0 465 049 and EP-A 0 683 028). The present invention typically requires suitable particle sizes of these emulsion polymers in the range from 10 to 150 nm, preferably from 20 to 120 nm, particularly preferably from 50 to 100 nm.

10 A three-layer or three-phase structure with a core and two shells can prepared as follows. The innermost (hard) shell can, for example, be composed in essence of methyl methacrylate, of small proportions of comonomers, e.g. ethyl acrylate, and of a proportion of crosslinking agent, e.g. allyl methacrylate. The middle (soft) shell can, for example, be composed of butyl acrylate and, if appropriate, styrene, while the outermost (hard) shell is in essence the same as the matrix
15 polymer, thus bringing about compatibility and good linkage to the matrix. The proportion of polybutyl acrylate in the impact modifier is decisive for the impact-modifying action and is preferably in the range from 20.0 to 40.0 wt.-%, particularly preferably in the range from 25.0 to 35.0 wt.-%.

20 A further preference is given to use of a system known in principle from EP 0 528 196 A1 which is a two-phase impact-modified polymer composed of:

- a1) from 10.0 to 95.0 wt.-% of a coherent hard phase whose glass transition temperature T_g is above 70°C, composed of
- 25 a11) from 80.0 to 100 wt.-% (based on a1) of methyl methacrylate and
- a12) from 0.0 wt.-% to 20.0 wt.-% of one or more other ethylenically unsaturated monomers capable of free-radical polymerization, and
- a2) from 90.0 to 5.0 wt.-% of a tough phase whose glass transition temperature T_g is below -10°C, distributed in the hard phase and composed of
- 30 a21) from 50.0 to 99.5 wt.-% of a C₁-C₁₀-alkyl acrylate (based on a2)
- a22) from 0.5 to 5.0 wt.-% of a crosslinking monomer having two or more ethylenically unsaturated radicals which are capable of free-radical polymerization, and
- a23) if appropriate, other ethylenically unsaturated monomers capable of free-radical polymerization,

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where at least 15.0 wt.-% of the hard phase a1) has a covalent linkage to the tough phase a2).

The two-phase impact modifier can be produced by a two-stage emulsion polymerization reaction in water, as described by way of example in DE-A 38 42 796. In the first stage, the tough phase a2)

is produced and is composed of at least 50.0 wt.-%, preferably more than 80.0 wt.-%, of lower alkyl acrylates, thus giving a glass transition temperature T_g below $-10\text{ }^{\circ}\text{C}$ for this phase. Crosslinking monomers a22) used comprise (meth)acrylates of diols, e.g. ethylene glycol dimethacrylate or 1,4-butanediol dimethacrylate, aromatic compounds having two vinyl or allyl groups, e.g. divinylbenzene, or other crosslinking agents having two ethylenically unsaturated radicals which are capable of free-radical polymerization, e.g. allyl methacrylate, as graft-linking agent. Crosslinking agents that may be mentioned by way of example and have three or more unsaturated groups which are capable of free-radical polymerization, e.g. allyl groups or (meth)acrylic groups, are triallyl cyanurate, trimethylolpropane triacrylate and trimethylolpropane tri(meth)acrylate, and pentaerythrityl tetraacrylate and pentaerythrityl tetra(meth)acrylate.

US 4,513,118 gives further examples thereof.

The ethylenically unsaturated monomers capable of free-radical polymerization and mentioned under a23) can, by way of example, be acrylic or methacrylic acid or else their alkyl esters having from 1 to 20 carbon atoms but not mentioned above, and the alkyl radical here can be linear, branched or cyclic. Furthermore, a23) can comprise further aliphatic comonomers which are capable of free-radical polymerization and which are copolymerizable with the alkyl acrylates a21). However, the intention is to exclude significant proportions of aromatic comonomers, such as styrene, α -methylstyrene or vinyltoluene, since they lead to undesired properties of the resulting product - especially on weathering.

When the tough phase is produced in the first stage, careful attention has to be paid to the setting of the particle size and its polydispersity. The particle size of the tough phase here is in essence dependent on the concentration of the emulsifier. The particle size can advantageously be controlled by the use of a seed latex. Particles whose average (weight-average) particle size is below 130 nm, preferably below 70 nm, and whose particle-size polydispersity P_{80} is below 0.5 (P_{80} being determined from cumulative evaluation of the particle-size distribution determined by ultracentrifuge; the relationship is: $P_{80} = [(r_{90} - r_{10})/r_{50}] - 1$, where r_{10} , r_{50} , r_{90} = average cumulative particle radius, being the value which is greater than 10, 50, 90% of the particle radii and is smaller than 90, 50, 10% of the particle radii), preferably below 0.2, are achieved using emulsifier concentrations of from 0.15 to 1.0 wt.-%, based on the aqueous phase. This applies especially to anionic emulsifiers, examples being the particularly preferred alkoxyated and sulphated paraffins. Examples of polymerization initiators used are from 0.01 to 0.5 wt.-% of alkali metal peroxodisulphate or ammonium peroxodisulphate, based on the aqueous phase, and the polymerization reaction is initiated at temperatures of from 20 to $100\text{ }^{\circ}\text{C}$. Preference is given to use of redox systems, an example being a combination composed of from 0.01 to 0.05 wt.-% of organic hydroperoxide and from 0.05 to 0.15 wt.-% of sodium hydroxymethylsulphinate, at temperatures of from 20 to $80\text{ }^{\circ}\text{C}$.

The glass transition temperature of the hard phase a1) of which at least 15 wt.-% has covalent bonding to the tough phase a2) is at least 70 °C and this phase can be composed exclusively of methyl methacrylate. Up to 20 wt.-% of one or more other ethylenically unsaturated monomers which are capable of free-radical polymerization can be present as comonomers a12) in the hard phase, and the amount of alkyl (meth)acrylates used here, preferably alkyl acrylates having from 1 to 4 carbon atoms, is such that the glass transition temperature is not below the glass transition temperature mentioned above.

The polymerization of the hard phase a1) proceeds likewise in emulsion in a second stage, using the conventional auxiliaries, for example those also used for polymerization of the tough phase a2).

Thermoplastic impact modifiers have a different mechanism of action than particulate impact modifiers. They are generally mixed with the matrix material. In the case that domains are formed, as occurs, for example, in the case of use of block copolymers, preferred sizes for these domains, the size of which can be determined, for example, by electron microscopy, correspond to preferred sizes for the core-shell particles.

There are various classes of thermoplastic impact modifiers. One example thereof are aliphatic TPUs (thermoplastic polyurethanes) e.g. Desmopan® products commercially available from Covestro AG. For instance, the TPUs Desmopan® WDP 85784A, WDP 85092A, WDP 89085A and WDP 89051D, all of which have refractive indices between 1.490 and 1.500, are particularly suitable as impact modifiers.

A further class of thermoplastic polymers for use according in the foil of the present invention as impact modifiers are methacrylate-acrylate block copolymers, especially acrylic TPE, which comprises PMMA-poly-*n*-butyl acrylate-PMMA triblock copolymers, and which are commercially available under the Kurarity® product name by Kuraray. The poly-*n*-butyl acrylate blocks form nanodomains in the polymer matrix having a size between 10 and 20 nm.

30 UV absorbers

The present invention is based on a surprising finding that by placing different UV absorbers in separate PMMA-based layers the weathering stability of the resulting multilayer foil can be dramatically improved. The choice of the first UV absorber and of the second UV absorber is thereby particularly important.

In one embodiment, the first UV absorber in the layer A is an organic UV absorber. The first UV absorber and its amount in the layer A is selected in such a way that the spectral transmittance of the layer A at any wavelength λ_A is not more than 10%; wherein $270 \text{ nm} \leq \lambda_A \leq 360 \text{ nm}$.

Preferably, the first UV absorber is triazine type UV absorber, whereby 2-(2-hydroxyphenyl)-1,3,5-triazines are particularly preferred. Preferably used 2-(2-hydroxyphenyl)-1,3,5-triazines include *inter alia* 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyl-oxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropoxy)phenyl]-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine, 2-(2-hydroxy-4-[3-(2-ethylhexyl-1-oxy)-2-hydroxypropyloxy]phenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(4-[2-ethylhexyloxy]-2-hydroxyphenyl)-6-(4-methoxyphenyl)-1,3,5-triazine. Triazine type UV absorbers such as 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-hexyloxyphenol, can also be used. These compounds are e.g. commercially available from BASF SE (Ludwigshafen, Germany) under trademarks Tinuvin® 1600, Tinuvin® 1577 or Tinuvin® 1545.

The amounts of the triazine type UV absorber in the layer A are from 0.1 to 5.0 wt.-%, preferably from 0.2 to 3.0 wt.-% and very particularly preferably from 0.5 to 2.0 wt.-%, based on the weight of the layer A. It is also possible to use mixtures of different triazine type UV absorbers.

In a further preferred embodiment, the first UV absorber in the layer A is an inorganic particulate material. Such material may be advantageously selected from zinc oxide, titanium dioxide, cerium dioxide, tin dioxide, iron oxides, silica or glass which may be in form of glass beads or glass powder. The first UV absorber and its amount in the layer A is selected in such a way that the spectral transmittance of the layer A at any wavelength λ_A is not more than 10% wherein $270 \text{ nm} \leq \lambda_A \leq 310 \text{ nm}$. Examples of suitable inorganic particulate materials are for instance Solasorb™ UV100 (titanium dioxide dispersion, contains 45 wt.-% of an inorganic and organic coated titanium dioxide, average particle size 40 nm), Solasorb™ UV200 (zinc oxide dispersion, contains 60 wt.-% zinc oxide, average particle size 60 nm) available from Croda International Plc (Snaith, United Kingdom).

In embodiments using glass as a first UV absorber, use of glass powder or glass beads having a particle size below 10 μm is particularly advantageous in terms of efficient UV absorption and high degree of transmission of visible light. Although the choice of the glass for this purpose is not

particularly limited, glass sorts such as GG395, GG400, GG420, GG435, GG475, OG515, OG 530, available from Schott AG (Mainz, Germany) showed to be particularly useful. Glass beads for use in the layer A will be described in a greater detail below in the section "Glass beads".

- 5 According to the present invention, the second UV absorber in the layer B is distinct from the first UV absorber in the layer A. The second UV absorber and its amount in the layer B is selected in such a way that the spectral transmittance of the layer B at any wavelength λ_B is not more than 10%; wherein $270 \text{ nm} \leq \lambda_B \leq 370 \text{ nm}$. Preferably, the optical transmittance of the layer B at the wavelength of 370 nm is not more than 10%.

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Preferably, the second UV absorber is an organic compound, which may be advantageously selected from the group of substituted benzophenones, salicylic esters, cinnamic esters, oxanilides, benzoxazinones, hydroxyphenylbenzotriazoles or benzylidenemalonate. However, it showed to be particularly advantageous to use a benzotriazole type UV absorber as the second UV absorber.

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In particular, a combination of a triazine type compound as a first UV absorber in the layer A with a benzotriazole type compound as a second UV absorber in the layer B surprisingly led to a particularly high weathering stability of the multi-layer foil of the present invention. For instance, the layer A may comprise from 0.5 to 3.0 wt.-%, based on the weight of the layer A, of a triazine type compound as a first UV absorber; the layer B may comprise from 0.5 to 4.0 wt.-%, based on the weight of the layer B, of a benzotriazole type compound as a second UV absorber.

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Benzotriazole type UV absorbers are known in the prior art and are typically 2-(2'-hydroxyphenyl)benzotriazoles. The corresponding compounds include in particular 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3',5'-di-*tert*-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-*tert*-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-*tert*-butyl-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-*tert*-butyl-2'-hydroxy-5'-methylphenyl)-5-chloro-benzotriazole, 2-(3'-*sec*-butyl-5'-*tert*-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-*tert*-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis-(α,α -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-*tert*-butyl-2'-hydroxy-5'-(2-octyloxy-carbonylethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-*tert*-butyl-5'-[2-(2-ethylhexyloxy)-carbonylethyl]-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-*tert*-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-*tert*-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)benzotriazole, 2-(3'-*tert*-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-*tert*-butyl-2'-hydroxy-5'-(2-isooctyloxy-carbonylethyl)phenyl)benzotriazole, 2,2'-methylene-bis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-ylphenol]; the transesterification product of 2-[3'-*tert*-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-2*H*-benzotriazole with polyethylene glycol 300; [R-

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CH₂CH₂-COO-CH₂CH₂- , where R = 3'-*tert*-butyl-4'-hydroxy-5'-2*H*-benzotriazol-2-ylphenyl, 2-[2'-hydroxy-3'-(α,α -dimethylbenzyl)-5'-(1,1,3,3-tetramethylbutyl)-phenyl]-benzotriazole; 2-[2'-hydroxy-3'-(1,1,3,3-tetramethylbutyl)-5'-(α,α -dimethylbenzyl)-phenyl]benzotriazole. Further examples of UV absorbers of benzotriazole type that can be used are 2-(2-hydroxy-5-methylphenyl)benzotriazole, 2-[2-hydroxy-3,5-di(α,α -dimethylbenzyl)phenyl]benzotriazole, 2-(2-hydroxy-3,5-di-*tert*-butylphenyl)benzotriazole, 2-(2-hydroxy-3,5-butyl-5-methylphenyl)-5-chlorobenzotriazole, 2-(2-hydroxy-3,5-di-*tert*-butylphenyl)-5-chlorobenzotriazole, 2-(2-hydroxy-3,5-di-*tert*-amylphenyl)benzotriazole, 2-(2-hydroxy-5-*tert*-butylphenyl)benzotriazole, 2-(2-hydroxy-3-*sec*-butyl-5-*tert*-butylphenyl)benzotriazole and 2-(2-hydroxy-5-*tert*-octylphenyl)benzotriazole, phenol, 2,2'-methylenebis[6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)]. These compounds are commercially available from BASF SE (Ludwigshafen, Germany) e.g. as Tinuvin® 360 and Tinuvin® 234.

Benzotriazole type UV absorber may also be used in combination with other UV absorbers, for instance with a bis-maloneate type UV absorber. An example of such combination is Eusorb® BLA 4200M (commercial product comprising Tinuvin® 329 and Hostavin® B-CAP), available from Eutec Chemical Co. Ltd.

The amounts the benzotriazole type UV absorber in the layer B of are from 0.1 to 5.0 wt.-%, preferably from 0.2 to 4.0 wt.-% and very particularly preferably from 0.5 to 3.0 wt.-%, based on the weight of the PMMA-based layer B. It is also possible to use mixtures of different benzotriazole type UV absorbers.

Suitable 2-hydroxybenzophenones may include *inter alia* 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

Suitable esters of substituted and unsubstituted benzoic acids are for example 4-*tert*-butyl-phenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-*tert*-butylbenzoyl)resorcinol, benzoyl resorcinol, 2,4-di-*tert*-butylphenyl 3,5-di-*tert*-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-*tert*-butyl-4-hydroxybenzoate, octadecyl 3,5-di-*tert*-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-*tert*-butylphenyl 3,5-di-*tert*-butyl-4-hydroxybenzoate.

Further additives

If desired, layers of the foil of the present invention may further contain one or more UV stabilisers which typically act as antioxidants, radical scavengers, etc. Particularly preferred UV stabilisers are sterically hindered phenols and HALS type additives.

Sterically hindered amines, HALS (Hindered Amine Light Stabilizer) UV stabilizers are per se known. They can be used to inhibit ageing phenomena in paints and plastics, especially in polyolefin plastics (Kunststoffe, 74 (1984) 10, pp. 620-623; Farbe + Lack, Volume 96, 9/1990, pp. 689-693). The tetramethylpiperidine group present in the HALS compounds is responsible for the stabilizing effect. This class of compound can have no substitution on the piperidine nitrogen or else substitution by alkyl or acyl groups on the piperidine nitrogen. The sterically hindered amines do not absorb in the UV region. They scavenge free radicals that have been formed, whereas the UV absorbers cannot do this. Examples of HALS compounds which have stabilizing effect and which can also be used in the form of mixtures are: bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro(4,5)-decane-2,5-dione, bis(2,2,6,6-tetramethyl-4-piperidyl) succinate, poly(*N*-β-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine succinate) or bis(*N*-methyl-2,2,6,6-tetramethyl-4-piperidyl) sebacate.

The amounts used of the HALS compounds in the layers are typically from 0.0 to 5.0 wt.-%, preferably from 0.1 to 3.0 wt.-% and very particularly preferably from 0.2 to 2.0 wt.-%, based on the weight of the layer. It is also possible to use mixtures of different HALS compounds.

Other co-stabilizers that can be used are the HALS compounds described above, disulphites, such as sodium disulphite, and sterically hindered phenols and phosphites. Such co-stabilizers may be present in a concentration of 0.1 to 5.0 wt.-%, based on the weight of each layer.

Sterically hindered phenols are also suitable for use in the foil of the present invention. Preferred sterically hindered phenols include *inter alia* 6-*tert*-butyl-3-methylphenyl derivatives, 2,6-di-*tert*-butyl-*p*-cresol, 2,6-*tert*-butyl-4-ethyl phenol, 2,2'-methylenebis-(4-ethyl-6-*tert*-butyl phenol), 4,4'-butylidenebis(6-*tert*-butyl-*m*-cresol), 4,4'-thiobis(6-*tert*-butyl-*m*-cresol), 4,4'-dihydroxy diphenyl cyclohexane, alkylated bisphenol, styrenated phenol, 2,6-di-*tert*-butyl-4-methyl phenol, *n*-octadecyl-3-(3',5'-di-*tert*-butyl-4'-hydroxy phenyl)propionate, 2,2'-methylenebis(4-methyl-6-*tert*-butyl phenol), 4,4'-thiobis(3-methyl-6-*tert*-butylphenyl), 4,4'-butylidenebis(3-methyl-6-*tert*-butylphenol), stearyl-β(3,5-di-4-butyl-4-hydroxy phenyl)propionate, 1,1,3-tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3-5-di-*tert*-butyl-4-hydroxybenzyl)benzene, tetrakis[methylene-3(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)propionate]methane. Commercially available sterically hindered phenols include Sumilizer™ BHT BP-76, WXR, GA-80 and BP-101 (Sumitomo Chemical, Osaka, Japan), Irganox® 1076, 565, 1035, 1425WL, 3114, 1330 and 1010 (BASF SE, Ludwigshafen, Germany), MARK AO-50,-80, -30, -20, -330 and -60 (ADEKA Polymer Additives, Mulhouse, France), and Tominox® SS, TT (Mitsubishi Chemical Corporation, Yoshitomi, Japan).

Adhesion-promoting copolymer

The adhesion-promoting copolymer in the layer B and/or in the layer C, if layer C is present, comprises:

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- (i) from 70.0 to 95.0 wt.-% methyl methacrylate;
- (ii) from 0.5 to 15.0 wt.-% maleic anhydride; and
- (iii) from 0.0 to 25.0 wt.-% of other vinyl-copolymerizable monomers having no functional groups other than the vinyl function, based on the weight of the adhesion-

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promoting copolymer.

The monomers (i) are selected from the group of alkyl(meth)acrylates having 1 to 6 carbon atoms in the ester group such as ethylmethacrylate, propylmethacrylate, isopropylmethacrylate, butylmethacrylate, isobutylmethacrylate, *tert*-butylmethacrylate, pentylmethacrylate, isopentylmethacrylate, hexylmethacrylate, 2,2-dimethylbutylmethacrylate, cyclopentylmethacrylate, and cyclohexylmethacrylate as well as the particularly preferred methylmethacrylate.

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The monomers (iii) can be selected from a group of vinyl aromatic substances such as α -halogen styrene, *p*-methylstyrene, *p-tert*-butylstyrene, vinylnaphthalene, as well as, preferably, α -methyl styrene and styrene, wherein styrene is particularly preferred.

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The adhesion-promoting monomers (ii) are those monomers capable of free-radical polymerization which have functional groups which can interact with the materials to be coated. This interaction is to be brought about at least via a chemical (covalent) bond. In addition, it may be promoted, by way of example, by hydrogen bonding, complexing, dipole forces or thermodynamic compatibility (*intertwining* of the polymer chains) or the like. These interactions generally involve heteroatoms, such as nitrogen or oxygen. Functional groups which may be mentioned are the amino group, in particular the dialkylamino group, (cyclic) amide group, imide group, hydroxy group, (ep)oxy group, carboxy group, (iso)cyno group, carboxylic acid group, anhydride group or imido group. These monomers are known per se (*cf.* H. Rauch Puntigam, Th. Völker, *Acryl und Methacrylverbindungen*, Springer-Verlag 1967; Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd. Ed., Vol. 1, pp. 394-400, J. Wiley 1978; DE-A 25 56 080; DE-A 26 34 003).

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The adhesion-improving monomers therefore preferably belong to the monomer class of the nitrogen-containing vinyl heterocycles preferably having 5-membered rings alongside 6-membered rings, and/or of the copolymerizable vinylic carboxylic acids and/or of the hydroxyalkyl-, alkoxyalkyl-, epoxy- or aminoalkyl substituted esters, anhydrides or amides of fumaric, maleic, itaconic, acrylic, or methacrylic acid. Nitrogen-heterocyclic monomers which may particularly be mentioned are those from the class of the vinylimidazoles, of the vinyl lactams, of the vinylcarbazoles, and of the

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vinylpyridines. Examples of these monomeric imidazole compounds, which are not intended to represent any form of restriction, are *N*-vinylimidazole (also termed vinyl-1-imidazole), *N*-vinylmethyl-2-imidazole, *N*-vinylethyl-2-imidazole, *N*-vinylphenyl-2-imidazole, *N*-vinylmethyl-2,4-imidazole, *N*-vinylbenzimidazole, *N*-vinylimidazoline (also termed vinyl-1-imidazoline), *N*-vinylmethyl-2-imidazoline, *N*-vinylphenyl-2-imidazoline and vinyl-2-imidazole.

Particular examples which may be mentioned of monomers derived from the lactams are compounds such as the following: *N*-vinylpyrrolidone, *N*-vinylmethyl-5-pyrrolidone, *N*-vinylmethyl-3-pyrrolidone, *N*-vinylethyl-5-pyrrolidone, *N*-vinylmethyl-5,5-pyrrolidone, *N*-vinylphenyl-5-pyrrolidone, *N*-allylpyrrolidone, *N*-vinylthiopyrrolidone, *N*-vinylpiperidone, *N*-vinyl-diethyl-6,6-piperidone, *N*-vinylcaprolactam, *N*-vinylmethyl-7-caprolactam, *N*-vinylethyl-7-caprolactam, *N*-vinylmethyl-7,7-caprolactam, *N*-allylcaprolactam, *N*-vinylcaprylactam.

Among the monomers which derive from carbazole mention may particularly be made of: *N*-vinylcarbazole, *N*-allylcarbazole, *N*-butenylcarbazole, *N*-hexenylcarbazole and *N*-(methyl-1-ethylene)carbazole. Among the copolymerizable vinylic carboxylic acids, mention may in particular be made of maleic acid, fumaric acid, itaconic acid and suitable salts, esters or amides of the same. Mention may also be made of the following epoxy-, oxy or alkoxy-substituted alkyl esters of (meth)acrylic acid: glycidyl methacrylate, 2-hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 2-butoxyethyl (meth)acrylate, 2-(2-butoxyethoxy)ethyl methacrylate, 2-(ethoxyethoxy)ethyl (meth)acrylate, 4-hydroxybutyl(meth)acrylate, 2-[2-(2-ethoxyethoxy)ethoxy]ethyl(meth)acrylate, 3-methoxybutyl-1-(meth)acrylate, 2-alkoxymethylethyl (meth)acrylate, 2-hexoxyethyl(meth)acrylate.

Mentioned may also be the following amine-substituted alkyl esters of (meth)acrylic acid: 2-dimethylaminoethyl (meth)acrylate, 2-diethylaminoethyl, (meth)acrylate, 3-dimethylamino-2,2-dimethylpropyl 1-(meth)acrylate, 3-dimethylamino-2,2-dimethylpropyl 1-(meth)acrylate, 2-morpholinoethyl(meth)acrylate, 2-*tert*-butylaminoethyl (meth)acrylate, 3-(dimethylamino)propyl (meth)acrylate, 2-(dimethylaminoethoxyethyl)(meth)acrylate.

Mention may be made by way of example of the following monomers which are representatives of the (meth)acrylamides: *N*-methyl(meth)acrylamide, *N*-dimethylaminoethyl(meth)acrylamide, *N*-dimethylaminopropyl(meth)acrylamide, *N*-isopropyl(meth)acrylamide, *N*-*tert*-butyl(meth)acrylamide, *N*-isobutyl(meth)acrylamide, *N*-decyl(meth)acrylamide, *N*-cyclohexyl(meth)acrylamide, *N*-[3-(dimethylamino)-2,2-dimethylpropyl]methacrylamide, *N*-[2-hydroxyethyl](meth)acrylamide.

It is particularly advantageous to use "adhesion promoting monomers" (ii) selected from the group consisting of GMA (glycidyl methacrylate), maleic acid derivatives, such as maleic acid, maleic anhydride (MA), methylmaleic anhydride, maleimide, methylmaleimide, maleamides (MAs),

phenylmaleimide and cyclohexylmaleimide, fumaric acid derivatives, methacrylic anhydride, acrylic anhydride.

Preferably, the adhesion-promoting monomer (ii) is maleic anhydride.

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The alkylacrylates (iv) may be optionally incorporated in amounts of up to 5.0 wt.-% to improve the rheological properties of the adhesion-promoting copolymer. Alkylacrylates having 1 to 6 carbon atoms in the ester group may be, for example, ethylacrylate, isopropylacrylate, propylacrylate, isobutylacrylate, *tert*-butylacrylate, pentylacrylate, hexylacrylate as well as, preferably, butylacrylate and the especially preferred methylacrylate.

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In a preferred embodiment, the adhesion-promoting copolymer comprises:

- 15 (i) from 50.0 to 95.0 wt.-%, preferably 60.0 to 90.0 wt.-%, more preferably from 70.0 to 85.0 wt.-%, even more preferably 70 to 80 wt.-% methyl methacrylate;
- (ii) from 0.2 to 25.0 wt.-%, preferably from 0.5 to 20.0 wt.-%, more preferably from 1.0 to 15.0 wt.-% and even more preferably 5.0 to 12.0 wt.-% maleic anhydride; and
- (iii) from 0.0 to 25.0 wt.-%, preferably from 2.0 to 15.0 wt.-% of other vinyl-copolymerizable monomers having no functional groups other than the vinyl function, based on the weight
20 of the copolymer.

In a particularly preferred embodiment, the adhesion-promoting copolymer is a copolymer of MMA, styrene and maleic anhydride.

- 25 The adhesion-promoting copolymer may be obtained in a manner known per se via free-radical polymerization. By way of example, EP 264 590 A1 describes a process for preparing a copolymer from a monomer mixture composed of methyl methacrylate, vinylaromatic compound, maleic anhydride and, where appropriate, from a lower alkyl acrylate, by carrying out the polymerization to 50 % conversion in the presence or absence of a non-polymerizable organic solvent, and
30 continuing the polymerization beyond a conversion of at least 50 % in the temperature range from 75 to 150 °C in the presence of an organic solvent to at least 80 % conversion, and then evaporating the low-molecular-weight volatile constituents.

- JP-A 60-147 417 describes a process for preparing a suitable adhesion-promoting copolymer by
35 feeding, at a temperature of from 100 to 180°C, a monomer mixture composed of methyl methacrylate, maleic anhydride and at least one vinylaromatic compound into a polymerization reactor suitable for solution polymerization or bulk polymerization, and polymerizing the material. DE-A 44 40 219 describes a further preparation process.

The adhesion-promoting copolymers described in EP 264 590 A1 and JP-A 60-147 417 may be advantageously used in the foil of the present invention.

Fluoropolymer

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Depending on the intended use of the foil of the present invention the fluoropolymer may be selected from polyvinylidene fluoride (PVDF), polyvinylfluoride (PVF), polytetrafluoroethylene (PTFE), polyethylenetetrafluoroethylene (ETFE), fluorinated ethylene-propylene (FEP) or a mixture or copolymers thereof. In order to additionally improve weathering stability of the foil of the present

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invention, the fluoropolymer may further comprise copolymerised UV absorbing agents.

The PVDF polymers used in the foil are generally transparent, semicrystalline, thermoplastic fluoroplastics. Advantageously, the PVDF has a high crystalline fusing point. The heat resistance of the foil is particularly high when, the crystalline fusing point of the PVDF is at least 150 °C and

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more preferably at least 160 °C. The upper limit of the crystalline fusing point is preferably approximately 175 °C, which is equal to the crystalline fusing point of PVDF. It is further preferred that the weight average molecular weight Mw of the PVDF ranges from 50 000 to 300 000 g/mol, more preferably from 80 000 to 250 000 g/mol, even more preferably from 150 000 to 250 000 g/mol as determined by GPC.

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The fundamental unit for PVDF is vinylidene fluoride, which is polymerized by means of a specific catalyst to give PVDF in high-purity water under controlled conditions of pressure and of temperature. Vinylidene fluoride is obtainable by way of example from hydrogen fluoride and methylchloroform as starting materials, using chlorodifluoroethane as precursor. In principle, any

commercial grade of PVDF such as Kynar® grades produced by Arkema, Dyneon® grades produced by Dyneon, or Solef® grades produced by Solvay is suitable for use in the present invention. For instance, the following commercial products may be employed: Kynar® 720 (vinylidene fluoride content: 100 wt.-%, crystalline fusing point: 169 °C) and Kynar® 710 (vinylidene fluoride content: 100 wt.-%, crystalline fusing point: 169 °C) manufactured by ARKEMA; T850 (vinylidene fluoride content: 100 wt.-%, crystalline fusing point: 173 °C) manufactured by KUREHA Corporation; Solef® 1006 (vinylidene fluoride content: 100 wt.-%, crystalline fusing point: 174 °C) and Solef® 1008 (trade name) (vinylidene fluoride content: 100 wt.-%, crystalline fusing point: 174 °C) manufactured by Solvay Solexis.

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PVDF has 3 linkage modes as linkage modes of monomer: head to head linkage; tail to tail linkage; and head to tail linkage, in which the head to head linkage and the tail to tail linkage are referred to as "*hetero linkage*". The chemical resistance of the layer A is particularly high when the "*rate of hetero linkage*" in the PVDF is not greater than 10 mol.-%. From the viewpoint of lowering the rate of hetero linkage, the PVDF is preferably a resin produced by suspension polymerization.

The rate of hetero linkage can be determined from a peak of a ^{19}F -NMR spectrum of the PVDF as specified in EP 2 756 950 A1.

- 5 Typically, the fluoropolymer is not cross-linked and it therefore suitable for thermoplastic processing.

- 10 The PVDF may include a flatting agent to such a degree that the transparency of the layer A is not deteriorated. As the flatting agent, an organic flatting agent and an inorganic flatting agent can be used.

- 15 In one embodiment, the fluoropolymer is a predominantly amorphous, or a microcrystalline PVDF with a haze value smaller than 5. The haze value is measured for this purpose on a pure fluoropolymer (PVDF) foil of thickness 30 μm at 23°C in accordance with ASTM D1003. Examples of types of PVDF having particularly good suitability with appropriately low haze value are Solef® 6008 from Solvay, T850 from Kureha and Kynar® 9000HD from Arkema.

Glass beads

- 20 The fluoropolymer-based layer D, if present, may optionally comprise glass beads. In this embodiment, the content of the glass beads dispersed in the polymeric matrix of the layer D is usually from 3.0 to 30.0 wt.-%, more preferred from 5.0 to 20.0 wt.-%, and particularly preferred from 7.0 to 15.0 wt.-%, based on the total weight of the layer D.

- 25 Furthermore, glass beads may be used as a first UV absorber in the layer A.

The glass beads may have an aspect ratio of at least about 4 : 1, more preferably at least about 2 : 1. Ideally, the glass beads are substantially spherical *i.e.* have an aspect ratio of about 1 : 1.

- 30 The glass beads advantageously have a narrow size distribution. The size distribution may be measured by conventional apparatus such as a Malvern particle size analyzer *e.g.* by Mastersizer 2000. Typically, the glass beads are solid (*i.e.* non-hollow) glass beads, are not limited to any chemical composition and can have either a smooth surface or an etched surface. The surface etching can be conveniently performed by contacting the glass beads with nitric acid for a time
35 sufficient to give the desired degree of etching of the surface. For achieving an optimal adhesion between the glass beads and the fluoropolymer-based matrix, the glass beads may also have a siloxane layer.

Depending on the desired optical properties of the foil and the desired surface roughness, the size of the glass beads (average diameter, weight averaged) is typically chosen to be from 2.0 μm to 30.0 μm , preferably from 3.0 μm to 20.0 μm , even more preferably from 5.0 μm to 15.0 μm .

- Typically, if glass beads with an average diameter below 2.0 μm are used, the surface of the resulting foil no longer appears matt. On the other hand, use of glass beads having an average diameter above 30.0 μm leads to a relatively high surface roughness, which is undesirable for many applications.

- The size of the glass beads – indicated as so-called d_{50} -value (that is 50 percent by volume of the particles have a particle size below the specified average particle size) can be measured in accordance with the standard norm for laser diffraction measurements ISO 13320 (2009). Typically, the size of the glass beads is determined in each case (at a dispersion of the particles in butyl acetate refractive index: 1,462) by laser light scattering (at room temperature 23 °C) using a Malvern Mastersizer 2000 from Malvern Instruments with the mini-dispersing MS1 at 2000 revolutions per minute and evaluation by Fraunhofer. A further equally suitable instrument for this purpose is Beckman Coulter LS 13 320 laser diffraction particle size analyser.

For the sake of achieving good mechanical properties of the foil, the glass beads are preferably non-hollow *i.e.* solid.

- The refractive index of the glass beads, measured for the Na-D line (589 nm) at 20 °C is selected to differ from the refractive index of the polymeric material matrix in the fluoropolymer-based layer A by from 0.01 to 0.2 units.

- The chemical composition of the glass beads is not particularly limited and substantially any commercially available sorts of glass can be employed. These include in particular fused silica glass, soda-lime-silica glass, sodium borosilicate glass, lead-oxide glass, aluminosilicate glass and oxide glass, wherein use of a soda-lime-silica glass is particularly preferred.

- The refractive index of a soda-lime-silica glass is usually from 1.51 to 1.52. In a particularly preferred embodiment, the glass beads have the following composition:

from 70.0 to 75.0 wt.% SiO_2

from 12.0 to 15.0 wt.% Na_2O

- from 0.0 to 1.5 wt.% K_2O

from 7.0 to 12.0 wt.% CaO

from 0.0 to 5.0 wt.% MgO

from 0.1 to 2.5 wt.% Al_2O_3

from 0.0 to 0.5 wt.% Fe_2O_3

Examples of suitable glass beads are Spherglass® products such as Spherglass® 7025 and Spherglass® 5000 available from Potters Industries LLC. or Omicron® glass beads Omicron® NP3 and Omicron® NP5 obtainable from Sovitec Mondial S.A. Furthermore, use of coloured glass beads having a particle size below 10 μm is particularly advantageous in terms of efficient UV absorption and high degree of transmission of visible light. Although the choice of the glass for this purpose is not particularly limited, glass sorts such as GG395, GG400, GG420, GG435, GG475, OG515, OG 530, available from Schott AG (Mainz, Germany) showed to be particularly useful.

Properties of the foil

Typically, the foil of the present invention has an average transmittance of not more than 40%, preferably not more than 30%, more preferably not more than 10% in a wavelength interval from 350 nm to 390 nm.

As already outlined above, the foil of the present invention has excellent weathering stability and mechanical properties. In particular, the elongation at break of the foil, measured by a common method such as the one described in the norm ISO 527-3 (2003), after accelerated weathering testing for 6 000 h, performed according to the norm ISO 4892-2, method A, cycle 1 (2013), is at least 60%, preferably at least 70%, even more preferably at least 90% of the initial elongation at break of the foil.

Furthermore, even upon use of relatively small amounts of the first and the second UV absorbers in the multilayer foil, after accelerated weathering testing for 15 000 h (30 GJ/m^2 radiant exposure), according to the norm ISO 4892-2 (2013), method A, cycle 1, the optical transmittance of the foil at any wavelength λ is usually is not more than 10%, preferably not more than 5%, more preferably not more than 2%, even more preferably not more than 1%; wherein $270 \text{ nm} \leq \lambda \leq 370 \text{ nm}$.

The weathering test is carried out according to DIN EN ISO 4892-2 (2013), method A with cycle No 1 under the following conditions:

Exposure period (dry / water spray) [min]	102 / 18
Black standard temperature [$^{\circ}\text{C}$]	65 +/- 3
Irradiance (300 – 400nm) [W/m^2]	60 +/- 2
Relative humidity [%]	65 +/-10
Chamber air temperature [$^{\circ}\text{C}$]	38 +/- 3

Typically, the foil of the present invention has a luminous transmittance (D_{65}) of more than 60%, preferably more than 70%, more preferably more than 80% for each wavelength from 400 nm to 800 nm, measured before a weathering test according to norm DIN EN ISO 13468-2 (2006).

5 Process for the manufacturing of the foil

Depending on the intended application, the foil of the present invention can be produced substantially at any desired thickness. A surprising factor here is the ability to obtain an exceptional weathering resistance and mechanical stability and a very high weathering and mechanical
10 protection provided to the substrate. However, for the purposes of the invention preference is given to a relatively thin foil, characterized by a thickness in the range from 10.0 to 200.0 μm , preferably in the range from 40.0 to 120.0 μm , particularly preferably in the range from 50.0 to 90.0 μm .

The mixtures of individual components of the layers can be prepared via dry blending of the
15 components, which are in pulverulent, granular, or preferably pelletized, form. Such mixtures may also be processed via melting and mixing of the individual components in the molten state or via melting of dry premixes of the individual components to give a ready-to-use moulding composition. By way of example, this may take place in single- or twin-screw extruders. The resultant extrudate may then be pelletized. Conventional additives, auxiliaries and/or fillers may be admixed directly or
20 added subsequently by the final user as required.

The multilayer foil of the present invention can then be produced by methods known per se, examples being co-extrusion or lamination or by extrusion lamination.

25 Application of the foil onto a substrate

The inventive foils have a broad range of applications. One preferred use of the foils is coating of plastics mouldings or metallic items. In particular, the substrate protected by the foil may be a melamine-resin-impregnated paper, a polymeric material which is optionally fibre-reinforced,
30 preferably polyvinyl chloride (PVC), polycarbonate (PC) or polypropylene (PP) or a metal, preferably steel or aluminium, and the co-extruded foil is directly applied to the substrate.

Here, it is particularly advantageous to coat plastics mouldings which comprise PVC, or are composed of PVC. The protected substrate is advantageously by way of example a window profile
35 composed of aluminium, of wood, of plastic or of a composite material, may bear a decorative foil, preferably composed of PC, SAN or PVC. This article is then protected from weathering by using the inventive foil. Another preferred use of the inventive foil is design of a high-specification, durable surface finish for substrate materials. Furthermore, the foils can be advantageously used in traffic control materials (TCM).

As will be readily appreciated by a skilled person, the foil of the present invention is applied to a substrate in such a way that the layer A is directed towards the outer surface of the coated substrate. In other words, if the foil of the present invention substantially consists of layers A and B, the layer B is located between the layer A and the substrate. In embodiments, in which the foil of the present invention further comprises the layer C, the layer C is located between the layer B and the surface of the coated substrate.

A further aspect of the present invention is a process for the manufacturing of a coated article, comprising a step of applying a foil onto the surface of said substrate. This coated article comprises a substrate and has an outer surface, wherein the substrate is at least partially covered by a foil, wherein said foil has layers arranged in the following order, beginning from the outer surface of the coated article:

- the layer D, if present,
- the layer A,
- the layer E, if present,
- the layer B, and
- the layer C, if present.

Application of the inventive foil onto a substrate is in all cases relatively simple. The foil is preferably applied by means of co-extrusion to the material to be protected. Application of the foil by means of foil lamination to the material to be protected is also possible. Preference is also given to a use which is characterized in that the foil is applied by means of extrusion lamination to the material to be protected. Preferably, extrusion lamination is carried out at a temperature greater than or equal to 120°C and upon application of a mechanical pressure greater than or equal to 1 MPa, preferably greater than or equal to 2 MPa, more preferably greater than or equal to 4 MPa, more preferably greater than or equal to 6 MPa, more preferably greater than or equal to 7 MPa.

In one embodiment of the present invention, the article itself may be a foil or a sheet, which can be conveniently stored and/or handled in form of a roll.

In some embodiments the coated article of the present invention may be a high-pressure laminate (HPL), a medium pressure laminate (MPL) or a continuous pressure laminate (CPL). In a particularly preferred embodiment, multi-layer materials obtainable using the foil of the invention are decorative high-pressure laminates (HPLs) according to EN 438-6, which are composed of layers of webs of fibrous material (e.g. paper), impregnated with curable resins, these being bonded to one another by means of the high-pressure process described below. The surface layer of the material, one or both sides of which have decorative colours or patterns, is impregnated with resins based on amino plastics, e.g. melamine resins. The amino or methylolamino groups present

in the decorative layer during the high-pressure process then serve as reaction partners for covalent bonding to the polymethacrylate layer (in this case foils) for surface finishing. The corresponding high-pressure laminates are described *inter alia* in US 2017/019 7391 A1.

- 5 Hence, one aspect of the present invention relates to a process for the manufacturing of a high-pressure laminate using the foil as described above.

The high-pressure process produces a long-lasting bond between the decorative layer and the polymethacrylate layer applied according to the invention. The temperature set during the process
10 and the associated interpenetration of the melamine-resin-saturated decorative paper into the foil ensures sufficient formation of covalent bonds and therefore long-lasting bonding to the material.

The high-pressure process is defined as simultaneous use of heat (temperature greater than or equal to 120 °C) and high pressure (greater than or equal to 3 MPa), the result being that the
15 curable resins flow and then harden to produce a homogeneous non-porous material of relatively high density (at least 1.35 g/cm³) having the required surface structure.

Typically, the coated article of the present invention has the following arrangement of layers within the multilayer foil:

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the layer D, if present, forms an outer surface of the coated article;
the layer A is located between the layer D and the substrate;
the layer E, if present, is located between the layer A and the layer B
the layer B is located between the layer A and the substrate; and
25 the layer C, if present, is located between the layer B and the substrate.

The following examples will illustrate the present invention in a greater detail without being limiting.

Examples

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The weathering tests were carried out according to DIN EN ISO 4892-2 (2013), method A with cycle No 1 at the wavelength range from 300 to 400 nm under the following conditions:

Exposure period (dry / water spray) [min]	102 / 18
35 Black standard temperature [°C]	65 +/- 3
Irradiance (300 – 400nm) [W/m ²]	60 +/- 2
Relative humidity [%]	65 +/-10
Chamber air temperature [°C]	38 +/- 3

Optical assessments were made after 0 h, 1 000 h, 2 000 h, 4 000 h, 6 000 h, 8 000 h, 10 000 h, 12 000 h, 14 000 h and 16 000 h.

5 The protective foils were produced by adapter co-extrusion using chill-roll process at 240-250 °C (melt temperature) at extrusion speed 7.3 m/min using a 35 mm-diameter single screw extruder and a 25 mm-diameter single screw co-extruder, in case of a 3-layer foil a second 25 mm-diameter single screw co-extruder was used. Alternatively, production can be achieved by way of a multiple-manifold co-extrusion process or a combination of adapter and multiple-manifold co-extrusion.

10 The adhesion promoter used was a copolymer of 75 wt.-% of MMA, 15 wt.-% of styrene and 10 wt.-% of maleic anhydride. The weight-average molar mass M_w of this copolymer was about 100 000 g/mol (determined by means of GPC against a PMMA standard).

15 Accelerated weathering testing was performed according to the norm ISO 4892-2 (2013) as described above.

Production Example 1 (comparative foil according to WO 2007/0074138 A1)

20 A PMMA monolayer foil having a total thickness of 53 μm was prepared by extrusion at 240-250 °C (melt temperature) at extrusion speed 7.3 m/min using a 35 mm-diameter single screw extruder and a 25 mm-diameter single screw co-extruder.

The monolayer foil had the following composition:

- 25 a) 85.7 wt.-% of a polymer acrylic core shell impact modifier with a composition of
61.3 wt.-% of methyl methacrylate,
38.0 wt.-% of butyl acrylate,
0.7 wt.-% of allyl methacrylate,
- b) 12.3 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- 30 c) 1.0 wt.-% of Tinuvin® 360 (phenol-2,2'-methylene-bis(6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl))), available from BASF SE (Ludwigshafen, Germany),
- d) 0.7 wt.-% of Tinuvin® 1600 (6-[4,6-bis(4-phenylphenyl)-1,2-dihydro-1,3,5-triazin-2-ylidene]-3-[(2-ethylhexyl)oxy]cyclohexa-2,4-dien-1-one), available from BASF SE
- 35 e) 0.3 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny]amino)-1,3,5-triazin-2-yl]amino]propyl]-*N'*,*N'*"-dibutyl-*N'*,*N'*"-bis(1,2,2,6,6-pentamethyl-4-piperidiny)]), available from Sabo S.p.A (Levate, Italy).

Production Example 2 (foil according to the invention)

PMMA-based bilayer foil having a thickness of 53 μm was prepared by co-extrusion under the same conditions as in Example 1.

5

The layer A had a thickness of 23 μm and the following composition:

- a) 85.7 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,
- b) 12.3 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- c) 1.72 wt.-% of Tinuvin® 1600, available from BASF SE
- d) 0.3 wt.-% of Sabo®stab UV 119, available from Sabo S.p.A.

15

The transmittance of the layer A at the wavelength of 360 nm was 1.7%. The spectral transmittance of the layer A at any wavelength λ_A was not more than 10%, wherein $270 \text{ nm} \leq \lambda_A \leq 360 \text{ nm}$.

- 20 The layer B had a thickness of 30 μm and the following composition:

- a) 85.7 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,
- b) 12.3 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- c) 1.7 wt.-% of Tinuvin® 360, available from BASF SE
- d) 0.3 wt.-% of Sabo®stab UV 119, available from Sabo S.p.A.

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- 30 The spectral transmittance of the layer B at any wavelength λ_B was not more than 10%, wherein $270 \text{ nm} \leq \lambda_B \leq 370 \text{ nm}$.

Production Example 3 (comparative foil)

- 35 PMMA-based bi-layer foil having a thickness of 58 μm was prepared by co-extrusion under the same conditions as in Example 1.

The layer D had a thickness of 5 μm and the following composition:

- a) 100.0 wt.-% of a KF Polymer 850 PVDF, available from KUREHA CORPORATION

The layer C had a thickness of 53 μm and the following composition:

- 5 a) 85.7 wt.-% of a polymer acrylic core shell impact modifier with a composition of
61.3 wt.-% of methyl methacrylate,
38.0 wt.-% of butyl acrylate,
0.7 wt.-% of allyl methacrylate,
b) 12.3 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
10 c) 1.0 wt.-% of Tinuvin® 360 (phenol-2,2'-methylene-bis(6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl))), available from BASF SE (Ludwigshafen, Germany),
d) 0.7 wt.-% of Tinuvin® 1600 (6-[4,6-bis(4-phenylphenyl)-1,2-dihydro-1,3,5-triazin-2-ylidene]-3-[(2-ethylhexyl)oxy]cyclohexa-2,4-dien-1-one), available from BASF SE
e) 0.3 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-ethanediybis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazin-2-yl]amino]propyl]-*N*',*N*'-dibutyl-*N*',*N*'-bis(1,2,2,6,6-pentamethyl-4-piperidinyl)]),
15 available from Sabo S.p.A (Levate, Italy).

Production Example 4 (foil according to the invention)

20

PMMA-based triple-layer foil having a thickness of 58 μm was prepared by co-extrusion under the same conditions as in Example 1.

The layer D had a thickness of 5 μm and the following composition:

25

- a) 100.0 wt.-% of a KF Polymer 850 PVDF, available from KUREHA CORPORATION

The layer A had a thickness of 23 μm and the following composition:

- 30 b) 85.7 wt.-% of a polymer acrylic core shell impact modifier with a composition of
61.3 wt.-% of methyl methacrylate,
38.0 wt.-% of butyl acrylate,
0.7 wt.-% of allyl methacrylate,
b) 12.3 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
35 c) 1.72 wt.-% of Tinuvin® 1600, available from BASF SE
d) 0.3 wt.-% of Sabo®stab UV 119, available from Sabo S.p.A.

The transmittance of the layer A at the wavelength of 360 nm was 1.7%. The spectral transmittance of the layer A at any wavelength λ_A was not more than 10%, wherein $270 \text{ nm} \leq \lambda_A \leq 360 \text{ nm}$.

5 The layer B had a thickness of 30 μm and the following composition:

- 10 b) 85.35 wt.-% of a polymer acrylic core shell impact modifier with a composition of

61.3 wt.-% of methyl methacrylate,

38.0 wt.-% of butyl acrylate,

0.7 wt.-% of allyl methacrylate,

 b) 12.3 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,

 c) 2.05 wt.-% of Tinuvin® 360, available from BASF SE

 d) 0.3 wt.-% of Sabo®stab UV 119, available from Sabo S.p.A.

15 The spectral transmittance of the layer B at any wavelength λ_B was not more than 10%; wherein $270 \text{ nm} \leq \lambda_B \leq 370 \text{ nm}$.

Production Example 5 (comparative foil)

20 PMMA-based bi-layer foil having a thickness of 58 μm was prepared by co-extrusion under the same conditions as in Example 1.

The layer D had a thickness of 5 μm and the following composition:

- 25 b) 100.0 wt.-% of a KF Polymer 850 PVDF, available from KUREHA CORPORATION

The layer C had a thickness of 53 μm and the following composition:

- 30 a) 83.0 wt.-% of a polymer acrylic core shell impact modifier with a composition of

61.3 wt.-% of methyl methacrylate,

38.0 wt.-% of butyl acrylate,

0.7 wt.-% of allyl methacrylate,

 b) 15.0 wt.-% of an adhesion promoter,

 c) 1.0 wt.-% of Tinuvin® 360 (phenol-2,2'-methylene-bis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl))), available from BASF SE (Ludwigshafen, Germany),

35 d) 0.7 wt.-% of Tinuvin® 1600 (6-[4,6-bis(4-phenylphenyl)-1,2-dihydro-1,3,5-triazin-2-ylidene]-3-[(2-ethylhexyl)oxy]cyclohexa-2,4-dien-1-one), available from BASF SE

 e) 0.3 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine,N2,N2"-1,2-ethanediybis[N2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-

triazin-2-yl]amino]propyl]-*N,N'*-dibutyl-*N,N'*-bis(1,2,2,6,6-pentamethyl-4-piperidiny)), available from Sabo S.p.A (Levate, Italy).

Production Example 6 (foil according to the invention)

5

PMMA-based triple-layer foil having a thickness of 58 μm was prepared by co-extrusion under the same conditions as in Example 1.

The layer D had a thickness of 5 μm and the following composition:

10

- c) 100.0 wt.-% of a KF Polymer 850 PVDF, available from KUREHA CORPORATION

The layer A had a thickness of 23 μm and the following composition:

15

- d) 85.7 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,

20

- b) 12.3 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- c) 1.72 wt.-% of Tinuvin® 1600, available from BASF SE
- d) 0.3 wt.-% of Sabo®stab UV 119, available from Sabo S.p.A.

The transmittance of the layer A at the wavelength of 360 nm was 1.7%. The spectral

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transmittance of the layer A at any wavelength λ_A was not more than 10%, wherein $270 \text{ nm} \leq \lambda_A \leq 360 \text{ nm}$.

The layer B had a thickness of 30 μm and the following composition:

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- c) 82.65 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,

- b) 15.0 wt.-% of an adhesion promoter,

35

- c) 2.05 wt.-% of Tinuvin® 360, available from BASF SE
- d) 0.3 wt.-% of Sabo®stab UV 119, available from Sabo S.p.A.

The transmittance of the layer B at the wavelength of 370 nm was 0.7 %. The spectral transmittance of the layer B at any wavelength λ_B was not more than 10%, wherein $270 \text{ nm} \leq \lambda_B \leq 370 \text{ nm}$.

- 5 The foils of Production Examples 1, 2, 3 and 4 were then laminated onto a PVC decorative foil, whereas the foil of Production Example 2 was laminated with the layer B onto the PVC foil (Example 2a). As a comparative example, the foil of Production Example 2 was laminated with the layer A onto the PVC foil (Example 2b). The foil of production Example 3 and 4 was laminated with the layer C or in the case of Example 4 with the layer B onto the PVC foil (Example 3 and
- 10 Example 4).

- The foils of Production Examples 5 and 6 were used for preparation of HPLs. The HPLs were produced by simultaneous lamination of the resin-impregnated paper layers and of the superposed protective foils (Production Examples 5 and 6). The core layer was composed of phenolic-resin-
- 15 impregnated papers. Between these and the protective foil there was a melamine-resin-impregnated decorative paper. An anthracite-coloured HPL was prepared and used for subsequent testing.

- The samples of Examples 1, 2a and 2b, 3, 4, 5 and 6 were subjected to accelerated weathering
- 20 test according to the norm ISO 4892-2 (2013), Method 1. Subsequently, the colour difference ΔE CIELAB 1976 (D_{65} , 10°) of each sample was determined according to the norm DIN EN ISO 11664-4:2011-07.

- The obtained data are summarized in Table 1 below:
- 25

Hours of accelerated weathering Samples	colour difference ΔE after					
	2 500 h	5 000 h	7 500 h	10 000 h	15 000 h	20 000 h
Example 1	0.42	1.23	1.86	2.31	3.54	6.15
Example 2a	0.22	0.34	0.42	0.57	0.76	1.25
Example 2b	0.63	1.45	2.46	2.73	3.84	6.23
Example 3	0.42	1.23	1.86	2.31	3.54	6.15
Example 4	0.22	0.34	0.42	0.57	0.76	1.25
Example 5	0.8	0.68	0.66	1.25	1.63	2.56
Example 6	0.69	0.53	0.69	0.77	0.85	1.25

Table 1. Results of accelerated weathering tests

- 5 In Examples 1, 2b and 3 (comparative examples) the UV protection at wavelengths lower than 360 nm provided by the foil was only moderate and therefore after about 10 000 h the colour difference of more than 2 after about 15 000 of more than 3 was observed. In Example 5 (comparative example) the UV protection at wavelengths lower than 360 nm provided by the foil was only moderate and therefore after about 20 000 h the colour difference of more than 2.5 was
- 10 observed. These values are readily recognisable by an observer, even with a naked eye, as a UV damage of the PVC decorative foil, or the ink on the HPL.

In contrast, the UV protection provided by the foils in Examples 2a, 4 and 6 (inventive examples) provide a significantly better UV protection. Even after a 20 000 h exposure the detected colour

15 difference was below 2 *i.e.* practically invisible to an observer. No visible damage of the foils took place.

In Production Examples 7-16 protective foils were produced by extrusion of monolayer foils using chill-roll process at 240-250 °C (melt temperature) at extrusion speed 7.3 m/min using a 35 mm-

20 diameter single screw extruder. To compare the different weathering behaviours monolayer foils which include all UV-absorbers were compared with and a foil made of laminated layers, each inhibiting one of the used UV-Absorbers. For example, a 90 µm monolayer foil with three UV-absorbers was compared against a 90 µm foil made of three layers each including one of the UV-absorbers. The lamination was done using a press at 140 °C, in which the stacked monolayer foils

25 each having a thickness of 30 µm were pressed together with a maximum press time of 1 minute.

The foils were placed between two rubber plates and separation sheets to prevent sticking of the foil to said rubber plates as shown in Figure 1.

5 The parts of the laminated foil with air bubbles were cut off and thickness of the obtained multi-layer foil was measured.

Alternatively, production can be achieved by way of a multiple-manifold co-extrusion process or a combination of adapter and multiple-manifold co-extrusion.

10 **Production Example 7** (comparative foil)

A PMMA monolayer foil having a total thickness of 90 µm was prepared by extrusion at 240-250 °C (melt temperature) at extrusion speed 7.3 m/min using a 35 mm-diameter single screw extruder.

15 The monolayer foil had the following composition:

- a) 85.69 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 20 0.7 wt.-% of allyl methacrylate,
- b) 12.0 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH (Darmstadt, Germany),
- c) 0.67 wt.-% of Tinuvin® 360 (phenol-2,2'-methylene-bis(6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl))), available from BASF SE (Ludwigshafen, Germany),
- d) 0.66 wt.-% of Tinuvin® 1577 (2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]-phenol),
 - 25 available from BASF SE,
- e) 0.66 wt.-% of nanoscale zinc oxide by using SolaSorb® UV 200 F, available from Croda GmbH (Nettetal, Germany),
- f) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-triazin-2-yl]amino]propyl]-*N*',*N*'-dibutyl-*N*',*N*'-bis(1,2,2,6,6-pentamethyl-4-piperidiny)]),
 - 30 available from Sabo S.p.A (Levate, Italy).

Production Example 8 (comparative foil)

35 A PMMA monolayer foil with having a total thickness of 60 µm was prepared by extrusion under the same conditions as in Example 7.

The monolayer foil had the following composition:

- a) 85.67 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,
- b) 12.0 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- c) 1.00 wt.-% of Tinuvin® 1577 (2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]-phenol), available from BASF SE,
- d) 1.00 wt.-% of nanoscale zinc oxide by using SolaSorb® UV 200 F, available from Croda GmbH,
- e) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazin-2-yl]amino]propyl]-*N'*,*N'*"-dibutyl-*N'*,*N'*"-bis(1,2,2,6,6-pentamethyl-4-piperidinyl)]), available from Sabo S.p.A (Levate, Italy).

Production Example 9 (comparative foil)

A PMMA monolayer foil with having a total thickness of 90 µm was prepared by extrusion under the same conditions as in Example 7.

The monolayer foil had the following composition:

- a) 85.68 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,
- b) 12.0 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- c) 0.67 wt.-% of Tinuvin® 360 (phenol-2,2'-methylene-bis(6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl))), available from BASF SE (Ludwigshafen, Germany),
- d) 0.66 wt.-% of Tinuvin® 1577 (2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]-phenol), available from BASF SE
- e) 0.67 wt.-% Eusorb® BLA 4200M (commercial product comprising Tinuvin® 329 and Hostavin® B-CAP), available from EUTEC CHEMICAL CO., LTD.
- f) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazin-2-yl]amino]propyl]-*N'*,*N'*"-dibutyl-*N'*,*N'*"-bis(1,2,2,6,6-pentamethyl-4-piperidinyl)]), available from Sabo S.p.A (Levate, Italy).

Production Example 10 (comparative foil)

A PMMA monolayer foil with having a total thickness of 90 µm was prepared by extrusion under the same conditions as in Example 7.

5

The monolayer foil had the following composition:

- a) 86.13 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,
- b) 12.193 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- c) 0.67 wt.-% of Tinuvin® 360 (phenol-2,2'-methylene-bis(6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl))), available from BASF SE (Ludwigshafen, Germany),
- d) 0.66 wt.-% of Tinuvin® 1577 (2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]-phenol), available from BASF SE,
- e) 0.017 wt.-% Oracet Yellow 180 (1,8-Bis(phenylthio)anthraquinone; 1,8-Bis(phenylthio)-9,10-anthracenedione), available from BASF SE,
- f) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazin-2-yl]amino]propyl]-*N*',*N*'-dibutyl-*N*',*N*'-bis(1,2,2,6,6-pentamethyl-4-piperidinyl)]), available from Sabo S.p.A (Levate, Italy).

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Production Example 11 (comparative foil)

- 25 A PMMA monolayer foil having a total thickness of 60 µm was prepared by extrusion under the same conditions as in Example 7.

The monolayer foil had the following composition:

- a) 86.3 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,
- b) 12.325 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- c) 1.02 wt.-% of Tinuvin® 360 (phenol-2,2'-methylene-bis(6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl))), available from BASF SE (Ludwigshafen, Germany),
- d) 0.025 wt.-% Oracet Yellow 180 (1,8-Bis(phenylthio)anthraquinone; 1,8-Bis(phenylthio)-9,10-anthracenedione), available from BASF SE,
- e) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-

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triazin-2-yl]amino]propyl]-*N',N''*-dibutyl-*N',N''*-bis(1,2,2,6,6-pentamethyl-4-piperidiny)), available from Sabo S.p.A (Levate, Italy).

Production Example 12 (inventive foil)

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A PMMA triple layer foil having a total thickness of 90 µm was prepared by lamination of three 30 µm thick monolayer foils, according the conditions given above.

The triple layer foil had the following composition:

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1. Monolayer foil having a thickness of 30 µm was prepared by extrusion under the same conditions as in Example 7 and having the following composition:

15

- a) 85.67 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,
- b) 12.0 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- c) 2.00 wt.-% of nanoscale zinc oxide by using SolaSorb® UV 200 F, available from Croda GmbH
- d) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N2,N2''*-1,2-ethanediybis[*N2*-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)]amino]-1,3,5-triazin-2-yl]amino]propyl]-*N',N''*-dibutyl-*N',N''*-bis(1,2,2,6,6-pentamethyl-4-piperidiny)), available from Sabo S.p.A (Levate, Italy).

25

2. Monolayer foil having a thickness of 30 µm was prepared by extrusion under the same conditions as in Example 7 and having the following composition:

30

- a) 85.67 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,
- b) 12.0 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- c) 2.00 wt.-% of Tinuvin® 1577 (2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]-phenol), available from BASF SE
- d) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N2,N2''*-1,2-ethanediybis[*N2*-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)]amino]-1,3,5-triazin-2-yl]amino]propyl]-*N',N''*-dibutyl-*N',N''*-bis(1,2,2,6,6-pentamethyl-4-piperidiny)), available from Sabo S.p.A (Levate, Italy).

35

3. Monolayer foil having a thickness of 30 µm was prepared by extrusion under the same conditions as in Example 7 and having the following composition:

- 5 a) 85.67 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,
- b) 12.0 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- 10 c) 2.00 wt.-% of Tinuvin® 360 (phenol-2,2'-methylene-bis(6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl))), available from BASF SE (Ludwigshafen, Germany),
- d) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-triazin-2-yl]amino]propyl]-*N'*,*N'*"-dibutyl-*N'*,*N'*"-bis(1,2,2,6,6-pentamethyl-4-piperidiny)]),
- 15 available from Sabo S.p.A (Levate, Italy).

Production Example 13 (inventive foil)

20 A PMMA dual layer foil having a total thickness of 60 µm was prepared by lamination of two 30 µm thick mono foils, according the conditions given above.

The dual layer foil had the following composition:

- 25 1. Monolayer foil having a thickness of 30 µm was prepared by extrusion under the same conditions as in Example 7 and having the following composition:
- b) 85.67 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 30 0.7 wt.-% of allyl methacrylate,
 - b) 12.0 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
 - c) 2.00 wt.-% of nanoscale zinc oxide by using SolaSorb® UV 200 F, available from Croda GmbH
 - d) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-triazin-2-yl]amino]propyl]-*N'*,*N'*"-dibutyl-*N'*,*N'*"-bis(1,2,2,6,6-pentamethyl-4-piperidiny)]),
 - 35 available from Sabo S.p.A (Levate, Italy).

2. Monolayer foil having a thickness of 30 μm was prepared by extrusion under the same conditions as in Example 7 and having the following composition:

- a) 85.67 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 5 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,
- b) 12.0 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- c) 2.00 wt.-% of Tinuvin® 1577 (2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]-phenol),
- 10 available from BASF SE
- d) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-triazin-2-yl]amino]propyl]-*N'*,*N'*"-dibutyl-*N'*,*N'*"-bis(1,2,2,6,6-pentamethyl-4-piperidiny)]),
- available from Sabo S.p.A (Levate, Italy).

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Production Example 14 (inventive foil)

A PMMA triple layer foil having a total thickness of 90 μm was prepared by lamination of three 30 μm thick monolayer foils, according the conditions given above.

20

The triple layer foil had the following composition:

- 1. Monolayer foil having a thickness of 30 μm was prepared by extrusion under the same conditions as in Example 7 and having the following composition:
 - 25 c) 85.67 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,
 - 30 b) 12.0 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
 - c) 2.00 wt.-% of Tinuvin® 1577 (2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]-phenol),
 - available from BASF SE
 - d) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-triazin-2-yl]amino]propyl]-*N'*,*N'*"-dibutyl-*N'*,*N'*"-bis(1,2,2,6,6-pentamethyl-4-piperidiny)]),
 - 35 available from Sabo S.p.A (Levate, Italy).
2. Monolayer foil having a thickness of 30 μm was prepared by extrusion under the same conditions as in Example 7 and having the following composition:

- 5 a) 85.67 wt.-% of a polymer acrylic core shell impact modifier with a composition of
61.3 wt.-% of methyl methacrylate,
38.0 wt.-% of butyl acrylate,
0.7 wt.-% of allyl methacrylate,
- b) 12.0 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- c) 2.00 wt.-% of Tinuvin® 360 (phenol-2,2'-methylene-bis(6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl))), available from BASF SE (Ludwigshafen, Germany),
- 10 d) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-triazin-2-yl]amino]propyl]-*N'*,*N''*-dibutyl-*N'*,*N''*-bis(1,2,2,6,6-pentamethyl-4-piperidiny)]), available from Sabo S.p.A (Levate, Italy).
- 15 3. Monolayer foil having a thickness of 30 µm was prepared by extrusion under the same conditions as in Example 7 and having the following composition:
- a) 85.67 wt.-% of a polymer acrylic core shell impact modifier with a composition of
61.3 wt.-% of methyl methacrylate,
38.0 wt.-% of butyl acrylate,
0.7 wt.-% of allyl methacrylate,
- 20 b) 12.0 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- c) 2.00 wt.-% of Eusorb® BLA 4200M (commercial product comprising Tinuvin® 329 and Hostavin® B-CAP), available from Eutec Chemical Co. Ltd,
- 25 d) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-triazin-2-yl]amino]propyl]-*N'*,*N''*-dibutyl-*N'*,*N''*-bis(1,2,2,6,6-pentamethyl-4-piperidiny)]), available from Sabo S.p.A (Levate, Italy).

Production Example 15 (inventive foil)

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A PMMA triple layer foil having a total thickness of 90 µm was prepared by lamination of three 30 µm thick monolayer foils, according the conditions given above.

35

The triple layer foil had the following composition:

1. Monolayer foil having a thickness of 30 µm was prepared by extrusion under the same conditions as in Example 7 and having the following composition:
- d) 85.67 wt.-% of a polymer acrylic core shell impact modifier with a composition of

- 61.3 wt.-% of methyl methacrylate,
 38.0 wt.-% of butyl acrylate,
 0.7 wt.-% of allyl methacrylate,
- 5 b) 12.0 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
 c) 2.00 wt.-% of Tinuvin® 1577 (2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]-phenol),
 available from BASF SE,
 d) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-
 ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-
 triazin-2-yl]amino]propyl]-*N*',*N*'-dibutyl-*N*',*N*'-bis(1,2,2,6,6-pentamethyl-4-piperidiny)]),
 10 available from Sabo S.p.A (Levate, Italy).
2. Monolayer foil having a thickness of 30 µm was prepared by extrusion under the same
 conditions as in Example 7 and having the following composition:
- 15 a) 85.67 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 61.3 wt.-% of methyl methacrylate,
 38.0 wt.-% of butyl acrylate,
 0.7 wt.-% of allyl methacrylate,
 b) 12.0 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
 20 c) 2.00 wt.-% of Tinuvin® 360 (phenol-2,2'-methylene-bis(6-(2*H*-benzotriazol-2-yl)-4-
 (1,1,3,3-tetramethylbutyl))), available from BASF SE (Ludwigshafen, Germany),
 d) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-
 ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-
 triazin-2-yl]amino]propyl]-*N*',*N*'-dibutyl-*N*',*N*'-bis(1,2,2,6,6-pentamethyl-4-piperidiny)]),
 25 available from Sabo S.p.A (Levate, Italy).
3. Monolayer foil having a thickness of 30 µm was prepared by extrusion under the same
 conditions as in Example 7 and having the following composition:
- 30 a) 86.97 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 61.3 wt.-% of methyl methacrylate,
 38.0 wt.-% of butyl acrylate,
 0.7 wt.-% of allyl methacrylate,
 b) 12.65 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
 35 c) 0.05 wt.-% of Oracet Yellow 180 (1,8-bis(phenylthio)anthraquinone; 1,8-Bis(phenylthio)-
 9,10-anthracenedione), available from BASF SE,
 d) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N*2,*N*2"-1,2-
 ethanediylbis[*N*2-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-

triazin-2-yl]amino]propyl]-*N',N''*-dibutyl-*N',N''*-bis(1,2,2,6,6-pentamethyl-4-piperidiny)), available from Sabo S.p.A (Levate, Italy).

Production Example 16 (inventive foil)

5

A PMMA dual layer foil with having a total thickness of 60 µm was prepared by lamination of two 30 µm thick monolayer foils, according the conditions given above.

The dual layer foil had the following composition:

10

1. Monolayer foil having a thickness of 30 µm was prepared by extrusion under the same conditions as in Example 7 and having the following composition:

15

- a) 85.67 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,
- b) 12.0 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- c) 2.00 wt.-% of Tinuvin® 360 (phenol-2,2'-methylene-bis(6-(2*H*-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl))), available from BASF SE (Ludwigshafen, Germany),
- d) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N2,N2''*-1,2-ethanediybis[*N2*-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-triazin-2-yl]amino]propyl]-*N',N''*-dibutyl-*N',N''*-bis(1,2,2,6,6-pentamethyl-4-piperidiny))], available from Sabo S.p.A (Levate, Italy).

25

2. Monolayer foil having a thickness of 30 µm was prepared by extrusion under the same conditions as in Example 7 and having the following composition:

30

- a) 86.97 wt.-% of a polymer acrylic core shell impact modifier with a composition of
 - 61.3 wt.-% of methyl methacrylate,
 - 38.0 wt.-% of butyl acrylate,
 - 0.7 wt.-% of allyl methacrylate,
- b) 12.65 wt.-% PLEXIGLAS® 7H, available from Röhm GmbH,
- c) 0.05 wt.-% of Oracet Yellow 180 (1,8-bis(phenylthio)anthraquinone; 1,8-bis(phenylthio)-9,10-anthracenedione), available from BASF SE,
- d) 0.33 wt.-% of Sabo®stab UV 119 (1,3,5-triazine-2,4,6-triamine, *N2,N2''*-1,2-ethanediybis[*N2*-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-triazin-2-yl]amino]propyl]-*N',N''*-dibutyl-*N',N''*-bis(1,2,2,6,6-pentamethyl-4-piperidiny))], available from Sabo S.p.A (Levate, Italy).

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