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(54) **Title**: COMPOSITE PIGMENT AND METHOD FOR PREPARATION THEREOF

(57) **Abstract**: The present invention relates to a composite pigment comprising at least one core particle wherein the surface of the core particle is at least in part covered with at least one layer comprising at least one solid UV filter having a mean particle size of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm. The composite pigment can be prepared by a method comprising a step of subjecting the core particle and at least one solid UV filter having a mean particle size of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm to a mechanochemical fusion process such as a hybridizer process. The composite pigment can be advantageously used as a component for a cosmetic composition.

DESCRIPTION

COMPOSITE PIGMENT AND METHOD FOR PREPARATION THEREOF

TECHNICAL FIELD

The present invention relates to a composite pigment comprising a core particle which is at least partially covered by solid UV filter(s) within a specific selected particle size range, as well as a method for preparing the composite pigment.

BACKGROUND ART

Many cosmetics include one or more UV filters in order to shield UV rays. In particular, skin cosmetics commonly include inorganic solid UV filters such as fine particles of TiO_2 for protecting the skin from UV rays.

However, inorganic solid UV filters such as fine particles of TiO_2 can easily aggregate and have poor dispersibility. Therefore, it is often difficult to uniformly disperse them in the form of primary particles in cosmetics. Therefore, the UV filtering property of cosmetics including inorganic solid UV filters is difficult to be enhanced.

JP-A-2007-254429 discloses composite pigments comprising a relatively large core particle covered with inorganic solid UV filters.

The composite pigments based on a relatively large core particle covered with inorganic solid UV filters can provide improved UV filtering effects, because the aggregation of the inorganic solid UV filters can be prevented.

However, the UV filtering effects provided by the above composite pigments are still insufficient, and thus further improvement in the UV filtering effects is desired. In particular, the improvement in filtering effects in the UVA region (wavelength region from 315 to 400 nm) is needed.

DISCLOSURE OF INVENTION

Thus, an objective of the present invention is to provide a novel composite pigment which is based on solid UV filter(s) and which

can provide better UV filtering effects, in particular in the UVA region.

The above objective of the present invention can be achieved by a composite pigment comprising
at least one core particle,
wherein the surface of the core particle is at least in part covered with at least one layer comprising at least one solid UV filter having a mean particle size of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm.

The core particle may have a mean particle size of from 300 nm to less than 30 μm, preferably from 300 nm to less than 20 μm, and more preferably from 300 nm to less than 15 μm.

The above at least one layer in the composite pigment according to the present invention may have a thickness of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm.

The solid UV filter may comprise at least one inorganic compound selected from the group consisting of silicon carbide, metal oxides, and mixtures thereof.

In a preferred embodiment, the solid UV filter is an inorganic solid UV filter, preferably made from a metal oxide.

On the other hand, the solid UV filter may comprise at least one organic compound selected from the group consisting of solid benzotriazole derivatives, oxanilide derivatives, solid triazine derivatives, triazole derivatives, vinyl-group containing amides, cinnamic acid amides, sulfonated benzimidazoles, and mixtures thereof.

The above at least one layer in the composite pigment according to the present invention may further comprise at least one additional UV filter. The additional UV filter may be selected from the group consisting of anthranilic derivatives; dibenzoylmethane derivatives, liquid cinnamic derivatives, salicylic derivatives, camphor derivatives, benzophenone derivatives, β,β-diphenylacrylate derivatives, liquid triazine derivatives, liquid benzotriazole derivatives, benzalmalonate derivatives, benzimidazole derivatives, imidazoline derivatives, bis-benzoazolyl derivatives, p-aminobenzoic acid (PABA) and

derivatives thereof, methylenebis(hydroxyphenylbenzotriazole) derivatives, benzoxazole derivatives, screening polymers and screening silicones, dimers derived from α-alkylstyrene, 4,4-diarylbutadienes, and octocrylene and derivatives thereof, guaiazulene and derivatives thereof, rutin and derivatives thereof, flavonoids, biflavonoids, oryzanol and derivatives thereof, quinic acid and derivatives thereof, phenols, retinol, cysteine, aromatic amino acids, peptides having an aromatic amino acid residue, and mixtures thereof.

The above at least one layer in the composite pigment according to the present invention may further comprise at least one coloring pigment. The coloring pigment may be selected from the group consisting of titanium dioxide, zirconium oxide, cerium oxide, zinc oxide, iron oxide, chromium oxide, manganese violet, ultramarine blue, chromium hydrate, ferric blue, aluminum powder, copper powder, silver powder, gold powder, barium sulfate, carbon black, pigments of D&C type, lakes, pearlescent pigments, silica, and mixtures thereof.

The core particle in the composite pigment according to the present invention may comprise at least one inorganic material and/or at least one organic material.

The inorganic material may be selected from the group consisting of mica, synthetic mica, talc, sericite, boron nitride, glass flake, calcium carbonate, barium sulfate, titanium oxide, hydroxyapatite, silica, silicate, zinc oxide, magnesium sulfate, magnesium carbonate, magnesium trisilicate, aluminum oxide, aluminum silicate, calcium silicate, calcium phosphate, magnesium oxide, bismuth oxychloride, kaolin, hydrotalcite, mineral clay, synthetic clay, iron oxide, and mixtures thereof.

In a preferred embodiment, the core particle is made from silica.

The organic material may be selected from the group consisting of poly(meth)acrylates, polyamides, silicones, polyurethanes, polyethylenes, polypropylenes, polystyrenes, polyhydroxyalkanoates, polycaprolactams, poly(butylene) succinates, polysaccharides, polypeptides, polyvinyl alcohols, polyvinyl resins, fluoropolymers, waxes, amidosulfonic acid polyvalent metal salts, acylated amino acids, and mixtures thereof.

In a preferred embodiment, the core particle is made from polyamides and poly(meth)acrylates.

The weight ratio of the core particle(s) to the solid UV filter(s) may be 90:10 to 10:90, preferably 80:20 to 20:80, and more preferably 70:30 to 30:70.

The composite pigment according to the present invention can be prepared by a method comprising a step of subjecting
at least one core particle,
at least one solid UV filter having a mean particle size of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm,
optionally at least one coloring pigment, and
optionally at least one additional UV filter,
to a mechanochemical fusion process.

The present invention also relates to a composite pigment composition comprising:
at least one small particle with a mean particle size of from 300 nm to less than 1 μm, preferably from 300 nm to less than 600 nm, and more preferably from 300 nm to less than 400 nm; and
at least one large particle with a mean particle size of 2 μm or more, preferably 3 μm or more, more preferably 5 μm or more, and even more preferably 10 μm or more;
wherein the surface of the small and large particle is at least in part covered with at least one layer comprising at least one solid UV filter having a mean particle size of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm.

The small and large particle may comprise at least one inorganic material and/or at least one organic material.

The weight ratio of the small particle(s) to the large particle(s) may be 90:10 to 10:90, preferably 80:20 to 20:80, and more preferably 70:30 to 30:70.

The composite pigment composition according to the present invention can be prepared by a method comprising a step of subjecting:
at least one small particle with a mean particle size of from 300 nm to less than 1 μm, preferably from 300 nm to less than 600 nm, and more preferably from 300 nm to less than 400 nm;

at least one large particle with a mean particle size of 2 μm or more, preferably 3 μm or more, more preferably 5 μm or more, and even more preferably 10 μm or more;
at least one solid UV filter having a mean particle size of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm;
optionally at least one coloring pigment; and
optionally at least one additional UV filter,
to a mechanochemical fusion process.

The present invention also relates to a cosmetic composition comprising a composite pigment according to the present invention or a composite pigment composition according to the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

After diligent research, the inventors have discovered that it is possible to obtain a new composite pigment providing enhanced UV filtering effects, in particular in the UVA region.

The new composite pigment according to the present invention comprises at least one core particle wherein the surface of the core particle is at least in part covered with at least one layer comprising at least one solid UV filter having a mean particle size of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm.

Surprisingly, it was discovered that a single core particle covered with a UV filter particle or particles with the above specific particle size can provide better UV filtering effects, in particular in the UVA region, than a single core particle covered with a smaller UV filter particle or particles having a mean particle size of less than 100 nm, and that the UV filtering effects, in particular in the UVA region, can be further enhanced when dual core particles with different particle sizes are used to form a composite pigment composition.

The composite pigment or composite pigment composition according to the present invention also has the following effects.

Since solid UV filter(s) is/are firmly bonded on the core particle, the UV filter(s) cannot penetrate into the skin via pores on the skin. In addition, even if solid UV filters may

irritate, a large amount of the solid UV filters cannot directly contact with the skin, because they are present on the core particle. Accordingly, the composite pigment or composite pigment composition according to the present invention is safer than the bulk of solid UV filters.

Further, the composite pigment or composite pigment composition according to the present invention can provide a better feeling on use, because fine particles of solid UV filter(s) are firmly fixed on the core particle so that it is possible to reduce free fine particles which have a high friction coefficient such that they do not easily spread on the skin and provide an unpleasant feeling on use.

Furthermore, a cosmetic composition comprising the composite pigment or composite pigment composition according to the present invention can exert advantageous cosmetic and/or practical effects due to the inclusion of the composite pigment or composite pigment composition according to the present invention. For example, the cosmetic composition according to the present invention has better UV shielding effects, in particular in the UVA region. In addition, the cosmetic composition according to the present invention in the form of a powder also has a smooth feeling on use due to reduced friction.

Hereafter, each of the elements constituting the composite pigment, and cosmetic composition, according to the present invention will be described in a detailed manner.

(Core Particle)

The core particle to be used for the composite pigment according to the present invention is not limited.

It is preferable that the core particle has a mean particle size or a mean particle diameter of from 300 nm to less than 30 μm, preferably from 300 nm to less than 20 μm, and more preferably from 300 nm to less than 15 μm.

The core particle can have a mean particle size or a mean particle diameter of from 300 nm to less than 1 μm, preferably from 300 nm to less than 600 nm, and more preferably from 300 nm to less than 400 nm. On the other hand, the core particle can have a mean particle size or a mean particle diameter of 2 μm or more, preferably 3 μm or more, more preferably 4 μm or more, and

even more preferably 5 μm or more. In this case, the mean particle size or a mean particle diameter of the core particle may be limited to 50 μm or less, preferably 30 μm or less, and more preferably 20 μm or less, and even more preferably 15 μm or less.

The mean particle size or mean particle diameter here is an arithmetric mean diameter, and can be determined, for example, by calculating the average of the dimensions of one hundred particles chosen on an image obtained with a scanning electron microscope.

The core particle can be in any shape. For example, the core particle may be a concave particle having at least one concavity, and preferably in a general concave shape. The concave is not a small dimple or pit, but a large hollow or crater which preferably includes a geometrical center or a center of gravity of the particle. Preferably, the core particle defines an inner concave surface and an outer convex surface which is opposite to the inner concave surface. In particular, the core particle is preferably in the form of a portion of a hollow sphere or a bowl. The substrate may have a transverse cross section with the shape of a horseshoe or arch.

On the other hand, it is possible to use a core particle in the form of a plate with an aspect ratio of at least 5, preferably more than 10, more preferably more than 20, and more preferably more than 50. The aspect ratio can be determined by the average thickness and the average length according to the formula: aspect ratio = length/thickness.

If a plate-like particle is used for the present invention, it is possible that the plate-like particle has a length ranging from 300 nm to less than 1 μm, preferably from 300 nm to less than 600 nm, and more preferably from 300 nm to less than 400 nm, or 2 μm or more, preferably 3 μm or more, more preferably 4 μm or more, and even more preferably 5 μm or more, but ranging 50 μm or less, preferably 30 μm or less, and more preferably 20 μm or less, and even more preferably 15 μm or less.

In a preferred embodiment, the core particle has a spherical shape.

The material of the core particle is not limited. The material can be at least one inorganic material and/or at least one organic material.

The inorganic material and/or organic material may be hollow or porous. The porosity of the material may be characterized by a specific surface area of from 0.05 m^2/g to 1,500 m^2/g, more preferably from 0.1 m^2/g to 1,000 m^2/g, and more preferably from 0.2 m^2/g to 500 m^2/g according to the BET method. However, it is preferable to use solid inorganic material(s) and/or solid organic material(s), preferably 'not hollow' materials.

Preferably, the inorganic material can be selected from the group consisting of mica, synthetic mica, talc, sericite, boron nitride, glass flakes, calcium carbonate, barium sulfate, titanium oxide, hydroxyapatite, silica, silicate, zinc oxide, magnesium sulfate, magnesium carbonate, magnesium trisilicate, aluminum oxide, aluminum silicate, calcium silicate, calcium phosphate, magnesium oxide, bismuth oxychloride, kaolin, hydrotalcite, mineral clay, synthetic clay, iron oxide, and mixtures thereof.

Natural mica, synthetic mica, sericite, kaolin, talc, silica and mixtures thereof are more preferable. Silica in the form of a spherical shape is most preferable.

In particular, silica particles such as P-1500 marketed by JGC C&C are preferable as inorganic particles.

Preferably, the organic material can be selected from the group consisting of poly(meth)acrylates, polyamides, silicones, polyurethanes, polyethylenes, polypropylenes, polystyrenes, polyhydroxyalkanoates, polycaprolactams, poly(butylene) succinates, polysaccharides, polypeptides, polyvinyl alcohols, polyvinyl resins, fluoropolymers, waxes, amidosulfonic acid polyvalent metal salts, acylated amino acids, and mixtures thereof.

Poly(meth)acrylates such as polymethylmethacrylates; polyamides such as Nylon®, silicones, polyurethanes, polyhydroxyalkanoates such as polylactic acids, fluoropolymers and mixtures thereof are more preferable. Poly(meth)acrylates, polyamides and mixtures thereof in the form of a spherical shape are most preferable.

As the polymethylmethacrylate particles, MP-2200, MP-2701 and MP-1451 marketed by Soken, and SJ touch 1 marketed by Sekisui Plastics are preferable.

As the polyamide particles, SP-500 marketed by Toray and Orgasol marketed by Arkema are preferable.

As the polyurethane particles, D-400 marketed by Toshiki Pigment are preferable.

As the fluoropolymers, for example, PTFE may be used. As the PTFE particles, Ceridust 9205F marketed by Clariant are preferable.

As the amidosulfonic acid polyvalent metal salts, for example, N-lauroyltaurine calcium may be used. As the acylated amino acids, lauroyllysine may be used.

The core particle may or may not be coated beforehand. In a particular embodiment, the core particle is coated. The material of a coating of the core particle is not limited, but an organic material such as an amino acid, an N-acylamino acid, an amido, a silicone, a modified silicone, and a polyolefin is preferable. As the organic material, mention may be made of lauroyl lysine, acryl-modified silicone, and polyethylene.

In particular, silica particles coated with polyethylene such as ACEMATT OK412 marketed by Degussa are preferable as the coated core particles.

(Layer on Core Particle)

The core particle is at least partially covered with at least one layer comprising at least one solid UV filter. The layer may be referred to as a coating layer. Preferably, 10% or more of the surface of the core particle can be covered by the coating layer(s). More preferably, 50% or more of the surface of the core particle can be covered by the coating layer(s). More preferably, 80% or more of the core particle can be covered by the coating layer(s). Most preferably, the entire surface of the core particle can be covered by the coating layer(s).

The solid UV filter in the coating layer on the core particle has a mean particle size of from 100 nm to less than 300 nm,

preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm.

Due to the use of the solid UV filter with the above particle size range, which corresponds to the medium level between so-called nano size UV filters and so-called pigment size UV filters, the UV filtering effects of the solid UV filter especially in the UVA region can be improved.

The thickness of the coating layer may vary depending on several factors such as the size of the core particle. Typically, depending on the mean particle size of the solid UV filter particle, the thickness of the coating layer may range from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm.

If there are two or more coating layers on the core particle, the thickness and the composition of the coating layers may be the same as or different from each other.

The coating layer(s) may comprise, other than the solid UV filter(s), any additional material(s) such as at least one additional UV filter and/or at least one coloring pigment. The additional material(s) may be present in an amount ranging from 1 to 50 wt% relative to the total weight of the additional material(s) and the solid UV filter(s).

(Inorganic Solid UV Filter)

The solid UV filter(s) in the coating layer on the core particle may be inorganic solid UV filter(s). If two or more inorganic solid UV filters are used, they may be the same or different, preferably the same. The inorganic solid UV filter may be hydrophilic and/or lipophilic. The inorganic solid UV filter is properly insoluble in solvents such as water and ethanol commonly used in cosmetics. The term "solid" means solid at 25°C under 1 atm.

It is preferable that the inorganic solid UV filter is in the form of a medium size fine particle such that the mean (primary) particle diameter thereof ranges from 100 nm to less than 300 nm, preferably 100 nm to less than 250 nm, and more preferably 100 nm to less than 200 nm. The mean (primary) particle size or mean (primary) particle diameter here is an arithmetic mean diameter.

The inorganic solid UV filter may comprise at least one inorganic compound selected from the group consisting of silicon carbide, metal oxides which may or may not be coated, and mixtures thereof.

Preferably, the inorganic solid UV filters are selected from pigments (mean size of the primary particles: generally from 100 nm to 300 nm, preferably from 100 nm to 250 nm) formed of metal oxides, such as, for example, pigments formed of titanium oxide (amorphous or crystalline in the rutile and/or anatase form), iron oxide, zinc oxide, zirconium oxide or cerium oxide, which are all UV photoprotective agents well known per se.

The inorganic solid UV filter may or may not be coated. The inorganic solid UV filter may have at least one coating. The coating may comprise at least one compound selected from the group consisting of alumina, silica, aluminum hydroxide, silicones, silanes, fatty acids or salts thereof(such as sodium, potassium, zinc, iron or aluminum salts), fatty alcohols, lecithin, amino acids, polysaccharides, proteins, alkanolamines, waxes such as beeswax, (meth)acrylic polymers, organic UV filters, and (per)fluoro compounds.

It is preferable for the coating to include at least one organic UV filter. As the organic UV filter in the coating, a dibenzoylmethane derivative such as butyl methoxydibenzoylmethane (Avobenzone) and 2,2'-Methylenebis[6-(2H-Benzotriazol-2-yl)-4-(1,1,3,3-Tetramethyl-Butyl)Phenol] (Methylene Bis-Benzotriazolyl Tetramethylbutylphenol) marketed as "TINOSORB" M by BASF may be preferable.

In a known manner, the silicones in the coating(s) may be organosilicon polymers or oligomers comprising a linear or cyclic and branched or crosslinked structure, of variable molecular weight, obtained by polymerization and/or polycondensation of suitable functional silanes and essentially composed of a repetition of main units in which the silicon atoms are connected to one another via oxygen atoms (siloxane bond), optionally substituted hydrocarbon radicals being connected directly to the said silicon atoms via a carbon atom.

The term "silicones" also encompasses silanes necessary for their preparation, in particular alkylsilanes.

The silicones used for the coating(s) can preferably be selected from the group consisting of alkylsilanes, polydialkylsiloxanes

and polyalkylhydrosiloxanes. More preferably still, the silicones are selected from the group consisting of octyltrimethylsilane, polydimethylsiloxanes and polymethylhydrosiloxanes.

Of course, the inorganic UV filters made of metal oxides may, before their treatment with silicones, have been treated with other surfacing agents, in particular with cerium oxide, alumina, silica, aluminum compounds, silicon compounds or their mixtures.

The coated inorganic solid UV filter may have been prepared by subjecting the inorganic solid UV filter to one or more surface treatments of a chemical, electronic, mechanochemical and/or mechanical nature with any of the compounds as described above, as well as polyethylenes, metal alkoxides (titanium or aluminum alkoxides), metal oxides, sodium hexametaphosphate, and those shown, for example, in Cosmetics & Toiletries, February 1990, Vol. 105, pp. 53-64.

The coated inorganic solid UV filters are preferable, because the UV filtering effects of the inorganic solid UV filters can be enhanced. In addition, the coating may function as a binder for fixing the UV filters on a core particle.

On the other hand, uncoated inorganic solid UV filters such as uncoated titanium oxide pigments such JA-1, JP-3 and JA-C marketed by TAYCA can be used as the inorganic solid UV filter.

The composite pigment according to the present invention has an effect that it can provide not a white appearance but a transparent or clear appearance, because the fine particles of the inorganic solid UV filters do not aggregate but spread on the core particle. It should be noted that free fine particles of inorganic solid UV filter(s) easily aggregate to give a white appearance to the skin.

The inorganic solid UV filter(s) may be used in the composite pigment according to the present invention in proportions such that the weight ratio of the core particle to the inorganic solid UV filter(s) is 90:10 to 10:90, preferably 80:20 to 20:80, and more preferably 70:30 to 30:70.

(Solid Organic UV Filter)

The solid UV filter(s) in the coating layer on the core particle may be organic solid UV filter(s). If two or more organic solid

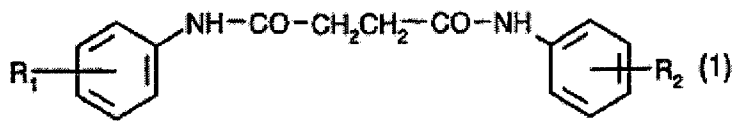
UV filters are used, they may be the same or different, preferably the same. The organic solid UV filter may be hydrophilic and/or lipophilic. The organic solid UV filter is properly insoluble in solvents such as water and ethanol commonly used in cosmetics. The term "solid" means solid at 25°C under 1 atm.

It is preferable that the organic solid UV filter is in the form of a medium size fine particle such that the mean (primary) particle diameter thereof ranges from 100 nm to less than 300 nm, preferably 100 nm to less than 250 nm, and more preferably 100 nm to less than 200 nm. The mean (primary) particle size or mean (primary) particle diameter here is an arithmetric mean diameter.

The material of the organic solid UV filter(s) is not limited as long as it is organic. If two or more organic solid UV filters are used, the material(s) of the organic solid UV filters may be the same as or different from each other.

The organic solid UV filter may comprise at least one organic compound selected from the group consisting of benzotriazole derivatives, oxanilide derivatives, triazine derivatives, triazole derivatives, vinyl-group containing amides, cinnamic acid amides, and sulfonated benzimidazoles.

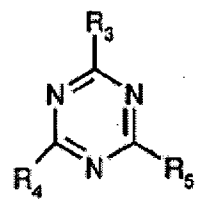
A preferred class of solid oxanilide UV absorbers is that having the formula:



(1)

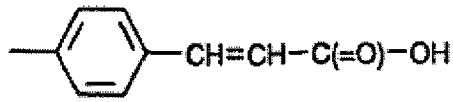
in which R_1 and R_2, independently, are C_1-C_{18} alkyl or C_1-C_{18} alkoxy. A preferred compound of formula (1) is N-(2-ethoxyphenyl)-N'-(2-ethylphenyl)-ethanediamide.

A preferred class of solid triazine UV absorbers is that having the formula:



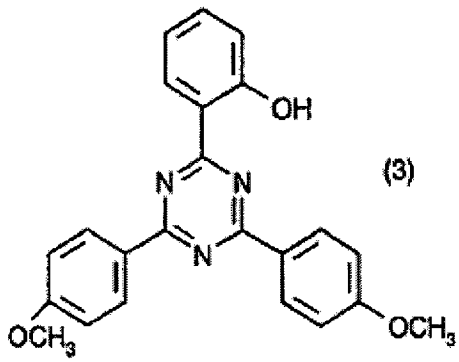
(2)

in which R_3, R_4 and R_5, independently, are H, OH, C_1-C_{18} alkoxy, NH_2, NH-R_6 or N(R_6)$_2$ in which R_6 is C_1-C_{18} alkyl, OR_6 in which R_6 is C_1-C_{18} alkyl, phenyl, phenoxy or anilino, or pyrrole, in which the respective phenyl, phenoxy or anilino, or pyrrolo moieties are optionally substituted by one, two or three substituents selected from OH, carboxy, CO-NH_2, C_1-C_{18} alkyl or alkoxy, C_1-C_{18} carboxyalkyl, C_5-C_8 cycloalkyl, a methylidenecamphor group, the group -(CH=CH)$_m$C(=O)-OR_6 in which m is 0 or 1 and R_6 has the same meaning above, or the group

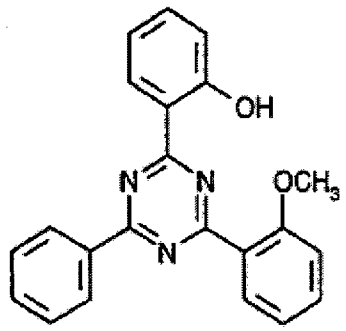


or the corresponding alkali metal, ammonium, mono-, di- or tri-C_1-C_4 alkylammonium, mono-, di- or tri-C_2-C_4 alkanolammonium salts, or the C_1-C_{18} alkyl esters thereof.

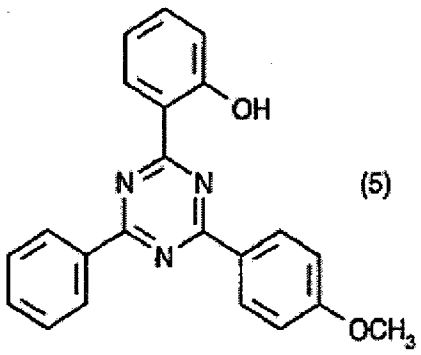
Preferred compounds of formula (2) are those having one of the formulae:



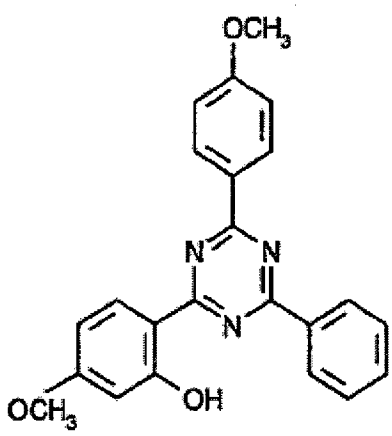
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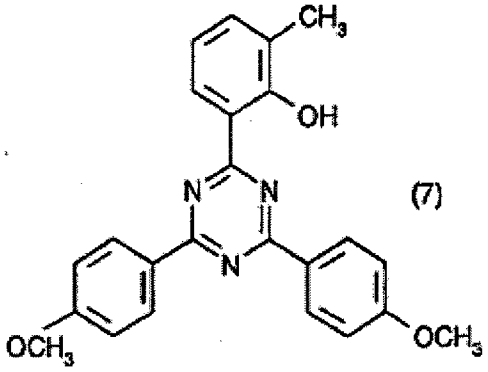
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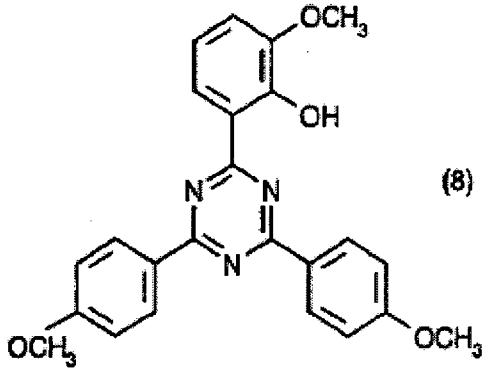
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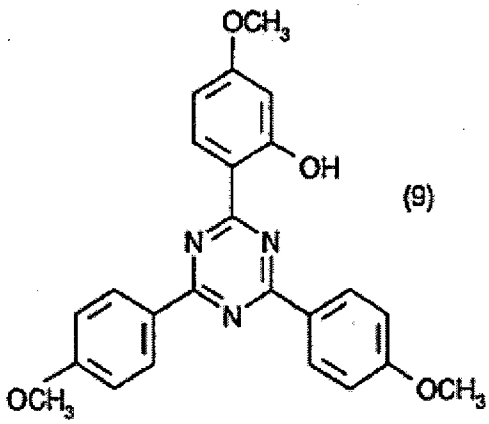
(6)


CH3
OH
N
N
N
OCH3
OCH3

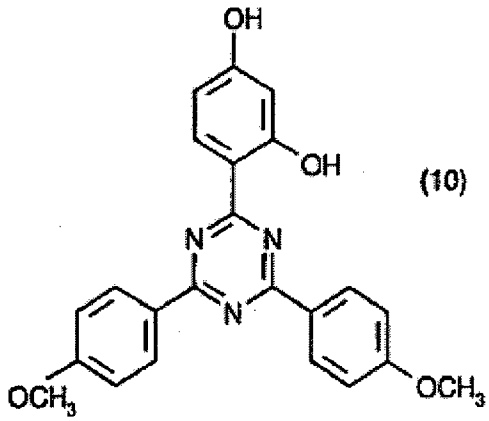
(7)


OCH3
OH
N
N
N
OCH3
OCH3

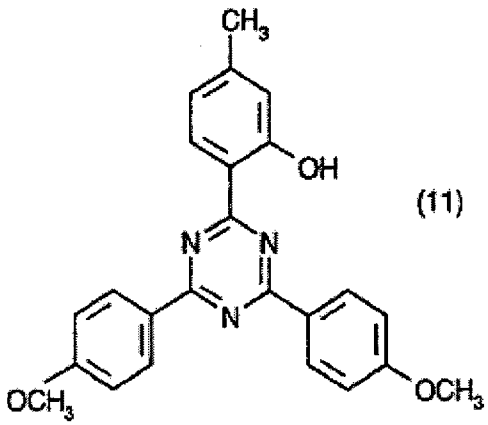
(8)


OCH3
OH
N
N
N
OCH3
OCH3

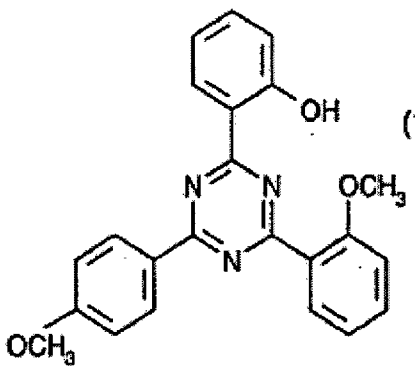
(9)


OH
OH
N
N
N
OCH3
OCH3

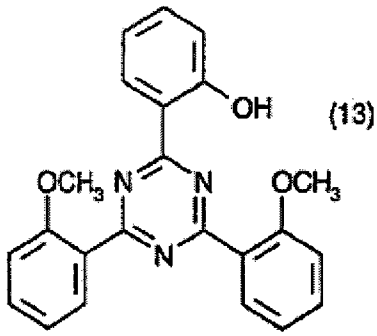
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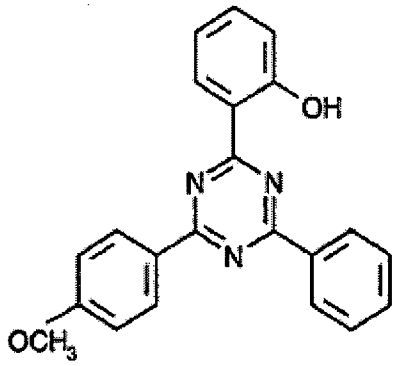

CH3
OH
N
N
N
OCH3
OCH3

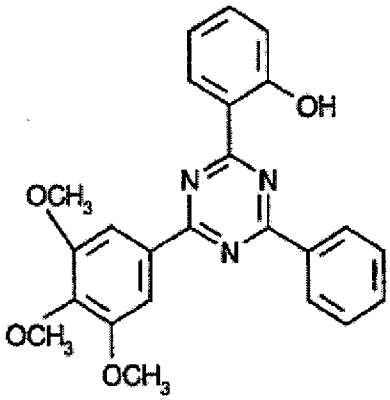
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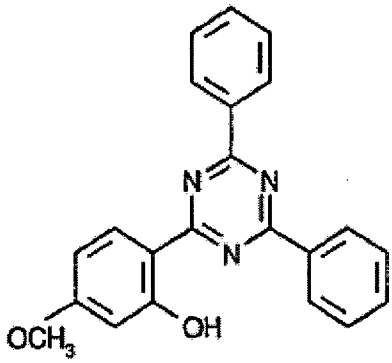

OH
N
N
N
OCH3
OCH3

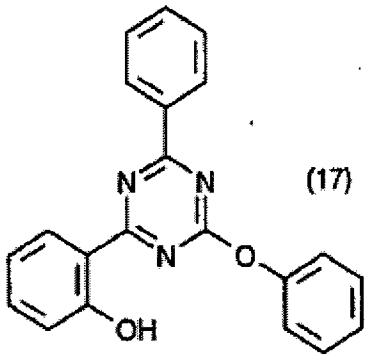
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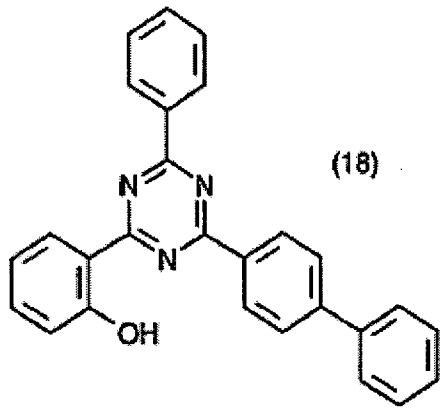

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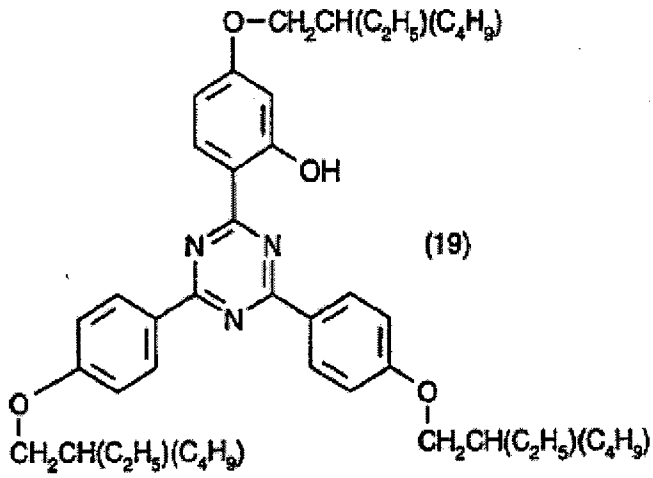

(14)


(15)

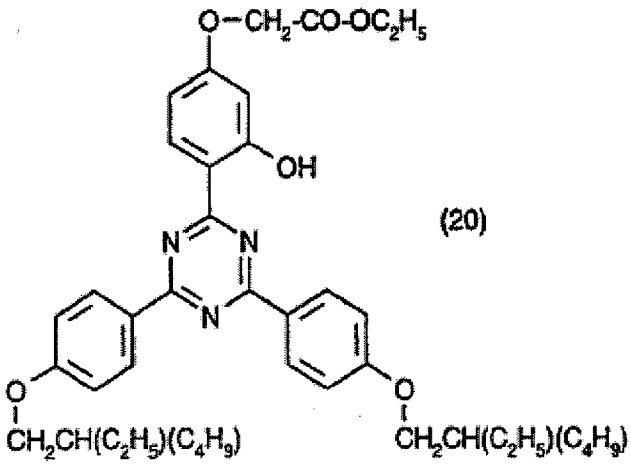

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(17)

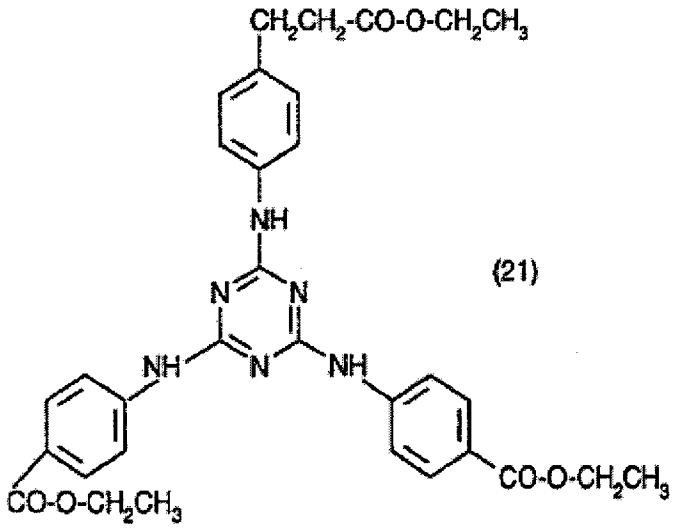

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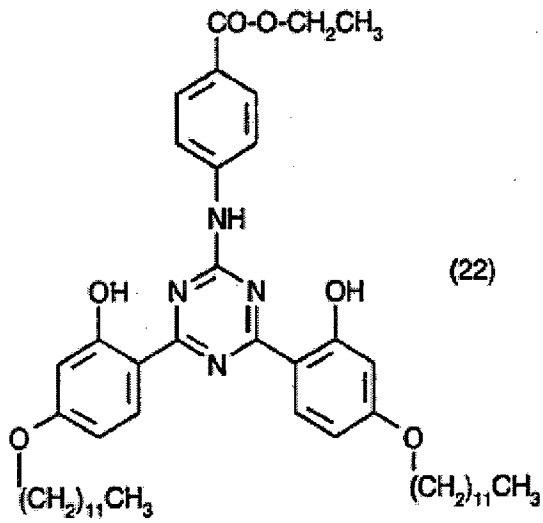
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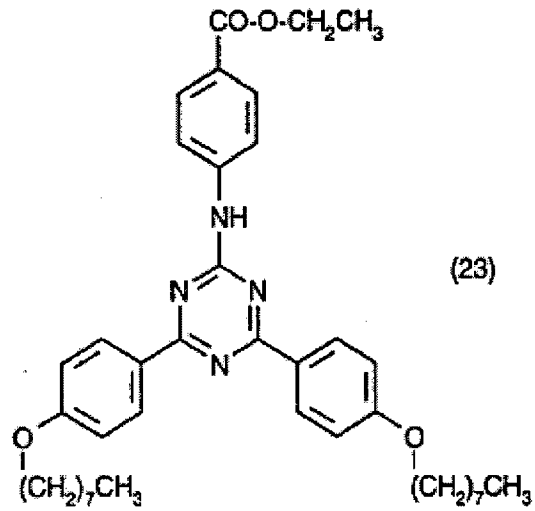
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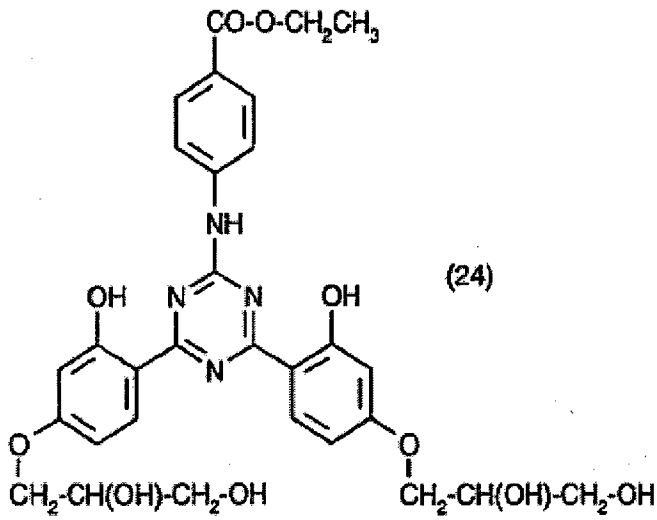
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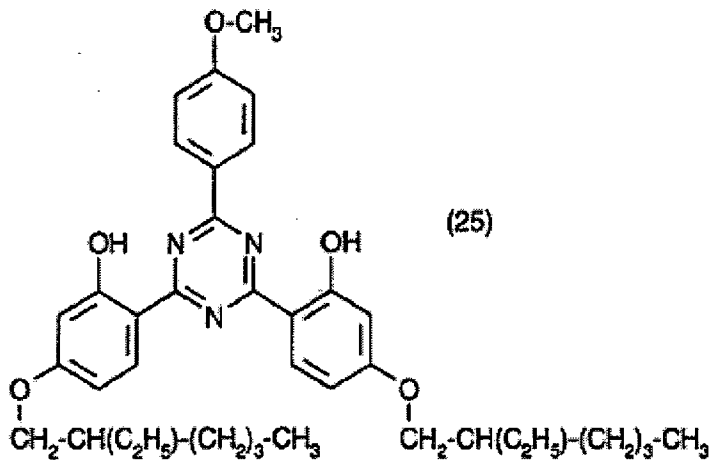
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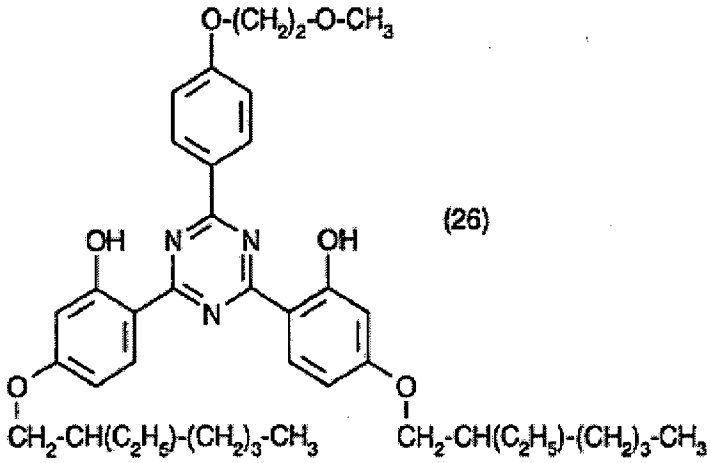
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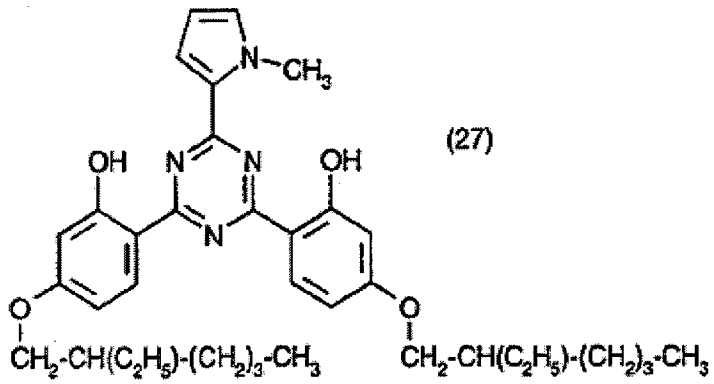
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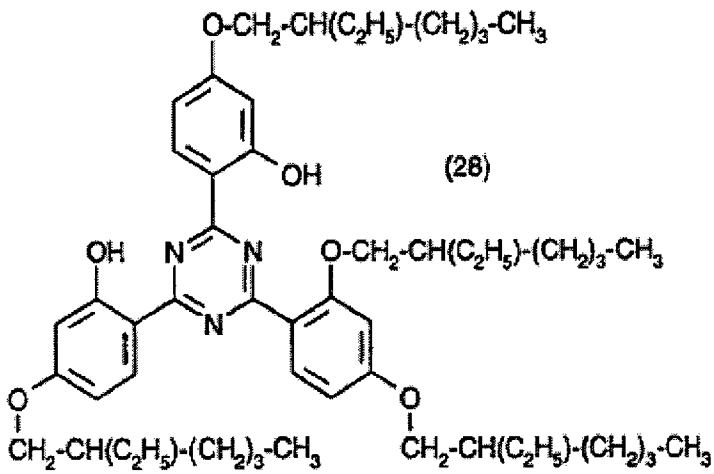
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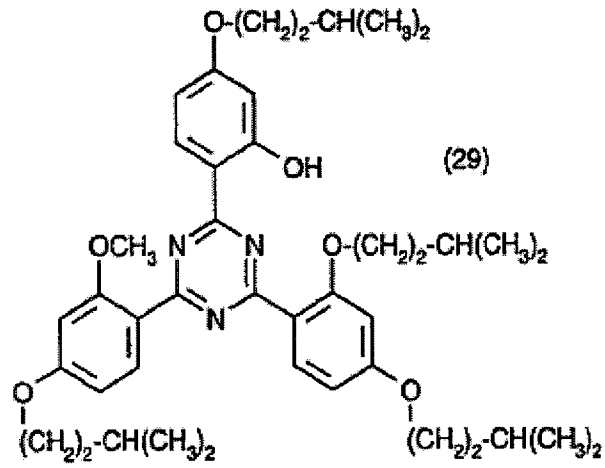
(26)



(27)

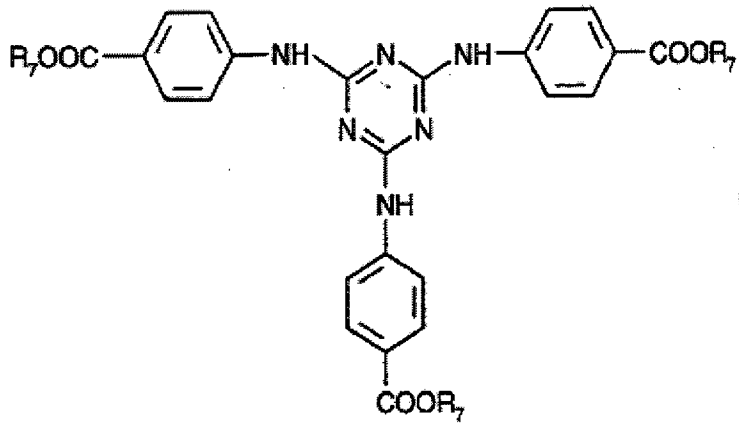


and



as well as 2,4,6-tris(diisobutyl-4'-aminobenzalmalonate)-s-triazine and 2,4-bis(diisobutyl-4-aminobenzalmalonate)-6-(4'-aminobenzylidenecamphor)-s-triazine. Bis-ethylhexyloxyphenol methoxyphenyl triazine, marketed under the trademark "Tinosorb S" by Ciba-Geigy is in particular preferable.

Particularly preferred compounds of formula (2) are those having the formula:

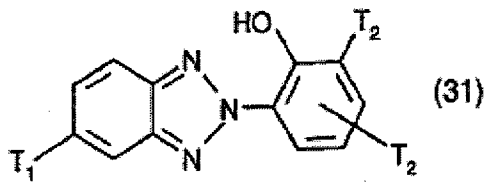


(30)

in which the individual radicals R_7 are the same or different and each is hydrogen; an alkali metal; an ammonium group $N(R_8)_4$ in which R_8 is hydrogen or an organic radical; C_1-C_{20} alkyl; or a polyoxyethylene radical which contains from 1 to 10 ethylene oxide units and the terminal OH group of which may be etherified by a C_1-C_3 alcohol.

In relation to the compounds of formula (30), when R_7 is an alkali metal it is preferably potassium or, especially sodium; when R_7 is the group $N(R_8)_4$ in which R_8 has its previous meaning, it is preferably a mono-, di- or tri-C_1-C_4 alkylammonium salt, a mono-, di- or tri-C_2-C_4 alkanolammonium salt or a C_1-C_{20} alkyl ester thereof; when R_8 is a C_1-C_{20} alkyl group, it is preferably a C_6-C_{12} alkyl group, more preferably a C_8-C_9 alkyl group, especially a 3,5,5-trimethylpentyl group or, most particularly, a 2-ethylhexyl group; and when R_8 is a polyoxyethylene group, this preferably contains from 2-6 ethylene oxide units.

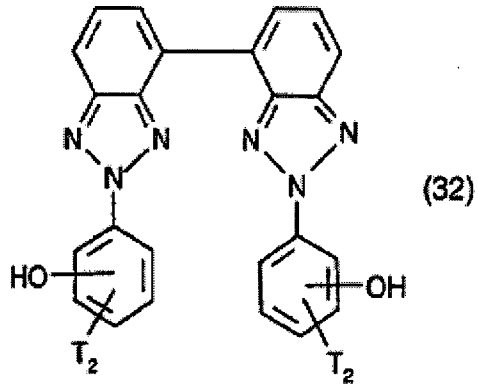
A preferred class of solid triazole UV absorbers is that having the formula:



(31)

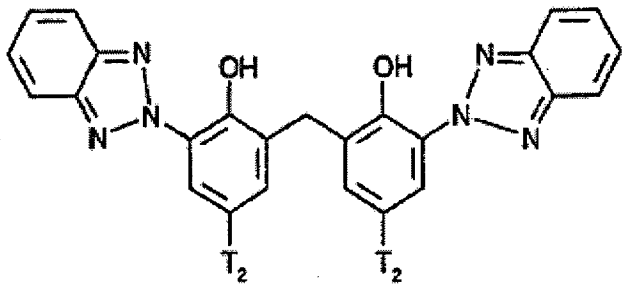
in which T_1 is C_1-C_{18} alkyl or, preferably, hydrogen; and T_2 is hydrogen, hydroxyl, or C_1-C_{18} alkyl, optionally substituted by phenyl, preferably α,α-dimethylbenzyl.

A further preferred class of solid triazole UV absorbers is that having the formula:


(32)

in which T_2 has its previous meaning.

A still further preferred class of solid triazole UV absorbers is that having the formula:


(33)

in which T_2 has its previous meaning and is preferably t-butyl.

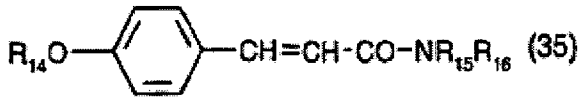
A preferred class of solid vinyl group-containing amide UV absorbers is that having the formula:

$$R_9-(Y)_m-CO-C(R_{10})=C(R_{11})-N(R_{12})(R_{13}) \quad (34)$$

in which R_9 is C_1-C_{18} alkyl, preferably C_1-C_5 alkyl, or phenyl optionally substituted by one, two or three substituents selected from OH, C_1-C_{18} alkyl, C_1-C_{18} alkoxy or $CO-OR_6$ in which R_6 has its previous meaning; R_{10}, R_{11}, R_{12} and R_{13} are the same or different and each is C_1-C_{18} alkyl, preferably C_1-C_5 alkyl, or hydrogen; Y is N or O; and m has its previous meaning.

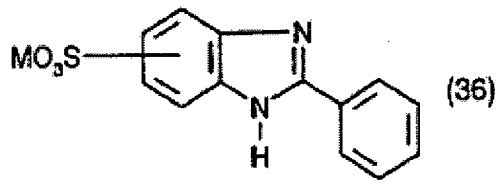
Preferred compounds of formula (34) are 4-octyl-3-penten-2-one, ethyl-3-octylamino-2-butenoate, 3-octylamino-1-phenyl-2-buten-1-one and 3-dodecylamino-1-phenyl-2-buten-1-one.

A preferred class of solid cinnamic acid amide UV absorbers is that having the formula:



in which R_{14} is hydroxy or C_1-C_4 alkoxy, preferably methoxy or ethoxy; R_{15} is hydrogen or C_1-C_4 alkyl, preferably methyl or ethyl; and R_{16} is $-(CONH)_m$-phenyl in which m has its previous meaning and the phenyl group is optionally substituted by one, two or three substituents selected from OH, C_1-C_{18} alkyl, C_1-C_{18} alkoxy or $CO-OR_6$ in which R_6 has its previous meaning. Preferably R_{16} is phenyl, 4-methoxyphenyl or the phenylaminocarbonyl group.

A preferred class of solid sulfonated benzimidazole UV absorbers is that having the formula:



in which M is hydrogen or an alkali metal, preferably sodium, an alkaline earth metal, such as magnesium or calcium, or zinc.

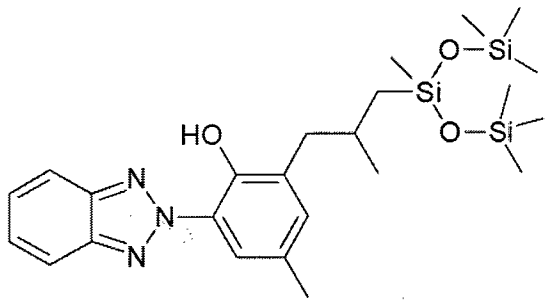
In the compounds of formula (1) to (35), C_1-C_{18} alkyl groups may be methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-amyl, n-hexyl, n-heptyl, n-octyl, iso-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, tetradecyl, hexydecyl or octadecyl; and C_1-C_{18} alkoxy groups include methoxy, ethoxy, propoxy, butoxy, n-hexoxy, n-heptoxy, n-octoxy, iso-octoxy, n-nonoxy, n-decoxy, n-undecoxy, n-dodecoxy, tetradecoxy, hexadecoxy or octadecoxy, methoxy and ethoxy being preferred.

C_1-C_{18} carboxyalkyl includes carboxymethyl, carboxyethyl, carboxypropyl, carboxyisopropyl, carboxybutyl, carboxyisobutyl, carboxybutyl, carboxyamyl, carboxyhexyl, carboxyheptyl, carboxyoctyl, carboxyisooctyl, carboxynonyl, carboxydecyl, carboxyundecyl, carboxydodecyl, carboxytetradecyl, carboxyhexadecyl and carboxyoctadecyl, carboxymethyl being preferred.

C_5-C_8 cycloalkyl includes cyclopentyl, cyclohexyl and cyclooctyl.

The compounds of formula (1) to (35) are known. The compounds of formula (30) are described, together with their production, in U.S. Pat. No. 4,617,390.

It is preferable that the organic solid UV filter(s) is a benzotriazole derivative, in particular, a phenylbenzotriazole derivative such as a drometrizole trisiloxane, marketed under the trademark "Silatrizole" by Rhodia Chimie or "Mexoryl XL" by L'Oreal, as represented below.



The composite pigment according to the present invention has an effect that it can provide a transparent or clear appearance, because the fine particles of the organic solid UV filter(s) do not aggregate but spread on the core particle. It should be noted that free fine particles of organic solid UV filter(s) can easily aggregate.

Further, if organic solid UV filter(s) is/are used with inorganic solid UV filter(s), the composite pigment according to the present invention has an additional effect that the particles of the inorganic solid UV filter(s) can be well dispersed in the coating layer due to the presence of the organic solid UV filter(s), and therefore, the inorganic solid UV filter(s) can be present in the coating layer in the form of primary particles. On the other hand, in the above case, the particles of the organic solid UV filter(s) can also be well dispersed in the coating layer due to the presence of the inorganic solid UV filter(s), and therefore, the organic solid UV filter(s) can be present in the coating layer in the form of primary particles. Accordingly, the UV filtering effects by the inorganic solid UV filter(s) as well as the organic solid UV filter(s) can be enhanced together.

The organic solid UV filter(s) may be used in the composite pigment according to the present invention in proportions such that the weight ratio of the core particle to the organic solid UV filter(s) is 90:10 to 10:90, preferably 80:20 to 20:80, and more preferably 70:30 to 30:70.

(Additional UV Filters)

As described above, the coating layer on the core particle may further comprise at least one additional UV filter. If two or more additional UV filters are used, they may be the same or different, preferably the same. The additional UV filter may be hydrophilic and/or lipophilic.

The additional UV filter may be solid or liquid. The terms "solid" and "liquid" mean solid and liquid, respectively, at 25°C under 1 atm. The additional UV filter may be made from at least one organic or inorganic material, preferably at least one inorganic material.

If solid UV filter(s) in the form of fine particles is/are used, as the additional UV filter(s), it is preferable that the solid UV filter is in the form of a fine particle such that the mean (primary) particle diameter thereof ranges from 1 nm to 50 nm, preferably 5 nm to 40 nm, and more preferably 10 nm to 30 nm.

The additional solid UV filter may comprise at least one inorganic compound selected from the group consisting of silicon carbide, metal oxides which may or may not be coated, and mixtures thereof. The metal oxides may be selected from the group consisting of titanium oxide, zinc oxide, zirconium oxide, cerium oxide and mixtures thereof.

The additional solid UV filter may or may not be coated. The additional solid UV filter may have at least one coating. The coating may comprise at least one compound selected from the group consisting of alumina, silica, aluminum hydroxide, silicones, silanes, fatty acids or salts thereof(such as sodium, potassium, zinc, iron or aluminum salts), fatty alcohols, lecithin, amino acids, polysaccharides, proteins, alkanolamines, waxes such as beeswax, (meth)acrylic polymers, organic UV filters, and (per)fluoro compounds.

It is preferable for the coating to include at least one organic UV filter. As the organic UV filter in the coating, a dibenzoylmethane derivative such as butyl methoxydibenzoylmethane (Avobenzone) and 2,2'-Methylenebis[6-(2H-Benzotriazol-2-yl)-4-(1,1,3,3-Tetramethyl-Butyl)Phenol] (Methylene Bis-Benzotriazolyl Tetramethylbutylphenol) marketed as "TINOSORB" M by BASF may be preferable.

The coated additional solid UV filter may have been prepared by subjecting the additional solid UV filter to one or more surface treatments of a chemical, electronic, mechanochemical and/or mechanical nature with any of the compounds as described above, as well as polyethylenes, metal alkoxides (titanium or aluminum alkoxides), metal oxides, sodium hexametaphosphate, and those shown, for example, in Cosmetics & Toiletries, February 1990, Vol. 105, pp. 53-64.

The coated inorganic solid UV filters may be titanium oxides coated:
with silica, such as the product "Sunveil" from Ikeda;
with silica and with iron oxide, such as the product "Sunveil F" from Ikeda;
with silica and with alumina, such as the products "Microtitanium Dioxide MT 500 SA" from Tayca, "Tioveil" from Tioxide, and "Mirasun TiW 60" from Rhodia;
with alumina, such as the products "Tipaque TTO-55 (B)" and "Tipaque TTO-55 (A)" from Ishihara, and "UVT 14/4" from Kemira;
with alumina and with aluminum stearate, such as the product "Microtitanium Dioxide MT 100 T, MT 100 TX, MT 100 Z or MT-01" from Tayca, the products "Solaveil CT-10 W" and "Solaveil CT 100" from Uniqema, and the product "Eusolex T-AVO" from Merck;
with alumina and with aluminum laurate, such as the product "Microtitanium Dioxide MT 100 S" from Tayca;
with iron oxide and with iron stearate, such as the product "Microtitanium Dioxide MT 100 F" from Tayca;
with zinc oxide and with zinc stearate, such as the product "BR351" from Tayca;
with silica and with alumina and treated with a silicone, such as the products "Microtitanium Dioxide MT 600 SAS", "Microtitanium Dioxide MT 500 SAS" and "Microtitanium Dioxide MT 100 SAS" from Tayca;
with silica, with alumina and with aluminum stearate and treated with a silicone, such as the product "STT-30-DS" from Titan Kogyo;
with silica and treated with a silicone, such as the product "UV-Titan X 195" from Kemira;
with alumina and treated with a silicone, such as the products "Tipaque TTO-55 (S)" from Ishihara or "UV Titan M 262" from Kemira;
with triethanolamine, such as the product "STT-65-S" from Titan Kogyo;

with stearic acid, such as the product "Tipaque TTO-55 (C)" from Ishihara; or
with sodium hexametaphosphate, such as the product "Microtitanium Dioxide MT 150 W" from Tayca.

Other titanium oxide pigments treated with a silicone are preferably TiO_2 treated with octyltrimethylsilane and for which the mean size of the individual particles is from 25 and 40 nm, such as that marketed under the trademark "T 805" by Degussa Silices, TiO_2 treated with a polydimethylsiloxane and for which the mean size of the individual particles is 21 nm, such as that marketed under the trademark "70250 Cardre UF TiO_2Si_3" by Cardre, anatase/rutile TiO_2 treated with a polydimethylhydrosiloxane and for which the mean size of the individual particles is 25 nm, such as that marketed under the trademark "Microtitanium Dioxide USP Grade Hydrophobic" by Color Techniques.

Preferably, the following coated TiO_2 can be used as the coated inorganic UV filter:
Stearic acid (and) Aluminum Hydroxide (and) TiO_2, such as the product "MT-100 TV" from Tayca, with a mean primary particle diameter of 15 nm;
Dimethicone (and) Stearic Acid (and) Aluminum Hydroxide (and) TiO_2, such as the product "SA-TTO-S4" from Miyoshi Kasei, with a mean primary particle diameter of 15 nm;
Silica (and) TiO_2, such as the product "MT-100 WP" from Tayca, with a mean primary particle diameter of 15 nm;
Dimethicone (and) Silica (and) Aluminum Hydroxide (and) TiO_2, such as the product "MT-Y02" and "MT-Y-110 M3S" from Tayca, with a mean primary particle diameter of 10 nm;
Dimethicone (and) Aluminum Hydroxide (and) TiO_2, such as the product "SA-TTO-S3" from Miyoshi Kasei, with a mean primary particle diameter of 15 nm;
Dimethicone (and) Alumina (and) TiO_2, such as the product "UV TITAN M170" from Sachtleben, with a mean primary particle diameter of 15 nm; and
Silica (and) Aluminum Hydroxide (and) Alginic Acid (and) TiO_2, such as the product "MT-100 AQ" from Tayca, with a mean primary particle diameter of 15 nm.

In terms of UV filtering ability, TiO_2 coated with at least one organic UV filter is more preferable. For example, Avobenzone (and) Stearic Acid (and) Aluminum Hydroxide (and) TiO_2, such as the product "HXMT-100ZA" from Tayca, with a mean primary particle diameter of 15 nm, can be used.

The uncoated titanium oxide pigments are, for example, marketed by Tayca under the trademarks "Microtitanium Dioxide MT500B" or "Microtitanium Dioxide MT600B", by Degussa under the trademark "P 25", by Wacker under the trademark "Oxyde de titane transparent PW", by Miyoshi Kasei under the trademark "UFTR", by Tomen under the trademark "ITS" and by Tioxide under the trademark "Tioveil AQ".

The uncoated zinc oxide pigments are, for example:
those marketed under the trademark "Z-cote" by Sunsmart;
those marketed under the trademark "Nanox" by Elementis; and
those marketed under the trademark "Nanogard WCD 2025" by Nanophase Technologies.

The coated zinc oxide pigments are, for example:
those marketed under the trademark "Oxide Zinc CS-5" by Toshiba (ZnO coated with polymethylhydrosiloxane);
those marketed under the trademark "Nanogard Zinc Oxide FN" by Nanophase Technologies (as a 40% dispersion in Finsolv TN, C_{12}-C_{15} alkyl benzoate);
those marketed under the trademark "Daitopersion Zn-30" and "Daitopersion Zn-50" by Daito (dispersions in oxyethylenated polydimethylsiloxane/cyclopolymethylsiloxane comprising 30% or 50% of zinc nano-oxides coated with silica and polymethylhydrosiloxane);
those marketed under the trademark "NFD Ultrafine ZnO" by Daikin (ZnO coated with phosphate of perfluoroalkyl and a copolymer based on perfluoroalkylethyl as a dispersion in cyclopentasiloxane);
those marketed under the trademark "SPD-Z1" by Shin-Etsu (ZnO coated with a silicone-grafted acrylic polymer dispersed in cyclodimethylsiloxane);
those marketed under the trademark "Escalol Z100" by ISP (alumina-treated ZnO dispersed in an ethylhexyl methoxycinnamate/PVP-hexadecene copolymer/methicone mixture); and
those marketed under the trademark "Fuji ZnO-SMS-10" by Fuji Pigment (ZnO coated with silica and polymethylsilsesquioxane);
those marketed under the trademark "Nanox Gel TN" by Elementis (ZnO dispersed at 55% in C_{12}-C_{15} alkyl benzoate with hydroxystearic acid polycondensate).

The uncoated cerium oxide pigments are marketed, for example, under the trademark "Colloidal Cerium Oxide" by Rhone-Poulenc.

The uncoated iron oxide pigments are, for example, marketed by Arnaud under the trademarks "Nanogard WCD 2002 (FE 45B)", "Nanogard Iron FE 45 BL AQ", "Nanogard FE 45R AQ" and "Nanogard WCD 2006 (FE 45R)", or by Mitsubishi under the trademark "TY-220".

The coated iron oxide pigments are, for example, marketed by Arnaud under the trademarks "Nanogard WCD 2008 (FE 45B FN)", "Nanogard WCD 2009 (FE 45B 556)", "Nanogard FE 45 BL 345" and "Nanogard FE 45 BL" or by BASF under the trademark "Oxyde de fer transparent".

Mention may also be made of mixtures of metal oxides, in particular of titanium dioxide and of cerium dioxide, including a mixture of equal weights of titanium dioxide coated with silica and of cerium dioxide coated with silica marketed by Ikeda under the trademark "Sunveil A", and also a mixture of titanium dioxide and of zinc dioxide coated with alumina, with silica and with silicone, such as the product "M 261" marketed by Kemira, or coated with alumina, with silica and with glycerol, such as the product "M 211" marketed by Kemira.

If liquid UV filter(s) is/are used as the additional UV filter(s), the additional UV filter(s) may be organic liquid filter(s) selected from the group consisting of anthranilic derivatives; dibenzoylmethane derivatives; liquid cinnamic derivatives; salicylic derivatives; camphor derivatives; benzophenone derivatives; β,β-diphenylacrylate derivatives; liquid triazine derivatives; liquid benzotriazole derivatives; benzalmalonate derivatives; benzimidazole derivatives; imidazoline derivatives; bis-benzoazolyl derivatives; p-aminobenzoic acid (PABA) and derivatives thereof; methylenebis(hydroxyphenylbenzotriazole) derivatives; benzoxazole derivatives; screening polymers and screening silicones; dimers derived from α-alkylstyrene; 4,4-diarylbutadienes; octocrylene and derivatives thereof, guaiazulene and derivatives thereof, rutin and derivatives thereof, flavonoids, biflavonoids, oryzanol and derivatives thereof, quinic acid and derivatives thereof, phenols, retinol, cysteine, aromatic amino acids, peptides having an aromatic amino acid residue, and mixtures thereof.

Mention may be made, as examples of the organic liquid UV filters, of those denoted below under their INCI names, and mixtures thereof.

Anthranilic derivatives: Menthyl anthranilate, marketed under the trademark "Neo Heliopan MA" by Haarmann and Reimer.

Dibenzoylmethane derivatives: Butyl methoxydibenzoylmethane, marketed in particular under the trademark "Parsol 1789" by Hoffmann-La Roche; and isopropyl dibenzoylmethane.

Liquid cinnamic derivatives: Ethylhexyl methoxycinnamate, marketed in particular under the trademark "Parsol MCX" by Hoffmann-La Roche; isopropyl methoxycinnamate; isopropoxy methoxycinnamate; isoamyl methoxycinnamate, marketed under the trademark "Neo Heliopan E 1000" by Haarmann and Reimer; Cinoxate (2-ethoxyethyl-4-methoxy cinnamate); DEA methoxycinnamate; diisopropyl methylcinnamate; and glyceryl ethylhexanoate dimethoxycinnamate.

Salicylic derivatives: Homosalate (homomentyl salicylate), marketed under the trademark "Eusolex HMS" by Rona/EM Industries; ethylhexyl salicylate, marketed under the trademark "Neo Heliopan OS" by Haarmann and Reimer; glycol salicylate; butyloctyl salicylate; phenyl salicylate; dipropyleneglycol salicylate, marketed under the trademark "Dipsal" by Scher; and TEA salicylate, marketed under the trademark "Neo Heliopan TS" by Haarmann and Reimer.

Camphor derivatives, in particular, benzylidenecamphor derivatives: 3-benzylidene camphor, manufactured under the trademark "Mexoryl SD" by Chimex; 4-methylbenzylidene camphor, marketed under the trademark "Eusolex 6300" by Merck; benzylidene camphor sulfonic acid, manufactured under the trademark "Mexoryl SL" by Chimex; camphor benzalkonium methosulfate, manufactured under the trademark "Mexoryl SO" by Chimex; terephthalylidene dicamphor sulfonic acid, manufactured under the trademark "Mexoryl SX" by Chimex; and polyacrylamidomethyl benzylidene camphor, manufactured under the trademark "Mexoryl SW" by Chimex.

Benzophenone derivatives: Benzophenone-1 (2,4-dihydroxybenzophenone), marketed under the trademark "Uvinul 400" by BASF; benzophenone-2 (tetrahydroxybenzophenone), marketed under the trademark "Uvinul D50" by BASF; benzophenone-3 (2-hydroxy-4-methoxybenzophenone) or Oxybenzone, marketed under the trademark "Uvinul M40" by BASF; benzophenone-4 (hydroxymethoxy benzophonene sulfonic acid), marketed under the trademark "Uvinul MS40" by BASF; benzophenone-5 (sodium hydroxymethoxy benzophenone sulfonate); benzophenone-6 (dihydroxy dimethoxy benzophenone);

marketed under the trademark "Helisorb 11" by Norquay; benzophenone-8, marketed under the trademark "Spectra-Sorb UV-24" by American Cyanamid; benzophenone-9 (disodium dihydroxy dimethoxy benzophenonedisulfonate), marketed under the trademark "Uvinul DS-49" by BASF; benzophenone-12, and n-Hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate.

β,β-diphenylacrylate derivatives: Octocrylene, marketed in particular under the trademark "Uvinul N539" by BASF; and etocrylene, marketed in particular under the trademark "Uvinul N35" by BASF.

Liquid triazine derivatives: Diethylhexyl butamido triazone, marketed under the trademark "Uvasorb HEB" by Sigma 3V; 2,4,6-tris(dineopentyl 4'-aminobenzalmalonate)-s-triazine; and the symmetrical triazine screening agents described in U.S. Pat. No. 6,225,467, WO 2004/085412 (see Compounds 6 and 9) or the document "Symmetrical Triazine Derivatives", IP.COM Journal, IP.COM INC, WEST HENRIETTA, NY, US (20 Sep. 2004), in particular the 2,4,6-tris(biphenyl)-1,3,5-triazines (especially 2,4,6-tris(biphenyl-4-yl)-1,3,5-triazine) and 2,4,6-tris(terphenyl)-1,3,5-triazine, which is taken up again in WO 06/035000, WO 06/034982, WO 06/034991, WO 06/035007, WO 2006/034992 and WO 2006/034985.

Liquid benzotriazole derivatives, in particular, phenylbenzotriazole derivatives: 2-(2H-benzotriazole-2-yl)-6-dodecyl-4-methylpheno, branched and linear; and those described in USP 5240975.

Benzalmalonate derivatives: Dineopentyl 4'-methoxybenzalmalonate, and polyorganosiloxane comprising benzalmalonate functional groups, such as polysilicone-15, marketed under the trademark "Parsol SLX" by Hoffmann-LaRoche.

Benzimidazole derivatives, in particular, phenylbenzimidazole derivatives: Phenylbenzimidazole sulfonic acid, marketed in particular under the trademark "Eusolex 232" by Merck, and disodium phenyl dibenzimidazole tetrasulfonate, marketed under the trademark "Neo Heliopan AP" by Haarmann and Reimer.

Imidazoline derivatives: Ethylhexyl dimethoxybenzylidene dioxoimidazoline propionate.

bis-benzoazolyl derivatives: The derivatives as described in EP-669,323 and U.S. Pat. No. 2,463,264.

para-aminobenzoic acid and derivatives thereof: PABA (p-aminobenzoic acid), ethyl PABA, ethyl dihydroxypropyl PABA, pentyl dimethyl PABA, ethylhexyl dimethyl PABA, marketed in particular under the trademark "Escalol 507" by ISP, Glyceryl PABA, and PEG-25 PABA, marketed under the trademark "Uvinul P25" by BASF.

Methylenebis(hydroxyphenylbenzotriazole) derivatives: Methylene bis-benzotriazolyl tetramethylbutylphenol, marketed in the solid form under the trademark "Mixxim BB/100" by Fairmount Chemical or in the micronized form in aqueous dispersion under the trademark "Tinosorb M" by Ciba Specialty Chemicals, and the derivatives as described in U.S. Pat. Nos. 5,237,071, 5,166,355, GB-2,303,549, DE-197,26,184 and EP-893,119.

Benzoxazole derivatives: 2,4-bis[5-1(dimethylpropyl)benzoxazol-2-yl-(4-phenyl)imino]-6-(2-ethylhexyl)imino-1,3,5-triazine, marketed under the trademark of Uvasorb K2A by Sigma 3V.

Screening polymers and screening silicones: The silicones described in WO 93/04665.

Dimers derived from α-alkylstyrene: The dimers described in DE-19855649.

4,4-diarylbutadiene Derivatives: 1,1-Dicarboxy(2,2'-dimethylpropyl)-4,4-diphenylbutadiene.

Octocrylene and derivatives thereof: Octocrylene.

Quaiazulene and derivatives thereof: Guaiazulene and sodium guaiazulene sulfonate.

Rutin and derivatives thereof: Rutin and glucosylrutin.

Flavonoids: Robustin (isoflavonoid), genistein (flavonoid), tectochrysin (flavonoid) and hispidone (flavonoid).

Biflavonoids: Lanceolatin A, lanceolatin B and hypnumbiflavonoid A.

Oryzanol and derivatives thereof: Γ-oryzanol.

Quinic acid and derivatives thereof: Quinic acid.

Phenols: Phenol.

Retinols: Retinol.

Cysteines: L-cysteine.

Peptides having an aromatic amino acid residue: Peptides having tryptophan, tyrosine or phenylalanine.

The preferred organic liquid UV filter(s) is/are selected from: butyl methoxydibenzoylmethane, ethylhexyl methoxycinnamate, homosalate, ethylhexyl salicylate, octocrylene, phenylbenzimidazole sulfonic acid, benzophenone-3, benzophenone-4, benzophenone-5, n-hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate, 4-methylbenzylidene camphor, terephthalylidene dicamphor sulfonic acid, disodium phenyl dibenzimidazole tetrasulfonate, ethylhexyl triazone, bis-ethylhexyloxyphenol methoxyphenyl triazine, diethylhexyl butamido triazone, 2,4,6-tris(dineopentyl 4'-aminobenzalmalonate)-s-triazine, 2,4,6-tris(diisobutyl 4'-aminobenzalmalonate)-s-triazine, 2,4,6-tris(biphenyl-4-yl)-1,3,5-triazine, 2,4,6-tris(terphenyl)-1,3,5-triazine, methylene bis-benzotriazolyl tetramethylbutylphenol, polysilicone-15, dineopentyl 4'-methoxybenzalmalonate, 1,1-dicarboxy(2,2'-dimethylpropyl)-4,4-diphenylbutadiene, 2,4-bis[5-1(dimethylpropyl)benzoxazol-2-yl-(4-phenyl)imino]-6-(2-ethylhexyl)imino-1,3,5-triazine, and their mixtures. More preferable organic liquid UV filter is butyl methoxydibenzoylmethane(Avobenzone).

The additional UV filter(s) may be used in the composite pigment according to the present invention in proportions such that the weight ratio of the core particle to the additional UV filter(s) is 50:50 to 90:10, preferably 50:50 to 80:20, and more preferably 50:50 to 70:30.

(Coloring Pigments)

As described above, the coating layer(s) on the core particle may comprise at least one coloring pigment.

The term "coloring pigment(s)" should be understood as meaning white or colored, inorganic or organic particle(s) of any shape which is/are insoluble and is/are intended to color a composition comprising them.

If coloring pigment(s) is/are used, the composite pigment according to the present invention has an effect in that it can provide a clearer appearance with high chroma, because the coloring pigments do not aggregate but spread on the substrate. It should be noted that free coloring pigments easily aggregate to give a dark appearance with low chroma to the skin.

The pigments can be white or colored, inorganic and/or organic.

Among the inorganic pigments that may be used, non-limiting mention may be made of titanium dioxide, optionally surface treated, zirconium or cerium oxide, as well as zinc, (black, yellow or red) iron or chromium oxide, manganese violet, ultramarine blue, chromium hydrate and ferric blue, barium sulfate, or metal powders, such as aluminum, copper, silver or gold powder.

The particle size of the coloring pigment is not limited. In a particular embodiment, the coloring pigment may have a mean particle size of from 100 nm to less than 1 μm, preferably from 100 nm to less than 500 nm, and more preferably from 100 nm to less than 300 nm.

Among organic pigments that may be used, non-limiting mention may be made of carbon black, pigments of D&C type and lakes, such as lakes-based on cochineal carmine and on barium, strontium, calcium or aluminum. For example, Red 202 (Calcium bis[2-(3-carboxy-2-hydroxynephthylazo)-5-methylbenzenesulfonate) may be used as the pigment of D&C type.

Preferably, the coloring pigment is chosen from titanium dioxide, zirconium oxide, cerium oxide, zinc oxide, iron oxide, chromium oxide, manganese violet, ultramarine blue, chromium hydrate, ferric blue, aluminum powder, copper powder, silver powder, gold powder, barium sulfate, carbon black, pigments of D&C type, lakes, pearlescent pigments, and mixtures thereof.

The term "pearlescent pigments" should be understood as meaning iridescent particles of any shape, such as particles produced by certain shellfish in their shells or else synthesized.

The pearlescent agents can be chosen from white pearlescent agents, such as mica covered with titanium dioxide or with bismuth oxychloride; colored pearlescent agents, such as titanium

oxide-coated mica covered with iron oxide, titanium oxide-coated mica covered with ferric blue or chromium oxide, or titanium oxide-coated mica covered with an organic pigment of the abovementioned type; and pearlescent agents based on bismuth oxychloride.

The coloring pigment(s) may be used in the composite pigment according to the present invention in proportions such that the weight ratio of the core particle to the coloring pigment(s) is 50:50 to 90:10, preferably 50:50 to 80:20, and more preferably 50:50 to 70:30.

(Method for Preparing Composite Pigment)

The composite pigment according to the present invention can be prepared by subjecting at least one core particle; at least one solid UV filter having a mean particle size of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm; optionally at least one additional UV filter; and optionally at least one coloring pigment, to a mechanochemical fusion process.

Mechanochemical fusion process means a process in which mechanical power such as impact force, friction force or shear force is applied to a plurality of subjects to cause fusion between the subjects.

The mechanochemical fusion process may be performed by, for example, an apparatus comprising a rotating chamber and a fixed inner piece with a scraper, such as a mechanofusion system marketed by Hosokawa Micron Corporation in Japan.

It is preferable to use a hybridizer process as the mechanochemical fusion process.

The hybridizer process was developed in the 1980s. The hybridizer process is a class of mechanochemical fusion processes in which strong mechanical power is applied to a plurality of particles to cause a mechanochemical reaction to form a composite particle.

According to the hybridizer process, the mechanical power is imparted by a high speed rotor which can have a diameter from 10 cm to 1 m, and can rotate at a speed of 1,000 rpm to 100,000 rpm. Therefore, the hybridizer process can be defined as a

mechanochemical fusion process using such a high speed rotor. The hybridizer process is performed in air or under dry conditions. Thus, due to the high speed rotation of the rotor, high speed air flow may be generated near the rotor. However, some liquid materials may be subjected to the hybridizer process together with solid materials. The term "hybridizer process" has been used as a technical term.

The hybridizer process can be performed by using a hybridization system marketed by, for example, Nara Machinery in Japan, in which at least two types of particles, typically core particles and fine particles, are fed into a hybridizer equipped with a high speed rotor having a plurality of blades in a chamber under dry conditions, and the particles are dispersed in the chamber and mechanical and thermal energy (e.g., compression, friction and shear stress) are imparted to the particles for a relatively short period of time such as 1 to 10 minutes, preferably 1 to 5 minutes. As a result, one type of particles (e.g., fine particles) is embedded or fixed on the other type of particles (e.g., core particle) to form composite particles. It is preferable that the particles have been subjected to electrostatic treatment(s) such as shaking to form an "ordered mixture" in which one type of particles is spread to cover the other type of particles. The hybridizer process can also be performed by using a theta composer marketed by Tokuju Corporation in Japan.

The hybridizer process can also be performed by using a Composi Hybrid or a Mechano Hybrid marketed by Nippon coke.

According to the present invention, a core particle and solid UV filter(s), as well as optionally coloring pigment(s) and optionally additional material(s) such as additional UV filter(s) if necessary, can be fed into such a hybridizer to form a composite pigment. The hybridizer process can be performed by using a rotor rotating at about 8,000 rpm (100 m/sec) for about 5 minutes.

The core particle and solid UV filter(s) can be used in proportions such that the weight ratio of the core particle to the solid UV filter(s) is 90:10 to 10:90, preferably 80:20 to 20:80, and more preferably 70:30 to 30:70.

The hybridizer process enables to provide a composite pigment in which a core particle is at least in part covered with at least

one layer comprising at least one solid UV filter with a medium particle size, and optionally at least one additional UV filter and/or at least one coloring pigment.

Furthermore, the hybridizer process can provide ordered array (e.g., uniform coverage) of solid UV filter(s) as well as optional additional UV filter(s) and/or coloring pigment(s) on a core particle and provides strong bonds at the surface of the core particle and a layer comprising the solid UV filter(s) as well as the optional additional UV filter(s) and/or coloring pigment(s).

It should be noted that the hybridizer process is quite different from other processes using, for example, a beads mill and a jet mill. In fact, a beads mill causes pulverization or aggregation of core particles, and a jet mill causes pulverization of core particles and uniform coating of a core particle by fine particles is difficult to be formed.

If necessary, an additional process for further coating the composite pigment with UV filter(s) and/or coloring material(s) may be performed. As a result of this additional process, the composite pigment according to the present invention may be coated with a further layer comprising UV filter(s) and/or coloring material(s), preferably consisting of UV filter(s) and/or coloring material(s).

(Composite Pigment Composition)

The present invention also relates to a composite pigment composition in which a composite pigment according to the present invention including a small core particle is combined with another composite pigment according to the present invention including a large core particle.

The composite pigment composition according to the present invention comprises
at least one small particle with a mean particle size of from 300 nm to less than 1 μm, preferably from 300 nm to less than 600 nm, and more preferably from 300 nm to less than 400 nm, and
at least one large particle with a mean particle size of 2 μm or more, preferably 3 μm or more, more preferably 5 μm or more, and even more preferably 10 μm or more,
wherein the surface of the small and large particles is at least in part covered with at least one layer comprising at least one

solid UV filter having a mean particle size of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm.

The mean particle size or mean particle diameter of the small or large particle is an arithmetric mean diameter, and can be determined by, for example, calculating the mean or average of the dimensions of one hundred particles chosen on an image obtained with a scanning electron microscope.

The small and large particles can be in any shape. For example, the core particle may be a concave particle having at least one concavity, and preferably in a general concave shape. The concave is not a small dimple or pit, but a large hollow or crater which preferably includes a geometrical center or a center of gravity of the particle. Preferably, the core particle defines an inner concave surface and an outer convex surface which is opposite to the inner concave surface. In particular, the core particle is preferably in the form of a portion of a hollow sphere or a bowl. The substrate may have a transverse cross section with the shape of a horseshoe or arch.

On the other hand, it is possible to use a small and/or large particle in the form of a plate with an aspect ratio of at least 5, preferably more than 10, more preferably more than 20, and more preferably more than 50. The aspect ratio can be determined by the average thickness and the average length according to the formula: aspect ratio = length/thickness.

If a plate-like particle is used for the present invention, it is possible that the plate-like particle has a length ranging from 300 nm to less than 1 μm, preferably from 300 nm to less than 600 nm, and more preferably from 300 nm to less than 400 nm, or 2 μm or more, preferably 3 μm or more, more preferably 4 μm or more, and even more preferably 5 μm or more, but ranging 50 μm or less, preferably 30 μm or less, and more preferably 20 μm or less, and even more preferably 15 μm or less.

In a preferred embodiment, the small and/or large particle has a spherical shape.

The material of the small and large particles is not limited. The material can be at least one inorganic material and/or at least one organic material. It is preferable that the small particle comprises at least one organic material.

The inorganic material and/or organic material may be hollow or porous. The porosity of the material may be characterized by a specific surface area of from 0.05 m^2/g to 1,500 m^2/g, more preferably from 0.1 m^2/g to 1,000 m^2/g, and more preferably from 0.2 m^2/g to 500 m^2/g according to the BET method. However, it is preferable to use solid inorganic material(s) and/or solid organic material(s), preferably 'not hollow' materials.

Preferably, the inorganic material can be selected from the group consisting of mica, synthetic mica, talc, sericite, boron nitride, glass flake, calcium carbonate, barium sulfate, titanium oxide, hydroxyapatite, silica, silicate, zinc oxide, magnesium sulfate, magnesium carbonate, magnesium trisilicate, aluminum oxide, aluminum silicate, calcium silicate, calcium phosphate, magnesium oxide, bismuth oxychloride, kaolin, hydrotalcite, mineral clay, synthetic clay, iron oxide, and mixtures thereof. Natural mica, synthetic mica, sericite, kaolin, talc, silica and mixtures thereof are more preferable.

Preferably, the organic material can be selected from the group consisting of poly(meth)acrylates, polyamides, silicones, polyurethanes, polyethylenes, polypropylenes, polystyrenes, polyhydroxyalkanoates, polycaprolactams, poly(butylene) succinates, polysaccharides, polypeptides, polyvinyl alcohols, polyvinyl resins, fluoropolymers, waxes, amidosulfonic acid polyvalent metal salts, acylated amino acids, and mixtures thereof. As the fluoropolymers, for example, PTFE may be used. As the amidosulfonic acid polyvalent metal salts, for example, N-lauroyltaurine calcium may be used. As the acylated amino acids, lauroyllysine may be used. Polyamides such as Nylon®, polyhydroxyalkanoates such as polylactic acids, poly(meth)acrylates such as polymethylmethacrylates, silicones, fluoropolymers, and mixtures thereof are more preferable.

In particular, it is preferable that the small particles are made from poly(meth)acrylates such as polymethylmethacrylate particles such as MP-2200, MP-2701 and MP-1451 marketed by Soken, and that the large particles are made from polyamides such as Nylon®-12 particles such as SP-500 marketed by Toray and Orgasol marketed by Arkema; silica particles such as P-1500 marketed by JGC C&C; polyurethane particles such as D-400 marketed by Toshiki Pigment; and poly(meth)acrylates such as polymethylmethacrylates particles, such as SJ touch 1 marketed by Sekisui plastic.

The small and/or large particles may or may not be coated beforehand. In a particular embodiment, the small and/or large particles are coated. The material of a coating of the small or large particle is not limited, but an organic material such as an amino acid, an N-acylamino acid, an amido, a silicone, a modified silicone and a polyolefin, is preferable. As the organic material, mention may be made of lauroyl lysine, acryl-modified silicone and polyethylene.

In the composite pigment composition, the weight ratio of the small particle(s) to the large particle(s) may be 10:90 to 90:10, preferably 20:80 to 80:20, and more preferably 30:70 to 70:30.

The weight ratio of the small particle(s)/the large particle(s)/the inorganic solid UV filter(s) may be 9:81:10 to 27:3:70, preferably 8:72:20 to 45:5:50, and more preferably 7:63:30 to 63:7:30.

In a particular embodiment, the weight ratio of the small particle(s)/the large particle(s)/the inorganic solid UV filter(s) may be 20:50:30 to 50:20:30, preferably 35:15:50 to 15:35:50.

In a preferred embodiment, the weight ratio of the small particle(s)/the large particle(s)/the inorganic solid UV filter(s) may be 35:35:30.

(Method for Preparing Composite Pigment Composition)

The composite pigment composition according to the present invention can be prepared by subjecting at least one small particle with a mean particle size of from 300 nm to less than 1 μm, preferably from 300 nm to less than 600 nm, and more preferably from 300 nm to less than 400 nm; at least one large particle with a mean particle size of 2 μm or more, preferably 3 μm or more, more preferably 5 μm or more, and even more preferably 10 μm or more; at least one solid UV filter having a mean particle size of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm; optionally at least one additional UV filter, and optionally at least one coloring pigment, to a mechanochemical fusion process as explained above.

The small particle, the large particle, the solid UV filter, the additional UV filter, and the coloring pigment are as explained above.

In the mechanochemical fusion process, preferably a hybridizer process using a hybridization system marketed by, for example, Nara Machinery in Japan, the small particle(s) and the large particle(s) can be used in proportions such that the weight ratio of the small particle to the large particle(s) is 10:90 to 90:10, preferably 20:80 to 80:20, and more preferably 30:70 to 70:30.

The weight ratio of the small particle(s)/the large particle(s)/the inorganic solid UV filter(s) may be 9:81:10 to 27:3:70, preferably 8:72:20 to 45:5:50, and more preferably 7:63:30 to 63:7:30.

In a particular embodiment, the weight ratio of the small particle(s)/the large particle(s)/the inorganic solid UV filter(s) may be 20:50:30 to 50:20:30, preferably 35:15:50 to 15:35:50.

In a preferred embodiment, the weight ratio of the small particle(s)/the large particle(s)/the inorganic solid UV filter(s) may be 35:35:30.

When the small and large particles are used in combination, the solid UV filter particle(s), and the optional additional UV filter(s) and/or coloring pigment(s), can be effectively bound on the surface of the small and large particles due to the anchor effects by the collision of the small and large particles. In addition, the specific surface on which the solid UV filter particle(s) can be bound will increase. Therefore, the UV filtering effects, in particular in the UVA region, can be further enhanced.

Accordingly, it is preferable that both small and large particles are used as core particles to prepare a composite pigment composition according to the present invention.

(Cosmetic Composition)

The composite pigment or composite pigment composition, as described above, according to the present invention can be present in the cosmetic composition according to the present invention in an amount ranging from 0.01% to 99% by weight,

preferably 0.1% to 50% by weight, and more preferably 1% to 30% by weight, relative to the total weight of the composition.

Preferably, the composite pigment or the composite pigment composition according to the present invention can be used in cosmetic compositions to be applied to keratin substances such as skin, hair, and nails, providing superior UV shielding effects, and/or coloring effects, because the composite pigment or the composite pigment composition can exhibit good UV filtering effects, in particular in the UVA region, possibly with a transparent or clear appearance and/or good coloring effects such as more transparent or clearer and more bright coloring, without the risk of affecting keratin substances.

Since the composite pigment or the composite pigment composition according to the present invention can reduce free particles which have a high friction coefficient such that they do not easily spread on the skin and provide an unpleasant feeling on use, the cosmetic composition according to the present invention has reduced friction, and therefore, can provide the effect of a better feeling on use.

The cosmetic composition according to the present invention may further comprise at least one filler and/or at least one oil.

As used herein, the term "filler" should be understood as meaning colorless natural or synthetic particles of any shape which are insoluble in the medium of the composition, whatever the temperature at which the composition is manufactured. Thus, the filler is different from the coloring pigment as described above.

The fillers may be inorganic or organic and of any shape(for instance, platelet, spherical, and oblong shapes) and with any crystallographic form (for example, sheet, cubic, hexagonal, orthorhombic, and the like). Examples of suitable additional fillers include, but are not limited to, talc; mica; silica; kaolin; powders of polyamide such as Nylon®; poly-β-3-alanine powders; polyethylene powders; polyurethane powders, such as the powder formed of hexamethylene diisocyanate and trimethylol hexyllactone copolymer sold under the name Plastic Powder D-400 by Toshiki; the powders formed of tetrafluoroethylene polymers (Teflon®); lauroyllysine; starch; boron nitride; polymeric hollow microspheres, such as microspheres of poly(vinylidene chloride)/acrylonitrile, for example Expancel® (Nobel Industrie), and microspheres of acrylic acid copolymers; silicone resin

powders, for example, silsesquioxane powders (for instance, silicone resin powders disclosed in European Patent No. 0 293 795 and Tospearls® from Toshiba); poly(methyl methacrylate) particles; precipitated calcium carbonate; magnesium carbonate; basic magnesium carbonate; hydroxyapatite; hollow silica microspheres; glass microcapsules; ceramic microcapsules; metal soaps derived from organic carboxylic acids comprising from 8 to 22 carbon atoms, for example, from 12 to 18 carbon atoms, such as zinc stearate, magnesium stearate, lithium stearate, zinc laurate, and magnesium myristate; barium sulphate; and mixtures thereof.

The filler may be present in the composition in an amount ranging from 0.1% to 80% by weight, with respect to the total weight of the composition, for example, from 1% to 25% by weight, or from 3% to 15% by weight.

The term "oil" is understood to mean a fatty substance which is liquid at ambient temperature (25°C).

Use may be made, as oils which can be used in the composition of the invention, for example, of hydrocarbon oils of animal origin, such as perhydrosqualene (or squalane); hydrocarbon oils of vegetable origin, such as triglycerides of caprylic/capric acids, for example those marketed by Stearineries Dubois or those marketed under the trademarks Miglyol 810, 812 and 818 by Dynamit Nobel, or oils of vegetable origin, for example sunflower, maize, soybean, cucumber, grape seed, sesame, hazelnut, apricot, macadamia, arara, coriander, castor, avocado or jojoba oil or shea butter oil; synthetic oils; silicone oils, such as volatile or non-volatile polymethylsiloxanes (PDMSs) comprising a linear or cyclic silicone chain which are liquid or paste at ambient temperature; fluorinated oils, such as those which are partially hydrocarbon and/or silicone, for example those described in JP-A-2-295912; ethers, such as dicaprylyl ether (CTFA name); and esters, such as benzoate C_{12}-C_{15} fatty alcohols (Finsolv TN from Finetex); arylalkyl benzoate derivatives, such as 2-phenylethyl benzoate (X-Tend 226 from ISP); amidated oils, such as isopropyl N-lauroylsarcosinate (Eldew SL-205 from Ajinomoto), and their mixtures.

The oily phase can also comprise one or more fatty substances selected, for example, from fatty alcohols (cetyl alcohol, stearyl alcohol, cetearyl alcohol), fatty acids (stearic acid) or waxes (paraffin wax, polyethylene waxes, carnauba wax, beeswax).

The oily phase can comprise lipophilic gelling agents, surfactants or also organic or inorganic particles.

The oily phase can preferably represent from 1 to 70% of oil by weight, with respect to the total weight of the composition.

The composition according to the present invention may further comprise at least one additional conventional cosmetic ingredient which may be chosen, for example, from hydrophilic or lipophilic gelling and/or thickening agents, surfactants, antioxidants, fragrances, preservatives, neutralizing agents, sunscreens, vitamins, moisturizing agents, self-tanning compounds, antiwrinkle active agents, emollients, hydrophilic or lipophilic active agents, agents for combating pollution and/or free radicals, sequestering agents, film-forming agents, dermo-decontracting active agents, soothing agents, agents which stimulate the synthesis of dermal or epidermal macromolecules and/or which prevent their decomposition, antiglycation agents, agents which combat irritation, desquamating agents, depigmenting agents, antipigmenting agents, propigmenting agents, NO-synthase inhibitors, agents which stimulate the proliferation of fibroblasts and/or keratinocytes and/or the differentiation of keratinocytes, agents which act on microcirculation, agents which act on energy metabolism of the cells, healing agents, and mixtures thereof.

The composition according to the present invention may be in various forms, for example, suspensions, dispersions, solutions, gels, emulsions, such as oil-in-water (O/W), water-in-oil (W/O), and multiple (e.g., W/O/W, polyol/O/W, and O/W/O) emulsions, creams, foams, sticks, dispersions of vesicles, for instance, of ionic and/or nonionic lipids, two-phase and multi-phase lotions, sprays, powders, and pastes. The composition may be anhydrous; for example, it can be an anhydrous paste or stick. The composition may also be a leave-in composition.

According to one embodiment, the cosmetic composition according to the present invention may be in the form of a powdery composition or a liquid or solid composition such as an oily-solid cosmetic composition or an anhydrous composition.

In a particular embodiment, the composition is a powdery composition.

In another particular embodiment, the composition is a liquid composition.

In particular, the powdery cosmetic composition according to the present invention can have a reduced friction which provide a smooth feeling to use, and can have a good compactability which provides a high stability against physical impacts, due to the inclusion of the composite pigment or composite pigment composition according to the present invention.

In any event, the cosmetic composition according to the present invention has better UV filtering effects, in particular in the UVA region, in addition to reduce the risk of fine particles of solid UV filter(s) penetrating into the skin via pores on the skin.

According to another embodiment, the cosmetic composition according to the present invention may be in the form of, for example, a compact powder, a lotion, a serum, a milk, a cream, a base foundation, an undercoat, a make-up base coat, a foundation, a face powder, cheek rouge, a lipstick, a lip cream, an eye shadow, an eyeliner, a loose powder, a concealer, a nail coat, mascara, a sunscreen and the like.

It is to be understood that a person skilled in the art can choose the appropriate presentation form, as well as its method of preparation, on the basis of his/her general knowledge, taking into account the nature of the constituents used, for example, their solubility in the vehicle, and the application envisaged for the composition.

EXAMPLES

The present invention will be described in more detail by way of examples, which however should not be construed as limiting the scope of the present invention.

Examples 1 to 10 and Comparative Examples 1 to 3

The components shown in Table 1 were subjected to a hybridizer process using a Hybridizer equipped with a high speed rotor having a plurality of blades in a chamber in dry conditions, marketed by Nara Machinery Co., Ltd. in Japan to obtain a composite pigment.

In detail, for each of Examples 1-10 and Comparative Examples 1-3, the core particle and the UV filter shown in Table 1 were mixed at the mixing ratio (the numerals in Table 1 are based on parts by weight) shown in Table 1 in a plastic bag by hand shaking for a short period of time. The mixture was put in the Hybridizer, and the rotor was revolved at 8,000 rpm (100 m/s linear velocity) for 3 minutes to obtain the composite pigments according to Examples 1-10 and Comparative Examples 1-3.

[UV Absorbance Evaluation]

Absorbance of UV waves of each of the composite pigments according to Examples 1-10 and Comparative Examples 1-3 was measured by use of a UV/VIS spectrophotometer type V-550 (JASCO, Japan) as follows.

A solvent was prepared by mixing isododecane and polyhydroxystearic acid such that the concentration of polyhydroxystearic acid was 3 wt%.

Each of the composite pigments according to Examples 1-10 and Comparative Examples 1-3 was dispersed in the above solvent by using ultrasonic waves for 1 minute to obtain a sample, such that the concentration of the composite pigment in the sample was 0.1 wt%. If agglomerates were still present, the ultrasonic treatment was repeated.

The obtained sample was put into a quartz cell having a 2 mm light pathway. The UV absorbance of the sample in the wavelength of from 280 to 400 nm was measured by use of a UV/VIS spectrophotometer type V-550 (JASCO, Japan).

The results are shown in Table 1.

Table 1

	Core						UV filter		UVA	UVB
	PMMA*	Nylon 12*	Nylon 12**	Silica	PU	PMMA**	TiO_2(1)	TiO_2(2)		
Particle Size	350nm	5μm	10μm	3μm	12μm	7μm	180nm	15nm		
Ex. 1	-	90	-	-	-	-	10	-	8	2
Ex. 2	-	70	-	-	-	-	30	-	15	6
Ex. 3	-	50	-	-	-	-	50	-	22	8
Ex. 4	-	30	-	-	-	-	70	-	26	10
Ex. 5	35	35	-	-	-	-	30	-	19	6
Ex. 6	35	15		-	-	-	50	-	32	11
Ex. 7	-	-	70	-	-	-	30	-	16	6
Ex. 8	-	-	-	70	-	-	30	-	16	5
Ex. 9	-	-	-	-	70	-	30	-	10	3
Ex. 10	-	-	-	-	-	70	30	-	18	6
Comp. Ex. 1	-	70	-	-	-	-	-	30	8	5
Comp. Ex. 2	-	-	70	-	-	-	-	30	3	1
Comp. Ex. 3	-	-	-	70	-	-	-	30	7	4

PMMA*: MP-2200 marketed by Soken in Japan
Nylon 12*: SP-500 marketed by Toray in Japan
Nylon 12**: Orgasol marketed by Arkema in France
Silica: P1500 marketed by JGC C&C in Japan
PU(polyurethane): D-400 marketed by Tishiki Pigment in Japan
PMMA**: SJ touch 1 marketed by Sekisui Plastics in Japan
TiO_2(1): JA-C marketed by Tayca in Japan
TiO_2(2): MT-100 TV marketed by Tayca in Japan
UVA: UV absorbance in the wavelength region from 315 to 400 nm
UVB: UV absorbance in the wavelength region from 280 to 315 nm

It is clear from Table 1 that the composite pigments according to Examples 1-10 using medium size TiO_2 particles have higher UV absorbance, in particular UVA absorbance, than the composite pigments according to Comparative Examples 1-3 using small size TiO_2 particles. This will be clearer when Examples 2, 7 and 8 are compared with Comparative Examples 1, 2 and 3, respectively.

Further, it can be found by comparing Example 2 and Example 5 that when a small core particle is combined with a large core particle, the obtained composite pigment composition can give better UV absorbance, in particular UVA absorbance. Accordingly, it is clear that the composite pigment compositions according to the present invention can provide a better UV absorbance.

CLAIMS

1. A composite pigment comprising
at least one core particle,
wherein the surface of the core particle is at least in part covered with at least one layer comprising at least one solid UV filter having a mean particle size of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm.

2. The composite pigment according to Claim 1, wherein the core particle has a mean particle size of from 300 nm to less than 30 μm, preferably from 300 nm to less than 20 μm, and more preferably from 300 nm to less than 15 μm.

3. The composite pigment according to Claim 1 or 2, wherein the at least one layer has a thickness of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm.

4. The composite pigment according to any one of Claims 1 to 3, wherein the solid UV filter comprises at least one inorganic compound selected from the group consisting of silicon carbide, metal oxides, and mixtures thereof.

5. The composite pigment according to any one of Claims 1 to 4, wherein the solid UV filter comprises at least one organic compound selected from the group consisting of solid benzotriazole derivatives, oxanilide derivatives, solid triazine derivatives, triazole derivatives, vinyl-group containing amides, cinnamic acid amides, sulfonated benzimidazoles, and mixtures thereof.

6. The composite pigment according to any one of Claims 1 to 5, wherein the at least one layer further comprises at least one additional UV filter.

7. The composite pigment according to any one of Claims 1 to 6, wherein the at least one layer further comprises at least one coloring pigment.

8. The composite pigment according to any one of Claims 1 to 7, wherein the core particle comprises at least one inorganic material and/or at least one organic material.

9. The composite pigment according to Claim 8, wherein the inorganic material is selected from the group consisting of mica, synthetic mica, talc, sericite, boron nitride, glass flake, calcium carbonate, barium sulfate, titanium oxide, hydroxyapatite, silica, silicate, zinc oxide, magnesium sulfate, magnesium carbonate, magnesium trisilicate, aluminum oxide, aluminum silicate, calcium silicate, calcium phosphate, magnesium oxide, bismuth oxychloride, kaolin, hydrotalcite, mineral clay, synthetic clay, iron oxide, and mixtures thereof.

10. The composite pigment according to Claim 8, wherein the organic material is selected from the group consisting of poly(meth)acrylates, polyamides, silicones, polyurethanes, polyethylenes, polypropylenes, polystyrenes, polyhydroxyalkanoates, polycaprolactams, poly(butylene) succinates, polysaccharides, polypeptides, polyvinyl alcohols, polyvinyl resins, fluoropolymers, waxes, amidosulfonic acid polyvalent metal salts, acylated amino acids, and mixtures thereof.

11. The composite pigment according to any one of Claims 1 to 10, wherein the weight ratio of the core particle(s) to the solid UV filter(s) is 90:10 to 10:90, preferably 80:20 to 20:80, and more preferably 70:30 to 30:70.

12. A method for preparing a composite pigment, comprising a step of subjecting
at least one core particle,
at least one solid UV filter having a mean particle size of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm,
optionally at least one additional UV filter, and
optionally at least one coloring pigment
to a mechanochemical fusion process.

13. A composite pigment composition, comprising
at least one small particle with a mean particle size of from 300 nm to less than 1 μm, preferably from 300 nm to less than 600 nm, and more preferably from 300 nm to less than 400 nm, and
at least one large particle with a mean particle size of 2 μm or more, preferably 3 μm or more, more preferably 5 μm or more, and even more preferably 10 μm or more,
wherein the surface of the small and large particles is at least in part covered with at least one layer comprising at

least one solid UV filter having a mean particle size of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm.

14. The composite pigment composition according to Claim 13, wherein the small and large particles comprise at least one inorganic material and/or at least one organic material.

15. The composite pigment composition according to Claim 13 or 14, wherein the weight ratio of the small particle(s) to the large particle(s) is 90:10 to 10:90, preferably 80:20 to 20:80, and more preferably 70:30 to 30:70.

16. A method for preparing a composite pigment composition, comprising a step of subjecting
at least one small particle with a mean particle size of from 300 nm to less than 1 μm, preferably from 300 nm to less than 600 nm, and more preferably from 300 nm to less than 400 nm,
at least one large particle with a mean particle size of 2 μm or more, preferably 3 μm or more, more preferably 5 μm or more, and even more preferably 10 μm or more,
at least one solid UV filter having a mean particle size of from 100 nm to less than 300 nm, preferably from 100 nm to less than 250 nm, and more preferably from 100 nm to less than 200 nm,
optionally at least one additional UV filter, and
optionally at least one coloring pigment
to a mechanochemical fusion process.

17. A cosmetic composition, in particular in the form of a liquid or powdery cosmetic composition, comprising a composite pigment according to any one of Claims 1 to 11 or a composite pigment composition according to any one of Claims 13 to 15.

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2011/052961

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09B63/00 C09B67/00 A61K8/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2007 254429 A (KOSE CORP) 4 October 2007 (2007-10-04) the whole document -----	1-17
Y	JUDIN V P S ET AL: "Charakteristika von hochleistendem ultrafeinen Titandioxid benutzt als UV-Schutzfilter", SOEFW : SEIFEN, ÖLE, FETTE, WACHSE,, vol. 119, no. 8, 1 January 1993 (1993-01-01), pages 491,492-495,496, XP001525757, ISSN: 0173-5500 page 492, middle col. below fig.3 ----- -/--	1-17

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 June 2011	28/06/2011

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	AKIO NASU AND YASUFUMI OTSUBO: "Improvement of Preparation Method of UV-protecting Suspensions by the Use of Rheological Techniques", NIHON-REOROJÎ-GAKKAI-SHI = JOURNAL OF THE SOCIETY OF RHEOLOGY, KYOTO, JP, vol. 37, no. 1, 1 January 2009 (2009-01-01), pages 11-15, XP009149327, ISSN: 0387-1533 [retrieved on 2009-04-16] figure 7	1-17
A	EP 1 093 796 A1 (OREAL [FR]) 25 April 2001 (2001-04-25) paragraph [0103]	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

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