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Tanning aids with a high protection factor

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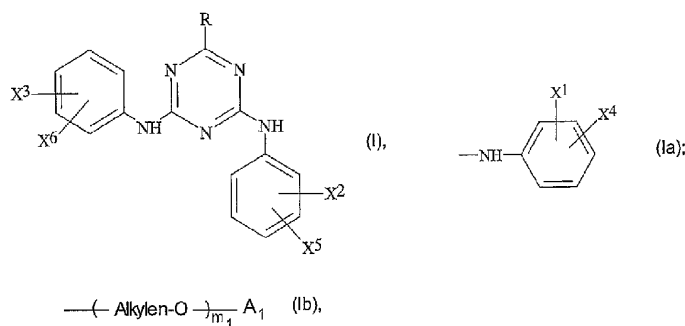
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(54) Title: TANNING AIDS WITH A HIGH PROTECTION FACTOR

(54) Bezeichnung: BRÄUNUNGSHILFEN MIT HOHEM SCHUTZFAKTOR



(57) Abstract: The invention relates to tanning aids exhibiting a high protection factor, comprising polymethylmethacrylate moulded bodies. The transparency of the polymethylmethacrylate moulded body at 380nm is at least 40% and the polymethylmethacrylate moulded body comprises 0.005-0.1 wt. % of at least one Triazin compound, in relation to the weight of said polymethylmethacrylate moulded body, according to formula (I) wherein R = Halogen, C₁-C₂₂-Alkyl, C₁-C₂₂-alkoxy, C₁-C₂₂-hydroxyalkoxy, C₁-C₂₂-alkoxyalkyl, -NHR¹, -N(R¹)₂, or a radical of (Ia) X¹, X² and X³ independently represent -CONHR¹, -NR²R³, -SO₂R⁴, -CN, -COR⁵ oder -COOR⁶; R¹ = hydrogen, C₁-C₂₂-alkyl, C₆-C₂₀-aryl, C₇-C₂₀-aralkyl, C₆-C₈-cycloalkyl, or a radical of formula (Ib) wherein A₁ = C₁-C₈-alkyl, C₇-C₈-cycloalkyl, C₆-C₂₀-aryl, C₇-C₂₀-aralkyl; and m₁ = 1-10, R² and R³ independently represent hydrogen, C₁-C₂₂-alkyl, C₆-C₈-cycloalkyl, C₆-C₂₀-aryl, C₇-C₂₀-aralkyl, a radical of formula (Ib) or a radical of formula COR¹; R⁴ = hydrogen, C₁-C₂₂-alkyl, C₆-C₈-cycloalkyl, C₆-C₂₀-aryl, C₇-C₂₀-aralkyl, a radical of formula NR²R³; R⁵ and R⁶ independently represent hydrogen, C₁-C₂₂-alkyl, C₆-C₈-cycloalkyl, C₆-C₂₀-aryl, C₇-C₂₀-aralkyl or a radical of formula (Ib); X⁴, X⁵ and X⁶ independently represent hydrogen or hydroxy.

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Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft Bräunungshilfen, einen Polymethylmethacrylat-Formkörper umfasst, wobei die Transparenz des Polymethylmethacrylat-Formkörpers bei 380nm mindestens 40% beträgt und der Polymethylmethacrylat-Formkörper 0,005 bis 0,1 Gew.-%, bezogen auf das Gewicht des Polymethylmethacrylat-Formkörpers, mindestens einer Triazinverbindung gemäss Formel (I) umfasst worin R Halogen, C₁-C₂₂-Alkyl, C₁-C₂₂-Alkoxy, C₁-C₂₂-Hydroxyalkoxy, C₁-C₂₂-Alkoxyalkyl, -N(R¹)₂, oder einen Rest der Formel (Ia) X¹, X² und X³ unabhängig voneinander -CONIR¹, -NR²R³, -SO₂R⁴, -CN, -COR⁵ oder -COOR⁶; R¹ Wasserstoff, C₁-C₂₂-Alkyl, C₆-C₂₀-Aryl, C₇-C₂₀-Aralkyl, C₅-C₈-Cycloalkyl, oder einen Rest der Formel (Ib) worin A₁ C₁-C₈-Alkyl, C₃-C₆-Cycloalkyl, C₆-C₂₀-Aryl, C₇-C₂₀-Aralkyl; und

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PCT Application PCT/EP2004/002064

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C. E. SITCH
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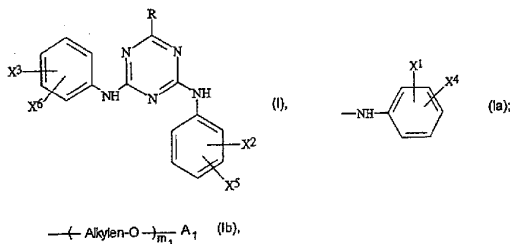
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For an explanation of the two-letter codes and the other abbreviations, reference is made to the explanations ("Guidance Notes on Codes and Abbreviations") at the beginning of each regular edition of the PCT Gazette.

(57) **Zusammenfassung:** Die vorliegende Erfindung betrifft Bräunungshilfen, einen Polymethylmethacrylat-Formkörper umfasst, wobei die Transparenz des Polymethylmethacrylat-Formkörpers bei 380nm mindestens 40% beträgt und der Polymethylmethacrylat-Formkörper 0,005 bis 0,1 Gew.-%, bezogen auf das Gewicht des Polymethylmethacrylat-Formkörpers, mindestens einer Triazinverbindung gemäß Formel (I) umfasst worin R Halogen, C₁-C₂₂-Alkyl, C₁-C₂₂-Alkoxy, C₁-C₂₂-Hydroxyalkoxy, C₁-C₂₂-Alkoxyalkyl, -NHR¹, -N(R¹)₂, oder einen Rest der Formel (Ia) X¹, X² und X³ unabhängig voneinander -CONHR¹, -NR²R³, -S(O)₂R⁴, -CN, -COR⁵ oder -COOR⁶; R¹ Wasserstoff, C₁-C₂₂-Alkyl, C₆-C₂₀-Aryl, C₇-C₂₀-Arylalkyl, C₅-C₈-Cycloalkyl, oder einen Rest der Formel (Ib) worin A₁ C₁-C₈-Alkyl, C₃-C₆-Cycloalkyl, C₆-C₂₀-Aryl, C₇-C₂₀-Arylalkyl; und

Tanning aids with-a high protection factor

The present invention relates to tanning aids with a high protection factor which comprise a polymethyl methacrylate shaped body.

A slightly tanned skin is a sign of holiday and health. In order to tan the skin, sunscreen creams and the like are usually used as tanning aids in order to protect the skin against damage by UV radiation. A disadvantage of these auxiliaries is that such creams can trigger allergies in sensitive people. Furthermore, many of these substances are not water-resistant. Accordingly, they are removed during bathing, and are then not applied again. This negligence can easily lead to skin damage.

Moreover, devices are known which bring about tanning of the skin with the help of incorporated UV emitters. Also known in this connection are lying devices for solarium applications made of PMMA, which comprise large amounts of UV stabilizers and/or UV absorbers in order to protect the plastic against degradation by UV radiation. Tanning with sunlight is not possible here, however. A disadvantage of such devices is the high energy consumption of the UV emitters. Moreover, these installations are not intended for operation outdoors, meaning that tanning is more likely to be perceived as boring.

In view of the prior art given and discussed here, it was consequently an object of the present invention to provide tanning aids which can be used to achieve natural tanning of the skin using sunlight without the skin coming into contact with sunscreen cream.

Moreover, it was an object of the present invention to provide a tanning aid which is particularly easy to maintain.

- 5 A further object of the invention was that the tanning aids have high durability, in particular high resistance to UV irradiation or weathering.

- 10 Furthermore, the object underlying the invention was to provide tanning aids which can be produced in a particularly simple manner. Thus, for the production of the tanning aids, it should be possible, in particular, to use substrates which are obtainable by extrusion, injection moulding, and by casting processes.

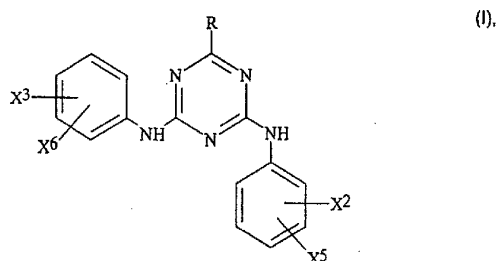
- 15 A further object of the present invention was to provide tanning aids whose sun protection can be adjusted in a particularly simple manner. For example, it should be possible to adjust the time spent under the tanning aid to a pregiven time for many skin types. With regard to classical sunscreen cream, it should be possible to adjust these tanning aids accordingly to a certain sun protection factor.

- 25 Moreover, it should be possible to adapt the tanning aids of the present invention in a particularly simple manner to different requirements and applications. Thus, for example, portable screens and built-in roofs should be available. In this connection, it should be possible to adapt the tanning aids to the requirements in a simple manner with respect to size and shape.

- 35 These objects and others which, while not specified in terms of words, can be derived quite naturally from the connections discussed herein or arise automatically from these, are achieved by the tanning aids described in Claim 1.

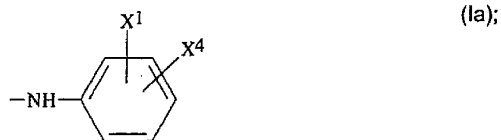
Advantageous modifications of the tanning aids according to the invention are protected in the dependent claims which relate back to Claim 1.

- 5 As a result of the fact that the tanning aid comprises a polymethyl methacrylate shaped body, where the transparency of the polymethyl methacrylate shaped body at 380 nm is at least 40%, and the polymethyl methacrylate shaped body comprises 0.005 to 0.1% by weight, based on the weight of the polymethyl methacrylate shaped body, of at least one triazine compound according to formula (I)



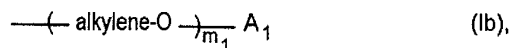
in which

- 15 R is halogen, C₁-C₂₂-alkyl, C₁-C₂₂-alkoxy, C₁-C₂₂-hydroxyalkoxy, C₁-C₂₂-alkoxyalkyl, -NHR₁-, -N(R¹)₂, or a radical of the formula (Ia)



X¹, X² and X³,

- 20 independently of one another, are -CONHR¹, -NR²R³, -SO₂R⁴, -CN, -COR⁵ or -COOR⁶, in which R¹ is hydrogen, C₁-C₂₂-alkyl, C₆-C₂₀-aryl, C₇-C₂₀-aralkyl, C₅-C₈-cycloalkyl, or a radical of the formula (Ib)



- 25 in which

- 4 -

A₁ is C₁-C₈-alkyl, C₅-C₆-cycloalkyl, C₆-C₂₀-aryl,
C₇-C₂₀-aralkyl;

and

m₁ is 1 to 10,

5 R² and R³, independently of one another,
are hydrogen, C₁-C₂₂-alkyl, C₆-C₈-cycloalkyl,
C₆-C₂₀-aryl, C₇-C₂₀-aralkyl, a radical of the
formula (Ib) or a radical of the formula -COR¹;

10 R⁴ is hydrogen, C₁-C₂₂-alkyl, C₆-C₈-cycloalkyl,
C₆-C₂₀-aryl, C₇-C₂₀-aralkyl, a radical of the
formula (Ib) or a radical of the formula -NR²R³;

15 R⁵ and R⁶, independently of one another,
are hydrogen, C₁-C₂₂-alkyl, C₆-C₈-cycloalkyl,
C₆-C₂₀-aryl, C₇-C₂₀-aralkyl or a radical of the
formula (Ib);

X⁴, X⁵ and X⁶, independently of one another,
are hydrogen or hydroxyl,

it is surprisingly possible to provide a tanning aid
with the help of which natural tanning with sunlight is
20 possible without the skin coming into contact with
sunscreen cream.

The measures according to the invention achieve, inter
alia, in particular the following advantages:

- 25
- The tanning aids according to the invention make
tanning outside possible.
 - 30 ➤ Furthermore, it is possible to dispense with
energy-intensive UV emitters during tanning.
 - 35 ➤ The tanning aids according to the invention are
easy to maintain and easy to produce. Thus, it is
possible, in particular, to use shaped bodies
which are obtainable by extrusion, injection
moulding and casting processes.
 - The tanning aids are weathering-resistant and, in
particular, resistant to UV radiation.

Furthermore, the tanning aids according to the invention have very good mechanical properties.

5 ➤ Furthermore, the tanning aids according to the invention can be adapted easily to very diverse requirements. Thus, it is possible to produce, in particular, transportable screens or solid roofs in any size in order to permit natural tanning of the skin without having to worry about skin damage
10 as a result.

 ➤ Moreover, the tanning aids can be produced for each skin type, meaning that different durations outside can be provided.

15 For the purposes of the present invention, the term tanning aid means a device which comprises at least one polymethyl methacrylate shaped body which can be brought between the sunlight and a skin surface to be
20 tanned. Accordingly, these may, in particular, be transparent roofs of buildings or screens which are, for example, immovably fixed. Moreover, roofs which can be fixed to boats, in particular paddle boats, electric boats and the like, are suitable as tanning aids.

25 Moreover, however, they may also be transportable screens which, depending on the thickness of the polymethyl methacrylate shaped body, are fixed in terms of their dimensions, or which can also be collapsed and
30 stored.

 The tanning aid according to the invention comprises a polymethyl methacrylate shaped body. Polymethyl methacrylate (PMMA) is known per se in the specialist
35 field. The polymethyl methacrylate shaped body preferably comprises at least 30% by weight, based on the weight of the polymethyl methacrylate shaped body, of polymethyl methacrylate.

Polymethyl methacrylates are generally obtained by free-radical polymerization of mixtures which comprise methyl methacrylate. In general, these mixtures comprise at least 40% by weight, preferably at least 5 60% by weight and particularly preferably at least 80% by weight, based on the weight of the monomers, of methyl methacrylate.

10 In addition, these mixtures for the preparation of polymethyl methacrylates can comprise further (meth)acrylates which are copolymerizable with methyl methacrylate. The expression (meth)acrylate includes methacrylates and acrylates, and mixtures of the two.

15 These monomers are also known. These include, inter alia, (meth)acrylates, which are derived from saturated alcohols, such as, for example, methyl acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate tert-butyl 20 (meth)acrylate, pentyl (meth)acrylate and 2-ethylhexyl (meth)acrylate;

(meth)acrylates which are derived from unsaturated alcohols, such as, for example, oleyl (meth)acrylate, 2-propynyl (meth)acrylate, allyl (meth)acrylate, vinyl 25 (meth)acrylate;

Aryl (meth)acrylates, such as benzyl (meth)acrylate or phenyl (meth)acrylate, where the aryl radicals may in each case be unsubstituted or substituted up to four times;

30 cycloalkyl (meth)acrylates, such as 2-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 35 (meth)acrylate;

glycol di(meth)acrylates, such as 1,4-butandiol (meth)acrylate, (meth)acrylates of ether alcohols, such as tetrahydrofurfuryl (meth)acrylate, vinyloxyethoxyethyl (meth)acrylate;

- amides and nitriles of (meth)acrylic acid, such as
N-(3-dimethylaminopropyl) (meth)acrylamide,
N-(diethylphosphono) (meth)acrylamide,
1-methacryloylamido-2-methyl-2-propanol;
5 sulphur-containing methacrylates, such as
ethylsulphinylethyl (meth)acrylate,
4-thiocyanatobutyl (meth)acrylate,
ethylsulphonylethyl (meth)acrylate,
thiocyanatomethyl (meth)acrylate,
10 methylsulphinylmethyl (meth)acrylate,
bis((meth)acryloyloxyethyl) sulphide;
polyvalent (meth)acrylates, such as
trimethyloxypropane tri(meth)acrylate.
- 15 As well as the (meth)acrylates listed above, the
compositions to be polymerized can also have further
unsaturated monomers which are copolymerizable with
methyl methacrylate and the abovementioned
(meth)acrylates.
- 20 These include, inter alia, 1-alkenes, such as 1-hexene,
1-heptene; branched alkenes, such as, for example,
vinylcyclohexane, 3,3-dimethyl-1-propene, 3-methyl-1-
diisobutylene, 4-methyl-1-pentene;
- 25 acrylonitriles; vinyl esters, such as vinyl acetate;
styrene, substituted styrenes with an alkyl substituent
in the side chain, such as, for example, α -methyl-
styrene and α -ethylstyrene, substituted styrenes with
30 an alkyl substituent on the ring, such as vinyltoluene
and p-methylstyrene, halogenated styrenes, such as, for
example, monochlorostyrenes, dichlorostyrenes,
tribromostyrenes and tetrabromostyrenes;
heterocyclic vinyl compounds, such as 2-vinylpyridine,
35 3-vinylpyridine, 2-methyl-5-vinylpyridine, 3-ethyl-4-
vinylpyridine, 2,3-dimethyl-5-vinylpyridine,
vinylpyridimidine, 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, vinylthiolan, vinylthiazoles and hydrogenated vinylthiazoles, 5 vinyloxazoles and hydrogenated vinyloxazoles;

vinyl and isoprenyl ethers;
maleic acid derivatives, such as, for example, maleic anhydride, methylmaleic anhydride, maleinimide, 10 methylmaleinimide; and dienes, such as, for example, divinylbenzene.

In general, these comonomers are used in an amount of from 0 to 60% by weight, preferably 0 to 40% by weight 15 and particularly preferably 0 to 20% by weight, based on the weight of the monomers, where the compounds can be used individually or as a mixture.

The polymerization is generally started using known 20 free-radical initiators. Preferred initiators include, inter alia, the azo initiators known throughout the specialist field, such as AIBN and 1,1-azobiscyclohexanecarbonitrile, and peroxy compounds, such as methyl ethyl ketone peroxide, acetylacetone 25 peroxide, dilauryl peroxide, tert-butyl per-2-ethylhexanoate, ketone peroxide, methyl isobutyl ketone peroxide, cyclohexanone peroxide, dibenzoyl peroxide, tert-butyl peroxybenzoate, tert-butyl peroxyisopropylcarbonate, 2,5-bis(2-ethylhexanoylperoxy)-2,5- 30 dimethylhexane, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxy-3,5,5-trimethylhexanoate, 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- 35 butylcyclohexyl)peroxydicarbonate, mixtures of two or more of these specified compounds with one another, and mixtures of these specified compounds with unspecified compounds which can likewise form free radicals.

These compounds are often used in an amount of from 0.01 to 10% by weight, preferably from 0.5 to 3% by weight, based on the weight of the monomers.

- 5 In this connection, it is possible to use different poly(meth)acrylates which differ, for example, in their molecular weight or in the monomer composition.

- Furthermore, the polymethyl methacrylate shaped bodies
10 can comprise further polymers in order to modify the properties. These include, inter alia, polyacrylonitriles, polystyrenes, polyethers, polyesters, polycarbonates and polyvinyl chlorides. These polymers can be used individually or as a
15 mixture, where also copolymers which can be derived from the abovementioned polymers.

- The plastic substrates according to the invention can, for example, be prepared from moulding materials of the
20 abovementioned polymers. In this connection, use is generally made of thermoplastic moulding processes, such as extrusion or injection moulding.

- The weight-average of the molecular weight M_w of the
25 homopolymers and/or copolymers to be used according to the invention as moulding material for the preparation of the plastic substrates can vary within wide ranges, the molecular weight usually being matched to the intended use and the processing method of the moulding
30 material. However, it is generally in the range between 20 000 and 1 000 000 g/mol, preferably 50 000 to 500 000 g/mol and particularly preferably 80 000 to 300 000 g/mol, without being limited by this. This parameter can be determined, for example, by means of
35 gel permeation chromatography.

Furthermore, the plastic substrates can be produced by casting chamber processes. In this, suitable (meth)acrylic mixtures are, for example, placed into a

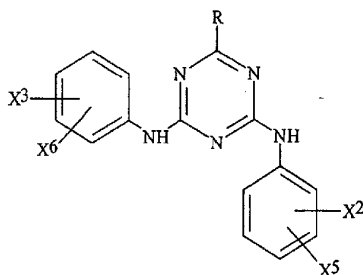
mould and polymerized. Such (meth)acrylic mixtures generally have the above-described (meth)acrylates, in particular methyl methacrylate.

- 5 Furthermore, the (meth)acrylic mixtures of the above-described copolymers and, particularly for adjusting the viscosity, polymers, in particular, poly(meth)acrylates, may be present.
- 10 The weight-average of the molecular weight M_w of the polymers which are prepared by casting chamber processes is generally higher than the molecular weight of polymers which are used in moulding materials. This gives rise to a number of known advantages. In general,
- 15 the weight average of the molecular weight of polymers which are prepared by casting chamber processes is in the range from 500 000 to 10 000 000 g/mol, without being limited by this.
- 20 According to a particular embodiment of the present invention, the matrix of the polymethyl methacrylate shaped body has at least 70%, preferably at least 80%, and particularly preferably at least 90% by weight, based on the weight of the polymethyl methacrylate
- 25 shaped body, of polymethyl methacrylate.

The polymethyl methacrylate shaped body comprises 0.005 to 0.4% by weight, in particular 0.005 to 0.1% by weight, preferably 0.01 to 0.04% by weight, based on

30 the total weight of the polymethyl methacrylate shaped body, of at least one triazine compound according to formula (I)

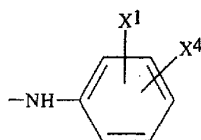
(I),



in which

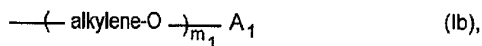
- 5 R is halogen, for example fluorine, chlorine, bromine or iodine, C₁-C₂₂-alkyl, C₁-C₂₂-alkoxy, C₁-C₂₂-hydroxyalkoxy, C₁-C₂₂-alkoxyalkyl, -NHR₁-, -N(R¹)₂, or a radical of the formula (Ia)

(Ia);



X¹, X² and X³,

- 10 independently of one another, are -CONHR¹, -NR²R³, -SO₂R⁴, -CN, -COR⁵ or -COOR⁶, in which R¹ is hydrogen, C₁-C₂₂-alkyl, C₆-C₂₀-aryl, C₇-C₂₀-aralkyl, C₅-C₈-cycloalkyl, or a radical of the formula (Ib)



in which

A₁ is C₁-C₈-alkyl, C₅-C₆-cycloalkyl, C₆-C₂₀-aryl, C₇-C₂₀-aralkyl;
and

- 20 m₁ is 1 to 10,

R² and R³, independently of one another, are hydrogen, C₁-C₂₂-alkyl, C₆-C₈-cycloalkyl, C₆-C₂₀-aryl, C₇-C₂₀-aralkyl, a radical of the formula (Ib) or a radical of the formula -COR¹;

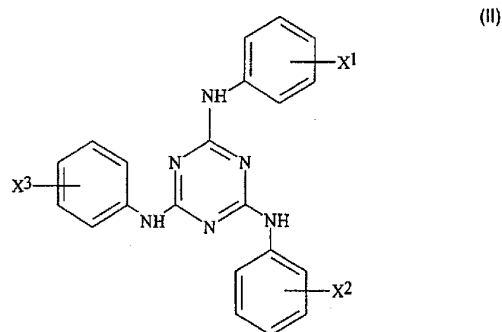
R^4 is hydrogen, C_1 - C_{22} -alkyl, C_6 - C_8 -cycloalkyl, C_6 - C_{20} -aryl, C_7 - C_{20} -aralkyl, a radical of the formula (Ib) or a radical of the formula $-NR^2R^3$;

5 R^5 and R^6 , independently of one another, are hydrogen, C_1 - C_{22} -alkyl, C_6 - C_8 -cycloalkyl, C_6 - C_{20} -aryl, C_7 - C_{20} -aralkyl or a radical of the formula (Ib);

X^4 , X^5 and X^6 , independently of one another, are hydrogen or hydroxyl.

10

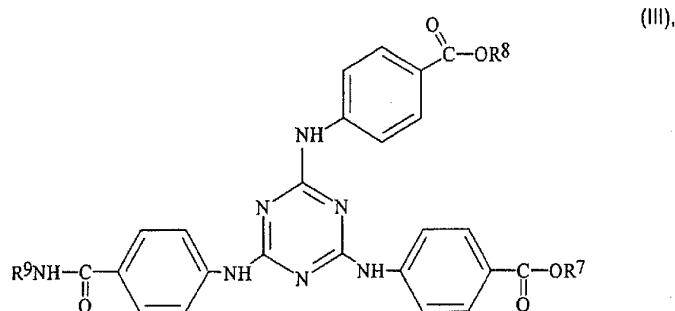
According to a particular aspect of the present invention, triazine compounds are used which can be represented by formula (II)



15

in which the radicals X^1 , X^2 , X^3 have the meanings given above.

20 According to a particular embodiment of the present invention, triazine compound are used which can be represented by formula (III)



in which the radicals R^7 , R^8 and R^9 , independently of one another, are C_1 - C_{22} -alkyl.

5

The alkyl radicals according to the abovementioned formulae (I) to (III) may be linear or branched. Furthermore, these radicals may have substituents, for example halogen atoms. Preferred straight-chain and
 10 branched C_1 - C_{22} -alkyl include, for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, t-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl,
 15 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl or eicosyl.

20

The alkoxy radicals according to the abovementioned formulae (I) and (II) may be linear or branched. Furthermore, these radicals may have substituents, for example halogen atoms.

25

Examples of straight-chain and branched C_1 - C_{22} -alkoxy are, for example, methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec-butoxy, tert-butoxy, pentoxy, isopentoxy, n-heptyloxy, n-octyloxy, isooctyloxy,

n-nonyloxy, isononyloxy, decyloxy, n-dodecyloxy, heptadecyloxy octadecyloxy or eicosyloxy.

5 Preferred cycloalkyl groups include the cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and the cyclooctyl group, which are optionally substituted by branched or unbranched alkyl groups.

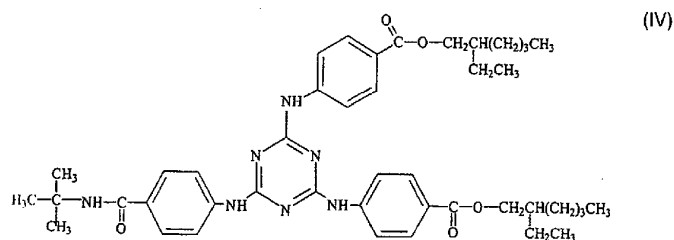
10 Preferred cycloalkoxy groups include cycloalkoxy groups whose hydrocarbon radical is one of the abovementioned preferred cycloalkyl groups.

15 The aryl radicals may be optionally substituted by one or more C₁-C₄-alkyl or alkoxy radicals. Examples of C₆-C₂₀-aryl are, in particular, phenyl, naphthyl and biphenyl.

20 The aralkyl radicals may be optionally substituted by one or more C₁- to C₄-alkyl or alkoxy radicals. Examples of C₇-C₂₀-aralkyl are benzyl, phenethyl, α -methylphenethyl or α,α -dimethylbenzyl.

25 "Alkylenes" means a bivalent alkylenes group having, preferably, 1 to 5, in particular 2 to 4, carbon atoms. These radicals include, inter alia, methylene, ethylene, n-propylene, isopropylene, n-butylene, isobutylene, pentylene, 2-ethylpropylene.

30 Particular preference is given to using the triazine compound which can be represented by formula (IV)



The compounds according to the above formulae and the preparation thereof are known per se and are described, for example, in EP-A 0 818 450.

The compound according to formula (IV), bis(2-ethylhexyl) 4,4'-[[6-[[4-[[1,1-dimethylethyl]-amino]carbonyl]phenyl]amino]-1,3,5-triazine-2,4-diyl]-diimino]bisbenzoacetate, can be obtained commercially from Ciba under the trade name ®Uvasorb HEB.

Furthermore, the polymethyl methacrylate shaped body can comprise further known additives, their amount, however, being restricted to the intended use of the tanning aids according to the invention. These include, inter alia, antistatics, antioxidants, mould-release agents, flame retardants, lubricants, dyes, flow improvers, fillers, light stabilizers, UV absorbers and organic phosphorus compounds, such as phosphites or phosphonates, pigments, anti-weathering agents and plasticizers.

Preferred additives include dyes which, dissolved in methyl methacrylate at a concentration of 0.01% by weight, display a transmission at 350 nm of at least 30%. Such dyes are known per se and are available, for example, under the trade name ®Makrolex blue RR, ®Makrolex violet B, ®Makrolex violet 3R, ®Makrolex green 5B, ®Makrolex green G, from Bayer, ®Sandoplast

blue 2B, @Sandoplast red BB, and @Sandoplast green G from Clariant, @Mikrolit violet BK from Ciba.

Furthermore, preferred additives include IR absorbers.

5 These include, inter alia, IR-Absorber 2052 from Bayer.

Furthermore, the polymethyl methacrylate shaped body can comprise spherical particles. For the purposes of the present invention, the term spherical means that
10 the particles preferably have a ball-like shape, it being obvious to the person skilled in the art that, due to the preparation methods, particles with a different shape may also be present, or that the shape of the particles can deviate from the ideal ball shape.

15 Accordingly, the term spherical means that the ratio of the largest dimension of the particles to the smallest dimension is at most 4, preferably at most 2, these dimensions in each case being measured through the
20 centre of gravity of the particles. Preferably at least 70%, particularly preferably at least 90%, based on the number of particles, are spherical.

The particles preferably have an average diameter
25 (weight-average) in the range from 5 to 50 μm , preferably in the range from 8 to 25 μm . More favourably, 75% of the particles are in the range from 5 to 35 μm .

30 These particles may, for example, be made of inorganic materials, in particular of BaSO_4 or plastic, preference being given to plastic particles. In this connection, the refractive index of the particles has a refractive number n_0 measured at the Na-D line (589 nm) and at 20°C
35 which differs from the refractive number n_0 of the matrix plastic by 0.02 to 0.2 unit.

The spherical plastic particles preferably comprise crosslinked polystyrene and/or crosslinked poly(meth)acrylates.

- 5 Mixtures from which the plastic particles are prepared particularly preferably have at least 80% by weight of styrene and at least 0.5% by weight of divinylbenzene.

- 10 The preparation of crosslinked plastic particles is known in the specialist field. For example, the scatter particles can be prepared by emulsion polymerization, as described, for example, in EP-A 342 283 or EP-A 269 324, very particularly preferably by polymerization in organic phase, as described, for
15 example, in German Patent Application P 43 27 464.1, where, in the case of the last-mentioned polymerization technique, particularly narrow particle size distributions or, put another way, particularly small deviations of the particle diameters from the average
20 particle diameter, arise.

The polymethyl methacrylate shaped body can comprise, for example, 2 to 50% by weight, preferably 4 to 10% by weight, of particles which develop a scattering effect.

- 25 As a result of this, a reduction in the dazzling effect by solar irradiation can surprisingly be achieved without tanning of the skin being impaired too much. This preferred embodiment of the tanning aid according
30 to the invention is particularly suitable for applications in which a dazzling effect of the sun is to be reduced.

- 35 According to a particular aspect of the present invention, the polymethyl methacrylate shaped body has an impact strength of at least 20 kJ/m² measured in accordance with DIN 53453 (standard test piece). To improve this mechanical property, known impact-resistance modifiers in particular can be used.

Preferred impact-resistant moulding materials which can be used to produce the polymethyl methacrylate shaped body comprise 1 to 30, preferably 2 to 20, particularly preferably 3 to 15, in particular 5 to 12, % by weight
5 of an impact-resistance modifying agent, which represents an elastomer phase of crosslinked polymer particles.

The impact-resistance modifying agent can be obtained
10 in a manner known per se by bead polymerization or by emulsion polymerization.

Preferred impact-resistance modifying agents represent crosslinked particles with an average particle size in
15 the range from 50 to 1 000 nm, preferably 60 to 500 nm and particularly preferably 80 to 120 nm.

Particles of this type can be obtained, for example, by the free-radical polymerization of mixtures which
20 generally at least 40% by weight, preferably 50 to 70% by weight, of methyl methacrylate, 20 to 80% by weight, preferably 25 to 35% by weight, of butyl acrylate, and 0.1 to 2% by weight, preferably 0.5 to 1% by weight, of a crosslinking monomer, e.g. a multifunctional
25 (meth)acrylate, such as, for example, allyl methacrylate and comonomers which can be copolymerized with the abovementioned vinyl compounds.

The preferred comonomers include, inter alia, C₁-C₄-alkyl (meth)acrylates, such as ethyl acrylate or butyl
30 methacrylate, preferably methyl acrylate, or other vinylically polymerizable monomers, such as, for example, styrene. The mixtures for the preparation of the abovementioned particles may preferably comprise 0
35 to 10% by weight, preferably 0.5 to 5% by weight, of comonomers.

Particularly preferred impact strength modifying agents are polymer particles which have a two-layer,

particularly preferably a three-layer, core-shell construction. Such core-shell polymers are described, inter alia, in EP-A 0 113 924, EP-A 0 552 351, EP-A 0 465 049 and EP-A 0 683 028.

5

Particularly preferred impact strength modifiers based on acrylate rubber have, inter alia, the following construction:

Core: Polymer with a methyl methacrylate fraction of at least 90% by weight, based on the weight of the core.

Shell 1: Polymer with a butyl acrylate fraction of at least 80% by weight, based on the weight of the first shell.

Shell 2: Polymer with a methyl methacrylate fraction of at least 90% by weight, based on the weight of the second shell.

10 As well as comprising the specified monomers, the core and the shells may in each case comprise further monomers. These have been described above, particularly preferred comonomers having a crosslinking effect.

15 For example, a preferred acrylate rubber modifier may have the following construction:

Core: Copolymer of methyl methacrylate (95.7% by weight), ethyl acrylate (4% by weight) and allyl methacrylate (0.3% by weight)

S1: Copolymer of butyl acrylate (81.2% by weight), styrene (17.5% by weight) and allyl methacrylate (1.3% by weight)

S2: Copolymer of methyl methacrylate (96% by weight) and ethyl acrylate (4% by weight)

The ratio of core to shell(s) in the acrylate rubber modifier may vary within wide ranges. The weight ratio of core to shell C/S is preferably in the range from 20:80 to 80:20, preferably from 30:70 to 70:30 to
5 modifiers with one shell, and the ratio of core to shell 1 to shell 2 C/S1/S2 is in the range from 10:80:10 to 40:20:40, particularly preferably from 20:60:20 to 30:40:30 in the case of modifiers with two shells.

10

The particle size of the core-shell modifiers is usually in the range from 50 to 1 000 nm, preferably 100 to 500 nm and particularly preferably from 150 to 450 nm, without being limited thereby.

15

According to a particular embodiment, the polymethyl methacrylate shaped body has a E modulus of at least 2 800 N/mm², preferably at least 3 300 N/mm² according to ISO 527/2.

20

The thickness of the polymethyl methacrylate shaped body can be within a wide range depending on the intended use. In general, this shaped body has a thickness in the range from 1 to 200 mm, preferably 2

25

to 20 mm.

The surface of the tanning aids may appear shiny or matt. According to a particular embodiment, the tanning aids may be equipped with a satin surface.

30

The size of the tanning aid can be adapted to the requirements. Thus, for example, roofs may be several 100 m² in size or smaller screens may comprise nearly 1 to 2 m².

35

The invention is illustrated in more detail by Example 1 below without the invention being limited to this example.

Example 1

A polymethyl methacrylate panel with a thickness of 3 mm was produced in a casting process. For this,
5 994.208 g of syrup (mixture of methyl methacrylate/polymethyl methacrylate with 8 to 10% conversion), 0.039 g of @Mikrolit violet BK, 0.03 g of Solvaperm red BB, 0.200 g of @Uvasorb HEB obtainable from Ciba Geigy and 0.55 g of
10 2,2-azodi(isobutyronitrile) (AIBN, from Akzo Nobel were mixed and poured into a casting glass mould. This mould was heated at 77°C for 150 minutes.

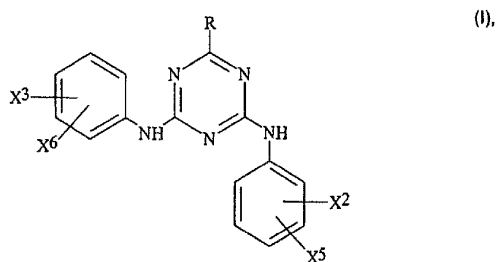
The panel obtained in this way had a UV transmission at
15 380 nm of more than 60% and at 330 nm a transmission of less than 0.1%. The calculated effective radiation intensity was 4.79 mW/m².

The effective irradiation intensity can be calculated
20 by the erythema function, which is expressed the efficiency of ultraviolet radiation for producing reddening of human skin. The evaluation is carried out by multiplying the transmitted irradiation spectrum by the erythema function.

25 The irradiation spectrum arises from the solar spectrum in accordance with standard DIN 67501. Integration of the evaluated spectrum over the wavelength gives the effective irradiation intensity, where the
30 effectiveness refers to the efficacy for producing sunburn. The original solar spectrum has an effective irradiation intensity of about 250.9 mW/m².

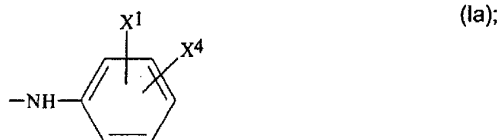
Patent Claims

1. Tanning aid, characterized in that the tanning aid comprises a polymethyl methacrylate shaped body, where the transparency of the polymethyl methacrylate shaped body at 380 nm is at least 40%, and the polymethyl methacrylate shaped body comprises 0.005 to 0.4% by weight, based on the weight of the polymethyl methacrylate shaped body, of at least one triazine compound according to formula (I)

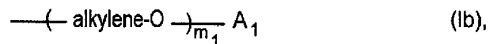


in which

- R is halogen, C₁-C₂₂-alkyl, C₁-C₂₂-alkoxy, C₁-C₂₂-hydroxyalkoxy, C₁-C₂₂-alkoxyalkyl, -NHR₁-, -N(R¹)₂, or a radical of the formula (Ia)



- X¹, X² and X³, independently of one another, are -CONHR¹, -NR²R³, -SO₂R⁴, -CN, -COR⁵ or -COOR⁶;
R¹ is hydrogen, C₁-C₂₂-alkyl, C₆-C₂₀-aryl, C₇-C₂₀-aralkyl, C₅-C₈-cycloalkyl, or a radical of the formula (Ib)



in which

A₁ is C₁-C₈-alkyl, C₅-C₆-cycloalkyl, C₆-C₂₀-aryl, C₇-C₂₀-aralkyl;

and

5 m₁ is 1 to 10,

R² and R³, independently of one another,

are hydrogen, C₁-C₂₂-alkyl, C₆-C₈-cycloalkyl, C₆-C₂₀-aryl, C₇-C₂₀-aralkyl, a radical of the formula (Ib) or a radical of the formula -COR¹;

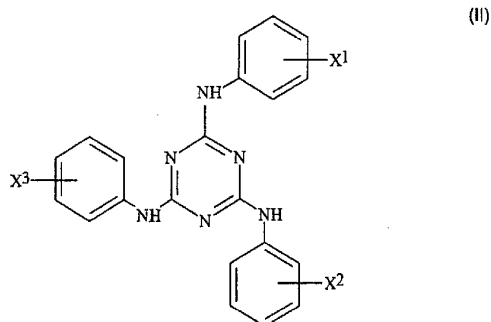
10 R⁴ is hydrogen, C₁-C₂₂-alkyl, C₆-C₈-cycloalkyl, C₆-C₂₀-aryl, C₇-C₂₀-aralkyl, a radical of the formula (Ib) or a radical of the formula -NR²R³;

R⁵ and R⁶, independently of one another,

15 are hydrogen, C₁-C₂₂-alkyl, C₆-C₈-cycloalkyl, C₆-C₂₀-aryl, C₇-C₂₀-aralkyl or a radical of the formula (Ib);

X⁴, X⁵ and X⁶, independently of one another, are hydrogen or hydroxyl.

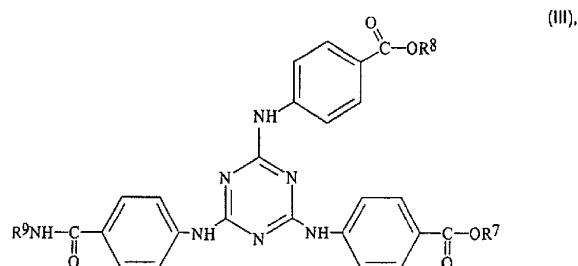
- 20 2. Tanning aid according to Claim 1, characterized in that the triazine compound can be represented by formula (II)



25 in which the radicals X¹, X², X³ have the meaning given in Claim 1.

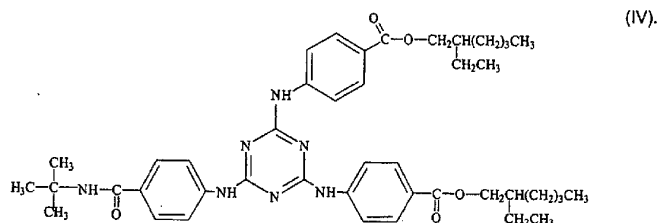
3. Tanning aid according to Claim 1, characterized in that the triazine compound can be represented by formula (III)

30



in which the radicals R^7 , R^8 and R^9 , independently of one another, are C_1-C_{22} -alkyl.

- 5 4. Tanning aid according to Claim 1, characterized in that the triazine compound can be represented by formula (VI)



- 10 5. Tanning aid according to one of the preceding claims, characterized in that the tanning aid comprises 0.01 to 0.04% by weight, based on the weight of the polymethacrylate shaped body, of triazine compound.
- 15 6. Tanning aid according to one of the preceding claims, characterized in that the plastic shaped body additionally comprises dyes which, dissolved in MMA at a concentration of 0.01% by weight, exhibit a transmission of at least 30% at 350 nm.
- 20 7. Tanning aid according to one of the preceding claims, characterized in that the transparency of
- 25

the polymethyl methacrylate shaped body at 400 nm is at least 30%.

- 5 8. Tanning aid according to one of the preceding claims, characterized in that the transparency of the polymethyl methacrylate shaped body at 330 nm is at most 30%.
- 10 9. Tanning aid according to one of the preceding claims, characterized in that the ratio of transparency of the polymethyl methacrylate shaped body at 400 nm to the transparency at 330 nm is at least 20.
- 15 10. Tanning aid according to one of the preceding claims, characterized in that the polymethyl methacrylate shaped body comprises an IR absorber.
- 20 11. Tanning aid according to one or more of the preceding claims, characterized in that the polymethyl methacrylate shaped body has an impact resistance of at least 20 kJ/m².
- 25 12. Tanning aid according to one or more of the preceding claims, characterized in that the polymethyl methacrylate shaped body has a thickness in the range from 1 to 200 mm.
- 30 14. Tanning aid according to one or more of the preceding claims, characterized in that the polymethyl methacrylate shaped body has an E modulus of at least 2 800 N/mm².
- 35 15. Tanning aid according to one of the preceding claims, characterized in that the polymethyl methacrylate shaped body comprises spherical particles.