

DESCRIPTION

TITLE OF INVENTION: GLAZING COMPRISING A TEMPORARY ORGANIC PROTECTIVE LAYER

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[0001] The invention relates to a material comprising a transparent substrate coated with a functional coating which can influence solar radiation and/or infrared radiation. The invention also relates to the glazings comprising these materials and also to the use of such materials for manufacturing glazings.

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[0002] In the following description, the term “functional” as used in “functional coating” means “capable of influencing solar radiation and/or infrared radiation”.

[0003] These functional coatings are used in so-called “solar control” glazings targeted at reducing the amount of solar energy entering and/or in so-called “low-emissivity” glazings targeted at reducing the amount of energy dissipated toward the outside of a building or of a vehicle due to their advantageous properties of electrical conduction and reflection of infrared (IR) radiation.

20 [0004] Functional coatings comprise one or more functional layers. These functional layers can be based on conductive oxide or metallic layers.

[0005] Conductive oxide-based functional coatings are typically based on ITO (Indium Tin Oxide). These coatings feature low emissivity, good chemical durability and good mechanical resistance. However, such functional coatings are relatively expensive.

25 [0006] Functional coatings comprising one or more silver-based metallic functional layers (hereinafter referred to as silver-based functional coatings) are considerably less expensive. However, the corrosion and mechanical resistance of these functional coatings is often insufficient. This low strength is reflected by the appearance in the short term of defects, such as sites of

corrosion, scratches, even the complete or partial tearing of the coating during its use under standard conditions. All defects or scratches, whether due to corrosion or mechanical stresses, are likely to affect not only the attractiveness of the coated substrate but also the optical and energy performance levels.

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[0007] Applications WO 2015/019022 and WO 2018/051029 disclose a substrate provided with a functional coating reflecting infrared radiation covered with a temporary protective layer intended to be removed following a heat treatment of the tempering type. These temporary protective coatings are acrylate-based organic polymer coatings of 10 to 20 μm in thickness. These thick, temporary protective layers prevent any occurrence of scratches on the functional coating that they protect. These layers are removed during heat treatment.

[0008] The solutions developed in these documents may be further improved. In particular, the following inconveniences are sometimes observed:

- the temporary layer is not always thoroughly burnt, especially when the rate of thermal degradation is too low with respect to the duration and/or temperature of the heat treatment,
- unpleasant odors are sometimes produced, especially in the tempering oven.

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[0009] The document WO 2019/123477 discloses a temporary protective layer based on (meth)acrylate compounds comprising solid particles such as polymeric beads or glass beads. Solid particles are used both as a replacement for costly oligomeric (meth)acrylate compounds and as a replacement for spacers and/or powders used between two glass substrates to prevent friction or adhesion phenomena, especially during storage.

[0010] Surprisingly, the applicant has discovered that these drawbacks can be avoided by using a polymeric protective layer based on specific acrylates, especially comprising a high proportion of acrylate compounds of defined molecular mass and functionality. This layer has a faster degradation rate and a lower degradation temperature. This layer effectively protects the

coated substrate from any defects or scratches, and is more easily removed during heat treatment.

[0011] The invention thus relates to a material comprising a substrate coated with a functional coating and a temporary organic protective layer deposited on at least part of the functional coating, the protective layer comprises a polymeric matrix obtained by crosslinking a polymerizable composition comprising (a) (meth)acrylate compounds and (b) optionally a polymerization initiator, characterized in that:

5 the temporary organic protective layer has a weight loss by thermogravimetric analysis (TGA) from 30°C to 450°C at a heating rate of 10°C/min in air of greater than 65%, preferably greater than 70%, or even greater than 75%. The polymerizable composition may comprise (meth)acrylate compounds (a1) comprising at least one alkyleneoxy group and a molecular mass comprised

10 between 100 and 800 g/mol. Preferably, these (meth)acrylate compounds (a1) represent at least 30% by mass of the total mass of the protective layer.

[0012] The invention also relates to a material comprising a substrate coated with a functional coating and a temporary organic protective layer deposited on at least part of the functional coating, the protective layer comprising a polymeric matrix obtained by crosslinking a polymerizable composition comprising (a) (meth)acrylate compounds and optionally (b) a polymerization initiator, characterized in that the polymerizable composition comprises (meth)acrylate compounds (a1) comprising at least one alkyleneoxy group and

20 a molecular mass of between 100 and 800 g/mol, these (meth)acrylate compounds (a1) representing, once crosslinked, at least 30% by mass of the total mass of the protective layer.

[0013] This is the same temporary organic protective layer, defined in two different ways, especially:

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- by its percentage of degradation by ATG at a given temperature,
- by the proportion of (meth)acrylate compounds of defined molecular mass.

[0014] The invention also relates to a material comprising a substrate coated with a functional coating and a temporary organic protective layer deposited on at least part of the functional coating, the protective layer is obtained by crosslinking a polymerizable composition comprising (a) (meth)acrylate compounds and optionally (b) a polymerization initiator, characterized in that: at least 50%, at least 60% or at least 70% by mass of the total mass of the protective layer comprises (meth)acrylate compounds with a molecular mass of between 100 and 800 g/mol, preferably between 100 and 500 g/mol.

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[0015] The organic protective layer is an organic polymeric layer. The organic protective layer is essentially of organic nature. It is obtained from a polymerizable composition. It results from the crosslinking of the polymerizable organic compounds present in the polymerizable composition.

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[0016] The (meth)acrylate compounds (a) and optionally (b) the polymerization initiator react with each other, and once crosslinked, form an organic polymeric matrix. When we consider that the protective layer comprises a certain proportion by mass of (meth)acrylate compounds (a) and optionally (b) a polymerization initiator, this corresponds to the proportion by mass of this organic polymer matrix. The polymerization initiator, when present, is incorporated into the resulting organic matrix.

[0017] The polymeric matrix represents at least 80%, at least 85%, at least 90%, at least 95%, at least 98% or 100% by mass of the total mass of the protective layer. The polymer matrix is obtained by crosslinking a polymerizable composition comprising (a) (meth)acrylate compounds and optionally (b). This means that these percentages may also correspond to the proportions of compounds (a) and (b) having reacted with each other. The compounds (a) and (b) that have reacted with one another represent at least 80%, at least 85%, at least 90%, at least 95%, at least 98% or 100% by mass of the polymer matrix. The compounds (a) and (b) that have reacted with one

another make up at least 80%, at least 85%, at least 90%, at least 95%, at least 98% or 100% by mass of the organic protective layer.

[0018] The invention also relates to a method for obtaining a material treated at a high temperature, the material comprising a substrate coated with a functional coating, said method comprising the following steps:

a step of protecting the article comprising:

- preparing a polymerizable composition comprising (a) (meth)acrylate compounds and optionally (b) a polymerization initiator, of which the (meth)acrylate compounds (a1) comprising at least one alkyleneoxy group and a molecular mass of between 100 and 800 g/mol, these (meth)acrylate compounds (a1) representing at least 30% by mass of the total mass of the protective layer,

[0019] - applying the polymerizable composition on at least one portion of the

- functional coating over a thickness of at least 1 micrometer,

- crosslinking the composition so as to form a temporary organic protective layer,

a same step of heat treating and deprotecting the article comprising:

- removing the temporary protective layer by heat treatment at a temperature

- above 200°C and sufficient to achieve the tempering of the article.

[0020] The invention also relates to a method for obtaining a material treated at a high temperature, the material comprising a substrate coated with a functional coating, said method comprising the following steps:

a step of protecting the article comprising:

- preparing a polymerizable composition comprising (a) (meth)acrylate compounds and optionally (b) a polymerization initiator,

- applying the polymerizable composition on at least one portion of the

- functional coating over a thickness of at least 1 micrometer,

- crosslinking the composition so as to form a temporary organic protective layer,

a same step of heat treating and deprotecting the article comprising:

- removing the temporary protective layer by heat treatment at a temperature above 200°C and sufficient to achieve the tempering of the article, characterized in that the temporary organic protective layer has a weight loss by thermogravimetric analysis (TGA) from 30°C to 450°C at a rate of 10°C/min in air of greater than 65%, preferably greater than 70% or even greater than 75%.

[0021] According to this method, the functional coating is preferably deposited by magnetron sputtering and in that the temporary protective layer is directly in contact with the functional coating.

[0022] The term "(meth)acrylate" is understood to mean an acrylate or a methacrylate. The expression "(meth)acrylate functions" is understood to mean an acrylate function ($\text{CH}_2=\text{CH}-\text{COO}-$) or a methacrylate function ($\text{CH}_2=\text{CH}(\text{CH}_3)-\text{COO}-$).

[0023] The (meth)acrylate compounds that have reacted with one another represent by mass, with respect to the total mass of the organic protective layer, in ascending order of preference:

- at least 50%, at least 60%, at least 70%, at least 80%, at least 90%, at least 95%, and/or
- up to 99%, up to 98%, up to 97%, up to 96%, up to 95%.

[0024] The expression "(meth)acrylate compounds" is understood to mean the esters of acrylic or methacrylic acid comprising at least one (meth)acrylate function. The (meth)acrylate compounds used according to the invention may be selected from amongst monofunctional and polyfunctional (meth)acrylates such as mono-, di-, tri-, poly-functional (meth)acrylates. These esters may be monomers, oligomers, prepolymers or polymers. These (meth)acrylate compounds, when they are subjected to the polymerization conditions, give a polymer network endowed with a solid structure.

[0025] The (meth)acrylate compounds have a molecular mass or average molecular mass (hereinafter molecular mass) of between 100 and 800 g/mol.

5 [0026] According to the invention, (meth)acrylate compounds are chosen from esters of acrylic or methacrylic acid.

[0027] The expression "(meth)acrylate compound comprising one alkyleneoxy group" is understood to mean a (meth)acrylate compound which comprises one or more alkyleneoxy groups. The expression "alkyleneoxy group" is
10 understood to mean a chemical group consisting of an allylene group bonded to an oxygen atom of the formula $-(C_nH_{2n})-O-$ preferably with n from 1 to 6. This definition does not include the group(s) involved in the formation of the ester group(s) of acrylic or methacrylic acid. Preferably, the alkylene-oxy groups are selected from an oxyethylene group $-CH_2-CH_2-O-$ and
15 oxypropylene $-CH_2-CH_2-CH_2-O-$, $-CH(CH_3)-CH_2-O-$ and $-CH_2-CH(CH_3)-O-$.

[0028] The expression "(meth)acrylate compounds (a1)" is understood to mean a (meth)acrylate compound comprising at least one alkyleneoxy group and a molecular mass of between 100 and 800 g/mol.

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[0029] The term "(meth)acrylate (a) compounds" includes:

[0030] - (meth)acrylate compounds containing no alkyleneoxy group and

[0031] - (meth)acrylate compounds (a1).

25 [0032] The methacrylate compounds (a1) containing an alkyleneoxy group of low molecular mass have the advantage of being less thermally stable at around 400°C than other (meth)acrylate compounds such as trimethylolpropane triacrylate. This lower stability allows the temporary protective layer to be degraded at a lower temperature and more effectively
30 during thermal tempering. This lower thermal stability may be attributed to the presence of "alkylene-oxy" groups in the polymer matrix of the temporary protective layer, compared to the mere presence of "alkylene" groups.

[0033] The (meth)acrylate compounds (a1) comprising at least one alkyleneoxy group and a molecular mass of between 100 and 800 g/mol used according to the invention have the following characteristics alone or in combination:

- 5 [0034] - they may represent at least 35%, at least 40%, at least 45%, at least 50%, at least 55%, at least 60%, at least 65% or at least 70%, by mass, of the total mass of the protective layer,

[0035] - the (meth)acrylate compounds (a1) are selected from (meth)acrylate compounds comprising:

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[0036] - a (meth)acrylate function,

[0037] - two (meth)acrylate functions,

[0038] - three (meth)acrylate functions,

[0039] - four (meth)acrylate functions,

- 15 [0040] - advantageously, the (meth)acrylate compounds (a1) are selected from (meth)acrylate compounds comprising:

[0041] - two (meth)acrylate functions,

[0042] - three (meth)acrylate functions,

- 20 [0043] - the (meth)acrylate compounds (a1) represent at least 35%, at least 40%, at least 45%, at least 50%, at least 55%, at least 60%, at least 65% or at least 70% by weight of the total weight of the protective layer,

[0044] - the (meth)acrylate compounds (a1) with 3 (meth)acrylate functions representing at least 40%, at least 50%, at least 60% or at least 70% by mass

- 25 with respect to the total mass of the organic protective layer,

[0045] - the (meth)acrylate compounds (a1) with an alkyleneoxy group are selected from:

[0046] - the (meth)acrylate compounds containing an ethylene-oxy group,

- 30 [0047] - the (meth)acrylate compounds containing a propylene-oxy group,

[0048] - the (meth)acrylate compounds (a1) are selected from (meth)acrylate compounds comprising at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 alkyleneoxy groups,

[0049] - the (meth)acrylate compounds (a1) have an average molecular mass
5 of between 300 and 800 g/mol, 350 and 800 g/mol or 350 to 500 g/mol,

[0050] - the methacrylate compounds with alkyleneoxy groups are selected from:

[0051] - polyethylene glycol diacrylates such as:

- 10 [0052] - triethylene glycol diacrylate,
- [0053] - tetra(ethylene glycol) diacrylate,
- [0054] - polyethylene glycol (200) diacrylate,
- [0055] - polyethylene glycol (300) diacrylate,
- [0056] - polyethylene glycol (400) diacrylate,
- 15 [0057] - polyethylene glycol (600) diacrylate,
- [0058] - hexanediol ethoxylated (5) diacrylate
- [0059] - polypropylene glycol di(meth)acrylates such as
- [0060] - dipropylene glycol diacrylate,
- [0061] - tripropylene glycol diacrylate,
- 20 [0062] - polypropylene glycol neopentyl glycol ether diacrylate,
- [0063] - 1,6-Hexanediol ethoxylated diacrylate
- [0064] - polyethylene glycol tri(meth)acrylates such as
- [0065] - ethoxylated trimethylolpropane (3) triacrylate,
- [0066] - ethoxylated trimethylolpropane (6) triacrylate,
- 25 [0067] - ethoxylated trimethylolpropane (9) triacrylate,
- [0068] - polypropylene glycol tri(meth)acrylates such as

[0069] The polyethylene glycol (PEG) diacrylates have the formula:
$$\text{H}_2\text{C}=\text{CHCOO}(\text{CH}_2\text{CH}_2)(\text{OCH}_2\text{CH}_2)_n\text{O}_2\text{CCH}=\text{CH}_2$$
 where n is 1 to 14,
30 preferably 2 to 10 and more preferably 2 to 5. Their molecular mass is between 200 and 800 g/mol⁻¹, especially 200, 300, 400, 500, 600 and 700. Reference may especially be made to triethylene glycol diacrylate (n=2) and

tetra(ethylene glycol) diacrylate with (n=3), polyethylene glycol (200) diacrylate, polyethylene glycol (300) diacrylate, polyethylene glycol (400) diacrylate, polyethylene glycol (600) diacrylate. It is customary to indicate the average molar mass of the PEG after the name, for example polyethylene glycol (200) or PEG-200 (200 g/mol).

[0070] Polypropylene glycol diacrylates correspond to the formula:

[0071] $\text{H}_2\text{C}=\text{CHCOO}(\text{C}_3\text{H}_6)(\text{OC}_3\text{H}_6)_n\text{O}_2\text{CCH}=\text{CH}_2$ where n is 1 to 10, preferably 2 to 5. Reference may especially be made to dipropylene glycol diacrylate, tripropylene glycol diacrylate and polypropylene glycol neopentyl glycol ether diacrylate. Their molecular mass is between 200 and 800 g/mol⁻¹, especially 200, 300, 400, 500, 600 and 700.

[0072] Di-ethoxylated 1,6 hexane diol diacrylate has CAS number 84170-27-4.

[0073] Polypropylene glycol triacrylates comprise three acrylate functions and at least one alkyleneoxy group. Reference may especially be made to ethoxylated (3) trimethylolpropane triacrylate (TMPEOTA) comprising 3 alkyleneoxy groups, ethoxylated (6) trimethylolpropane triacrylate and ethoxylated (9) trimethylolpropane triacrylate.

[0074] The list below contains the preferred alkyleneoxy (meth)acrylate compounds (a1) and some of their commercial names:

- [0075] - polyethylene glycol (200) diacrylate (PEG200DA) SR259®,
- [0076] - tetraethylene glycol diacrylate (TTEGDA) SR268G®,
- [0077] - triethylene glycol diacrylate (TIEGDA) SR272®,
- [0078] - tripropylene glycol diacrylate (TPGDA) SR306®,
- [0079] - polyethylene glycol (400) diacrylate (PEG400DA) SR344®,
- [0080] - polyethylene glycol 600 diacrylate (PEG600DA) SR610®,
- [0081] - dipropylene glycol diacrylate (DPGDA)
- [0082] - ethoxylated 3 bisphenol A diacrylate (BPA3EODA) SR349®, SR508®,
- [0083] - ethoxylated 4 bisphenol A diacrylate (BPA4EODA) SR601E®,

- [0084] - ethoxylated 10 bisphenol A diacrylate (BPA10EODA) SR602®,
[0085] - ethoxylated 3 trimethylolpropane triacrylate (TMP3EOTA) SR415®,
[0086] - ethoxylated 6 trimethylolpropane triacrylate (TMP6EOTA) SR499®,
[0087] - ethoxylated 9 trimethylolpropane triacrylate (TMP9EOTA) SR502®,
5 [0088] - propoxylated 3 trimethylolpropane triacrylate (TMP3POTA) SR492®,
[0089] - propoxylated 3 glyceryl triacrylate (GPTA) SR9020®,
[0090] - ethoxylated glyceryl triacrylate preferably comprising 1 to 11
ethyleneoxy groups,
[0091] - ethoxylated 12 glyceryl triacrylate (G12EOTA) SR9046®,
10 [0092] - glyceryl propoxy triacrylate.

[0093] The polymerizable composition may comprise (meth)acrylate compounds (a), some of which do not comprise an alkylene-oxy group.

- 15 [0094] The (meth)acrylate compounds (a) used according to the invention have the following characteristics alone or in combination:

[0095] - at least 50%, at least 60% or at least 70% by mass of the total mass of the protective layer comprises (meth)acrylate compounds (a) having a molecular mass of between 100 and 800 g/mol, preferably between 100 and

- 20 500 g/mol, and/or

[0096] - the composition comprises (meth)acrylate compounds (a) having 1 to 3 (meth)acrylate functions, and/or

[0097] - the (meth)acrylate compounds (a) with 1 to 3 (meth)acrylate functions represent by mass, with respect to the total mass of the organic protective layer:

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[0098] - at least 50%, at least 60% or at least 65%, and/or

[0099] - up to 90%, up to 85%, up to 80%, up to 75%, and/or

[0100] - the composition comprises (meth)acrylate compounds (a) having 3 (meth)acrylate functions representing by mass with respect to the total mass

- 30 of the organic protective layer:

[0101] - at least 40%, at least 50% or at least 60%, and/or

[0102] - up to 80%, up to 75%, up to 70%, or up to 65%, and/or

[0103] - the composition comprises (meth)acrylate compounds (a) having 1 or 2 (meth)acrylate functions representing by mass with respect to the total mass of the organic protective layer:

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[0104] - at least 5%, and/or

[0105] - up to 40%, up to 30%, up to 20%, or up to 10%, and/or

[0106] - the composition comprises (meth)acrylate compounds (a) having at least 4 (meth)acrylate functions which represent by mass with respect to the total mass of the organic protective layer:

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[0107] - at least 5%, at least 10% or at least 15%, and/or

[0108] - up to 40%, up to 35%, up to 30%, up to 25%, or up to 20%, and/or

[0109] - the compounds (a) and (b) that have reacted with one another represent, in ascending order of preference, at least 80%, at least 90%, at least 95%, at least 98% by mass of the organic protective layer.

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[0110] The list above includes (meth)acrylate compounds (a) not comprising an alkyleneoxy group. These compounds can be used in restricted proportions so as not to impact on good degradation properties:

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[0111] - 1,6-Hexanediol diacrylate,

[0112] - tricyclodecane dimethanol diacrylate (SR833S),

[0113] - decanediol diacrylate

[0114] - esterdiol diacrylate

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[0115] - trimethylolpropane triacrylate (TMPTA) SR351®,

[0116] - pentaerythritol triacrylate (PETIA) SR444D®,

[0117] - polybutadiene diacrylate,

[0118] - ethoxylated 15 trimethylolpropane triacrylate (TMP15EOTA) SR9035®,

[0119] - trimethylolpropane triacrylate (TMPTA) SR351®.

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[0120] The invention also relates to a material further comprising one or more of the following characteristics:

[0121] - the temporary organic protective layer has a weight loss by thermogravimetric analysis (TGA) from 30°C to 450°C at a heating rate of 10°C/min in air of more than 65%, preferably increasing to more than 70%, or even more than 75% o, and/or

- 5 [0122] - the temporary organic protective layer can also advantageously have a weight loss by thermogravimetric analysis (TGA) from 30°C to 400°C at a heating rate of 10°C/min in air greater than 50%, preferably greater than 60% and/or

- [0123] - the temporary organic protective layer can also advantageously have a weight loss by thermogravimetric analysis (TGA) from 30°C to 350°C at a
10 heating rate of 10°C/min in air greater than 25%, preferably greater than 30%, or even greater than 35%, and/or

[0124] - the organic protective layer has a thickness:

[0125] - less than 50 µm, less than 30 µm, less than 20 µm, and/or

- 15 [0126] - greater than 1 µm, greater than 5 µm, greater than 10 µm, and/or

[0127] - the temporary protective layer is directly in contact with the functional coating, and/or

- [0128] - the functional coating comprises a stack of thin layers successively comprising starting from the substrate an alternation of n functional metallic layers
20 based on silver or on a metal alloy containing silver, and of (n+1) dielectric coatings, each dielectric coating comprising at least one dielectric layer, such that each functional metallic layer is disposed between two dielectric coatings, and/or

[0129] - the functional coating is deposited by magnetron sputtering, and/or

- [0130] - the substrate bearing the functional coating has not undergone a heat
25 treatment at a temperature greater than 400°C.

[0131] According to advantageous embodiments of the invention, the polymerizable composition has the following features:

- it comprises at least one polymerization initiator, preferably a photoinitiator,
30 - it may comprise at least two different photoinitiators,

- the polymerization initiator represents 0.1 to 20%, or 2 to 15%, preferably 5 to 15% and better still 8 to 12% by mass with respect to the total mass of the organic protective layer,
- the(meth)acrylate compounds a) are chosen from monomers, oligomers, prepolymers or polymers comprising at least one (meth)acrylate function,
- the (meth)acrylate compounds a) are selected from esters of acrylic or methacrylic acid comprising at least two (meth)acrylate functions,
- the (meth)acrylate compounds a) do not comprise aromatic groups,
- the (meth)acrylate compounds a) comprise at least one oligomeric or prepolymeric monomer containing at least 1, at least 2, at least 3, at least 4 or at least 5 (meth)acrylate functions,
- the polymerizable composition further comprises at least one additive selected from plasticizers, absorbers, separating agents, heat and/or light stabilizers, thickeners, or surface modifiers,
- the sum of all additives is between 0 and 10%, preferably 0 and 5%, or even 0.05 to 2.00% by mass with respect to the total mass of the organic protective layer.

[0132] According to the invention, the polymerization initiators are not considered to be additives.

[0133] The organic protective layer is continuous. It has a thickness, in ascending order of preference:

- less than 50 μm , less than 40 μm , less than 30 μm , less than 20 μm , and/or
- greater than 5 μm , greater than 7 μm , greater than 8 μm , greater than 10 μm .

[0134] The organic protective layer according to the invention is preferably applied at the outlet of the manufacturing line for manufacturing substrates bearing functional coatings. The step of depositing the organic protective layer may be easily integrated into the method for manufacturing the substrate bearing the functional coating.

[0135] The polymerizable composition exhibits, by virtue of the judicious selection of (meth)acrylate compounds and optionally of solvent, a viscosity that is suitable for easily obtaining an organic protective layer with a thickness greater than or equal to 5 μm .

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[0136] The chemical nature, the degree of crosslinking, and the density of the organic protective layer contribute to obtaining effective protection against abrasion, the appearance of scratches and corrosion.

10 [0137] The organic protective layer is preferably deposited and crosslinked through suitable means that can be directly integrated at the outlet of the functional coating deposition chamber. This makes it possible to prevent any contamination of the coated substrates and to continuously manufacture protected materials.

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[0138] The polymerizable composition may be applied at ambient temperature by any known means and especially by roll coating, spraying, dipping, curtain coating or gun spraying.

20 [0139] This water-insoluble organic protective layer makes it possible to obtain effective protection even during the washing step.

[0140] Although the invention is very particularly suitable for the protection of substrates bearing mechanically weak functional coatings, the solution of the
25 invention may be applied to the protection of substrates bearing any type of functional coating.

[0141] The functional coating comprises at least one functional layer. The functional layer is preferably a layer that can act on solar radiation and/or
30 infrared radiation of long wavelength. These functional layers are for example metallic functional layers based on silver or on a metal alloy containing silver. They are deposited between dielectric coatings which generally comprise

several dielectric layers making it possible to adjust the optical properties of the stack. Furthermore, these dielectric layers make it possible to protect the silver layer from chemical or mechanical attacks.

5 [0142] The functional coating thus advantageously comprises at least one silver-based functional metal layer and at least two dielectric coatings, each dielectric coating comprising at least one dielectric layer, so that each functional metal layer is positioned between two dielectric coatings.

10 [0143] The substrate may comprise a functional coating comprising a stack of thin layers successively comprising starting from the substrate an alternation of n functional metallic layers based on silver or on a metal alloy containing silver, and of $(n+1)$ dielectric coatings, each dielectric coating comprising at least one dielectric layer, so that each functional metallic layer is positioned
15 between two dielectric coatings. Preferably, n is equal to 1, 2, 3 or 4. Even more preferably, n is greater than 1, in particular n is equal to 2 or 3.

[0144] The substrate may successively comprise starting from the substrate an alternation of two functional metallic layers, especially functional layers
20 based on silver or on a metal alloy containing silver, and of three dielectric coatings, each dielectric coating comprising at least one dielectric layer, so that each functional metallic layer is disposed between two dielectric coatings.

[0145] The substrate may also comprise a functional coating comprising a
25 stack of thin layers successively comprising starting from the substrate an alternation of three functional metallic layers based on silver or on a metal alloy containing silver, and of 4 dielectric coatings, each dielectric coating comprising at least one dielectric layer, so that each functional metallic layer is disposed between two dielectric coatings.

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[0146] The thickness of the functional coating is:

- greater than 50 nm, greater than 100 nm, preferably greater than 150 nm, and/or

- less than 350 nm, or less than 300 nm.

[0147] According to one particularly advantageous embodiment of the invention, the functional coating comprises a non-organic protective upper
5 layer selected from nitrides, oxides or oxynitrides of titanium and/or of zirconium. The upper layer of the functional coating is the layer furthest from the substrate and/or the layer in direct contact with the organic protective layer.

[0148] The thickness of these upper layers is preferably between 1 and 20 nm
10 and better still between 1 and 5 nm.

[0149] The top layer of the functional coating, especially when based on titanium oxide, is important as it promotes adhesion between the inorganic
15 layers of the functional coating and the organic protective layer.

[0150] The functional coating may be deposited by any known means such as by magnetron sputtering, by thermal evaporation, by CVD or PECVD, by pyrolysis,
by chemical deposition, by sol-gel deposition or wet deposition of inorganic layers.

20 [0151] The functional coating is preferably deposited by magnetron sputtering. According to this advantageous embodiment, all the layers of the functional coating are deposited by magnetron sputtering. The organic protective layer is advantageously directly in contact with the functional coating.

25 [0152] The substrate is preferably a glass substrate. The glass substrate may be flat or curved, colorless and/or colored. The thickness of the substrate is preferably between 1 and 19 mm, more particularly between 2 and 12 mm, or even between 3 and 12 mm.

30 [0153] The organic protective layer may be deposited:
- on each of the main surfaces of the substrate and/or
- on at least one edge of the substrate and/or

- on each of the edges of the substrate.

[0154] The invention also relates to the method for obtaining a material according to the invention. The method of the invention comprises one or more
5 of the following features:

- the functional coating is deposited by magnetron sputtering and the organic protective layer is directly in contact with the functional coating,
- the polymerizable composition is applied to the functional coating,
- the organic protective layer is obtained by UV crosslinking.

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[0155] Preferably, the functional coating is deposited by magnetron sputtering and the organic protective layer is directly in contact with the functional coating.

[0156] The organic protective layer may be formed immediately after the step
15 of depositing the functional coating. According to the invention, it is considered that the organic protective layer may be formed "immediately after", when the organic protective layer may be formed in less than 10 minutes, preferably less than 5 minutes and better still less than 1 minute after the step of depositing the functional coating.

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[0157] The invention also relates to a glazing comprising a material according to the invention. The glazing can be mounted on a vehicle or a building.

[0158] Glazing according to the invention is particularly suitable for use in
25 buildings or vehicles, especially as side windows, retractable roofs or rear windows. It is also suitable for use as a refrigerator door or window having an antifog (anticondensation) function, especially in showcases displaying frozen products in supermarkets.

30 [0159] The following examples illustrate the invention.

Examples

I. Substrates and functional coatings

- 5 [0160] Functional coatings defined below are deposited on substrates made of clear soda-lime glass with a thickness of 6 mm.

The functional coating was deposited by virtue of a magnetron sputtering device. The conditions for deposition of the layers deposited by sputtering (so-called "magnetron cathode" sputtering), are summarized in Table 1 below.

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Tab.1	Targets employed	Deposition pressure	Gas	Index*
SnZnOx	Sn:Zn (60:40% by wt)	$1.5 \cdot 10^{-3}$ mbar	Ar 39% - O ₂ 61%	2.09
ZnO:Al	Zn:Al (98:2% by wt)	$1.8 \cdot 10^{-3}$ mbar	Ar/(Ar + O ₂) at 63%	1.95
NiCr	Ni:Cr (80:20% at.)	$1.5 \cdot 10^{-3}$ mbar	Ar at 100%	-
Ag	Ag	$2.3 \cdot 10^{-3}$ mbar	Ar at 100%	-
TiO ₂	TiOx	$1.5 \cdot 10^{-3}$ mbar	Ar 88% - O ₂ 12%	2.32

[0161] at. : atomic; wt: weight; *: at 550 nm.

[0162] The materials and the physical thicknesses in nanometers (unless otherwise indicated) of each layer or coating of which the stack is composed are listed in the table below as a function of their positions with regard to the substrate bearing the stack.

15

Table 2: Glazing		
Upper protective layer	TiOx	2.5
Dielectric coating	SnZnOx	30
	ZnO:Al	6
Blocking layer BO	NiCr	0.4
Functional layer	Ag	12
Blocking layer BU	NiCr	0.1
Dielectric coating	ZnO:Al	6
	SnZnOx	30
Substrate (mm)	glass	6

II. Organic protective layer

1. Raw materials

- 5 [0163] Polymerizable compositions were prepared. They comprise (meth)acrylate compounds, polymerization initiators and, optionally, additives. The various constituents and additives are mixed by mechanical stirring.

a) (Meth)acrylate monomers and oligomers

10

[0164] These (meth)acrylate compounds comprise oligomers and monomers comprising at least one acrylate function. The following compounds marketed by the company Sartomer were used:

15 A - Isobornyl acrylate mono-functional acrylate monomer with a molecular mass of 208.30 g/mol ((meth)acrylate (a) compound),

B1 - Tricyclodecane dimethanol diacrylate (SR833S), a di-functional acrylate monomer with a molecular mass of 304 g/mol ((meth)acrylate (a) compound),

B2 - Dipropylene glycol diacrylate, a di-functional acrylate monomer with a molecular mass of 242.3 g/mol, ((meth)acrylate (a1) compound)

20 C1 - Trimethylolpropane ethoxy triacrylate, a tri-functional acrylate monomer with a molecular mass of 428 g/mol, ((meth)acrylate (a1) compound)

C2 - Trimethylolpropane triacrylate (SR351), a tri-functional acrylate monomer with a molecular mass of 296 g/mol, (meth)acrylate (a) compound)

25 D - Tetra-functional aliphatic urethane acrylate oligomer CN9276 (hereinafter 4-functional acrylate oligomer) with a molecular mass of 1,000 g/mol, ((meth)acrylate (a) compound)

E - Dipentaerythritol pentaacrylate, a penta-functional acrylate monomer with a molecular mass of 524.5 g/mol, ((meth)acrylate (a) compound)

30 **b) Photoinitiator**

[0165] The initiator may be selected from photoinitiators sold by BASF under the name Irgacure® such as Iragure 500, by Lambson under the name Speedcure 500, Speedcure 84 or by Lamberti under the name Esacure HB. The photoinitiators may also be 1-hydroxy-1-methylethyl phenyl ketone.

5

c) Additives

[0166] An adhesion promoter can be used.

10 2. Polymerizable compositions

[0167] The compositions tested are defined in the table below in parts by weight. The polymerizable compositions are liquid. They are filtered at 0.2 µm to avoid aggregates. Their dry extracts can be adapted by adding solvent, depending on the thickness of the protective layer required.

15

Compositions	Functions	CC	CI	CI2
A (a)	1	-	7.0	-
B1 (a)	2	18.1	-	-
B2 (a1)	2	-	-	17.0
C1 (a1)	3	-	65.0	73
C2 (a)	3	19.2	-	-
D (a)	4	53.0	-	-
E (a)	5	-	18.3	-
(b) UV initiator	-	9.5	9.5	9.8
(c) Adhesion promoter	-	0.2	0.2	0.2
Total dry matter	-	100	100	100
% monomer ≤ 3 acrylate functions by weight with respect to the sum of monomers	-	41%	80%	100%
weight % with respect to the sum of monomers with molecular mass < 800 g/mol	-	41%	100%	100%
% by weight of (meth)acrylate (a1) compounds in the protective layer	-	0%	65%	90%

[0168] The compositions are defined in terms of mass percentage.

The compositions are applied to glass substrates by spin coating or with a Meyer bar.

- The coatings cured by UV irradiation are cross-linked by UV radiation supplied
- 5 by a Light Hammer® lamp with H+ bulb at a rate of between 10 and 50 m/min.
- The polymerizable compositions are applied so as to have a thickness after curing of about 15 µm.

3. Preparation of the materials tested

10

[0169] The table below lists for each material comprising a substrate coated with a functional coating:

- the nature of the organic protective layer,
- the polymerizable composition used,
- 15 - the thickness of the organic protective layer after curing.

Materials	Comp.	Inv.1	Inv.2
Polymerizable comp.	CC	CI1	CI2
Functional rev.	Yes	Yes	Yes
Thickness (µm)	15	15	15

III. Characterization

- 20 [0170] **1. Assessment of removal by heat treatment**

1.a. Thermogravimetric analysis

- [0171] The thermal stability of the protective coatings was determined by
- 25 thermogravimetric analysis (TGA) at atmospheric pressure in air with a heating rate of 10°C/min at a temperature of 30°C to 700°C.

[Fig.1] shows the mass loss curves in % as a function of temperature after curing:

- of the comp. composition (CC),
- of the composition according to the invention (CI1).

This figure shows a shift in the C11 curve towards lower temperatures. The composition according to the invention begins to degrade at a significantly lower temperature. Due to its lower thermal stability, the composition degrades more rapidly in the tempering furnace.

5

[0172] Tempering tests using a vertical furnace were carried out. The vertical furnace makes it possible to simulate the tempering conditions in a laboratory. The glass is held vertically by means of a system of clamps, on a mobile support. This support is automatically inserted into the furnace situated above the required temperature. Once the tempering time has elapsed, the support comes back down and the glass is subjected to a jet of cold air on its two faces using a system of nozzles. The furnace has no convection and the temperature is regulated with the aid of 3 thermocouples located at 3 different locations. The following parameters are set:

15

- Oven temperature: 670°C,
- Heating time: Variable,
- Cooling time: 100 s,
- Cold air pressure: 0.7 bar.

20

[0173] For each material, the shortest tempering times were determined. These times correspond to the minimum times to:

- obtain a good-quality glazing especially with absence of breakage, absence of iridescence, absence of corrosion of the functional coating, good flatness,
- obtain a glazing having a satisfactory fragmentation, and

25

- remove the temporary protective layer.

Material	Tempering time
Comp.	330 s
Inv.1	315 s

[0174] With the polymerizable composition of the prior art (CC), the minimum tempering time is 330 s under our conditions. When these times are shortened, unburned composition is observed to still be present on the functional coating.

30

[0175] With the polymerizable composition of the invention (CI1), for tempering times of 315 s or even shorter, there is no residue and good fragmentation on breaking is observed.

5

[0176] **2. Odor assessment following heat treatment**

[0177] During heat treatment of the temporary protective layer of the prior art, volatile organic compounds ("VOCs") can be emitted and under certain
10 conditions:

- during edge trimming: an abrasive wheel removes the protective layer and the functional coating from the substrate and/or
- during high-temperature thermal treatment.

It is likely that the emission of these volatile compounds generates
15 unpleasant odors.

These negative effects are not observed materials according to the invention Inv.1 and Inv.2. This is probably due to the absence of compounds with a high molecular mass, that is, around 1,000 g/mol.

Claims

[Claim 1] A material comprising a substrate coated with a functional coating and a temporary organic protective layer deposited on at least part of the functional coating, the protective layer is obtained by crosslinking a polymerizable composition comprising (a) (meth)acrylate compounds and (b) optionally a polymerization initiator, characterized in that:

the temporary organic protective layer has a weight loss by thermogravimetric analysis (TGA) from 30°C to 450°C at a heating rate of 10°C/min in air of greater than 65%, preferably greater than 70%, or even greater than 75%.

[Claim 2] The material comprising a substrate coated with a functional coating and a temporary organic protective layer deposited on at least part of the functional coating, the protective layer comprises a polymeric matrix obtained by crosslinking a polymerizable composition comprising (a) (meth)acrylate compounds and optionally (b) a polymerization initiator, characterized in that the polymerizable composition comprises (meth)acrylate compounds (a1) comprising at least one alkyleneoxy group and a molecular mass of between 100 and 800 g/mol, these (meth)acrylate compounds (a1) representing at least 30% by mass of the total mass of the protective layer.

[Claim 3] The material according to any one of the preceding claims, characterized in that at least 70% by mass of the total mass of the protective layer comprises (meth)acrylate compounds (a) having a molecular mass of between 100 and 800 g/mol, preferably between 100 and 500 g/mol.

[Claim 4] The material according to any one of the preceding claims, characterized in that the polymerizable composition comprises (meth)acrylate compounds (a1) representing at least 50% by mass of the total mass of the protective layer.

[Claim 5] The material according to the preceding claim, characterized in that the (meth)acrylate compounds (a1) comprise 1 to 3 (meth)acrylate functions.

[Claim 6] The material according to any one of the preceding claims,
5 characterized in that the (meth)acrylate compounds (a1) are selected from (meth)acrylate compounds comprising at least 2 alkyleneoxy groups.

[Claim 7] The material according to any one of the preceding claims,
10 characterized in that the (meth)acrylate compounds (a1) have an average molecular mass of between 300 and 800 g/mol.

[Claim 8] The material according to any one of the preceding claims,
15 characterized in that (meth)acrylate compounds (a1) having 3 (meth)acrylate functions represent at least 40% by mass with respect to the total mass of the organic protective layer.

[Claim 9] The material according to any one of the preceding claims,
20 characterized in that the compounds (a) and (b) that have reacted with one another represent at least 90% by mass of the organic protective layer.

[Claim 10] The material according to any one of the preceding claims,
25 characterized in that the polymerizable composition comprises (meth)acrylate compounds (a) having 1 to 3 (meth)acrylate functions representing at least 50% by mass with respect to the total mass of the organic protective layer.

[Claim 11] The material according to any one of the preceding claims,
30 characterized in that the polymerizable composition comprises (meth)acrylate compounds (a) having 1 or 2 (meth)acrylate functions representing at least 5% by mass with respect to the total mass of the organic protective layer.

[Claim 12] The material according to any one of the preceding claims,
characterized in that the polymerizable composition comprises (meth)acrylate

compounds (a) having at least 4 (meth)acrylate functions, which represents at least 5% by mass with respect to the total mass of the organic protective layer.

[Claim 13] The material according to any one of the preceding claims,
5 characterized in that the organic protective layer has a thickness:

- less than 50 μm , and
- greater than 1 μm .

[Claim 14] The material according to any one of the preceding claims,
10 characterized in that the temporary protective layer is directly in contact with the functional coating.

[Claim 15] The material comprising a substrate according to any one of the preceding claims, characterized in that the functional coating is deposited by
15 magnetron sputtering.

[Claim 16] The material according to any one of the preceding claims, characterized in that the functional coating comprises at least one functional silver-based metallic layer.
20

[Claim 17] The material comprising a substrate according to any one of the preceding claims, characterized in that the functional coating comprises a stack of thin layers successively comprising, starting from the substrate, an alternation of n functional metallic layers based on silver or on a metal alloy
25 containing silver, and of (n+1) dielectric coatings, each dielectric coating comprising at least one dielectric layer, so that each functional metallic layer is positioned between two dielectric coatings.