COSMETIC TINTED SUNSCREEN COMPOSITION

The present invention relates to a tinted cosmetic sunscreen composition comprising the particulate sunscreen phenylene bis-diphenyltriazine.

TECHNICAL BACKGROUND

The field of photoprotection is a major public health issue to prevent skin damage from overexposure to the sun.

The potentially harmful effects of ultraviolet radiation on the skin are well known, and a multitude of sunscreen products, commonly called sunscreen products, are marketed to prevent these effects. Skin alterations are mainly induced by ultraviolet radiations (UVA and/or UVB), but also by visible light, including in particular the high-energy visible blue light, and the infrared, through damage to macromolecules resulting in damage to deoxyribonucleic acid (DNA), oxidative stress, lipid peroxidation and degradation of the dermal matrix.

Among the existing sunscreens, phenylene bis-diphenyltriazine is a particulate organic sunscreen (also referred to as an UV filter) having the particularity of absorbing and reflecting the harmful part of the solar spectrum, which includes UVB, short UVA, long UVA but also high energy blue light (Bacqueville et al., Photochemical & Photobiological Sciences (2021) 20: 1475–1486). Thus, its properties make it a particularly interesting sunscreen in the field of photoprotection and photoaging prevention.

Photoprotective systems combining phenylene bis-diphenyltriazine with other existing sunscreens have already been proposed by the prior art, and more particularly systems developed to optimize the number and total amount of sunscreens in order to obtain better results in terms of tolerance and toxicity for the user, and to reduce the environmental impact of sunscreen products (WO 2013/113745).

The phenylene bis-diphenyltriazine-based sunscreen compositions described and marketed to date are mainly emulsions, and more particularly oil-in-water emulsions. These compositions are available in untinted or weakly tinted form.

Pigments have become almost indispensable in cosmetics. They make it possible to color the compositions and give the face a unique dimension thanks to the shade thereof. Pigments are particulate insoluble solid chemicals that

bring color and nuance to compositions that contain them. Many commercial materials are available and offer a wide range of colors, shades, reflections, etc. depending on the optical properties thereof due to the nature of the pigment, the size thereof, the coating thereof, etc.

Tinted sunscreen products combine sunscreens with a colored base that traditionally consists of various preparations and concentrations of iron oxides and pigmentary titanium dioxide, which are also likely to optimize protection against visible light. To adapt to consumer demand while taking into account the skin phenotypes thereof, tinted products in different shades are available. The shade is obtained by mixing the three iron oxides – yellow, red and black – with pigmentary titanium dioxide.

Iron oxides are pigments produced from iron sulfate. Depending on the state of oxidation thereof, they may appear yellow, red or black. A yellow or red pigment appears as such due to the reflection of the corresponding wavelengths in the visible range. The black appearance of a pigment is due to absorption in the entire visible region, no photons being reflected in this range. Depending on the targeted shade, pigmentary titanium dioxide (i.e. titanium dioxide that is not nanometric) is another pigment that can be used to ensure coverage and opacity. It appears white because it reflects all photons of visible light.

There is currently a need for new tinted sunscreen cosmetic compositions comprising the sunscreen of interest phenylene bis-diphenyltriazine and responding to a larger panel of shades (including darker shades) than current tinted sunscreen compositions, so as to be able to respond to all skin phototypes. This may require incorporating a greater total amount of pigments into the sunscreen compositions. The aim of the present invention is to provide such tinted sunscreen cosmetic compositions, in particular of a darker shade than the tinted sunscreen cosmetic compositions of the prior art. Obtaining a good covering power for such compositions is also one of the objectives of the present invention.

Added to this is the appeal of consumers for light and fluid, non-sticky textures, which the invention also aims to satisfy.

In this context, having to suspend a larger amount of particulate fillers – including the particulate sunscreen which is phenylene bis-diphenyltriazine – in an oil-in-

water emulsion type composition, the formulator will be confronted with the risk of instability of the formula due to this significant amount of particulate fillers to be put and maintained into suspension; and this more particularly when the particulate fillers are distributed in each of the two phases of the emulsion. A problem of instability in the formulation can result in particular in the migration and separation of the pigments towards the surface of the composition, making it inhomogeneous and unsatisfactory.

The effectiveness of a composition in terms of sun protection indeed requires guaranteeing a stable and homogeneous suspension of all the solid particles it contains in order to prevent any agglomeration of said particles. This objective must not be achieved to the detriment of:

- neither the desired fluidity of the compositions, which must have a texture sufficiently fluid to be compatible with application by the fingers by the users, and therefore have easy spreading,
- nor the sensory properties thereof.

It has been discovered by the present Inventors that adding unmodified smectite, and in a specific amount, to a cosmetic composition in the form of an oil-in-water emulsion, containing 1 to 5% by weight of phenylene bis-diphenyltriazine, and pigments, allows, regardless of the amount of these pigments in the composition, and including for amounts greater than 2% by weight (and remaining less than or equal to 5% by weight) relative to the total weight of the composition, to obtain the different benefits sought in terms of:

- stability of the composition and homogeneity of suspension of the particulate fillers contained therein,
- sensoriality / fluidity / coverage (the degree of coverage conferred by the composition being related to the amount of pigments present in the composition),
- and Sun Protection Factor (SPF, in English Sun Protection Factor).

DESCRIPTION OF THE INVENTION

Thus, according to a first aspect of the invention, a tinted sunscreen cosmetic composition in the form of an emulsion is proposed, suitable for topical application on the skin, said composition comprising, the percentages being expressed by weight relative to the total weight of the composition:

- 30 to 50% of water,

- 1 to 5% of the particulate sunscreen phenylene bis-diphenyltriazine,
- at least one emulsifier,
- at least one oily emollient,
- at least one pigment, in particular of mineral origin, the total content of pigments in the composition being between 1 and 5%, preferably between 2 and 5%, by weight relative to the total weight of the composition,
- and a suspension agent selected from among unmodified smectites, the total amount of suspension agent(s) selected from among unmodified smectites in the composition being between 0.3 and 2% by weight relative to the total weight of the composition.

By "photoprotective system", it should be understood, within the meaning of the present invention, a combination of compounds that allows, after application to a surface (skin, hair, etc.), by mechanisms for absorption and/or reflection and/or scattering of UVA and/or UVB radiation and/or blue light, preventing, or at least limiting, the contact of said radiation with said surface.

The term “sunscreen” means a substance able to filter solar radiations to protect a surface, typically the skin or the hair, from the harmful effects of such radiations.

The term "ultraviolet radiation” or "UV radiation", commonly abbreviated to "UV", refers to the solar ultraviolet radiation but also the artificial ultraviolet radiation, generated by tanning lamps for example.

By "UVA radiation" or simply "UVA", it should be understood ultraviolet rays having a wavelength λ between 320 and 400 nm.

By "UVB radiation" or simply "UVB", it should be understood ultraviolet rays having a wavelength λ between 290 and 320 nm.

A sunscreen is referred to as a "UVA filter" or a "UVB filter" depending on whether it filters mostly UVA or UVB.

A so-called "broadband" or "broad spectrum" sunscreen filters both UVA and UVB.

According to the radiation filtering mechanism, i.e. according to whether the radiation is absorbed and/or reflected, or even scattered by the sunscreen, a distinction is made, in a thorough manner, between:

- stricto sensu filters, which mainly absorb the radiation, and
- screens, which absorb and reflect the radiation.

Nonetheless, in the following description, the term “sunscreen”, sometimes abbreviated to “filter”, will be used indifferently to designate a filter or a screen.

A sunscreen may be "liposoluble" or “water-soluble", depending on whether it is more easily soluble in lipids or water, or "insoluble". An insoluble sunscreen is typically in particulate form, and can nevertheless be integrated into a sunscreen composition, in particular in a dispersed form, in particular hydrodispersed when it is dispersed in an aqueous phase.

In the present description, “sun protection" means protection against the effects of ultraviolet radiations, in particular UVA and/or UVB, and/or blue light. The expression "sun protection", as used in the present description, encompasses not only protection against the harmful effects of solar radiations, but also against the artificial ultraviolet radiations, generated by tanning lamps for example. More particularly, sun protection is understood here to mean preventing, or at least limiting, the contact of ultraviolet radiation and/or blue light with the surface to be protected, by mechanisms of absorption and/or reflection and/or scattering UVA and/or UVB radiation and/or blue light.

Phenylene bis-diphenyltriazine, a commonly used name for 5,6,5',6'-tetraphenyl-3,3'-(1,4-phenylene)-bis[1,2,4]triazine, (CAS No.: 55514-22-2) is a sunscreen, more particularly an ultra-broad-spectrum sunscreen able to filter the harmful part of the solar spectrum, which includes UV radiation (UVB and UVA), but also visible high-energy blue light. In the remainder of the description, the designations 5,6,5',6'-tetraphenyl-3,3'-(1,4-phenylene)-bis[1,2,4]triazine and phenylene bis-diphenyltriazine are used indifferently.

Phenylene bis-diphenyltriazine is a particulate organic filter of the insoluble, hydrodispersible type.

This filter is typically in the form of an aqueous dispersion, comprising between 20% and 50%, in particular between 40% and 50%, by weight of active material relative to the total weight of the dispersion. Advantageously, the method for preparing such an aqueous dispersion consists in grinding the organic filter in the form of particles, using a grinding apparatus and in the presence of a grinding additive. Conventionally, wet grinding methods such as wet grinding or wet

mixing, well known to the person skilled in the art, are used for this purpose. The grinding apparatus may be for example a microbead mill, a vibrating mill or a ball mill. Depending on the grinding method, the grinding additive is selected from the group consisting of anionic, nonionic or amphoteric surfactants, emulsifiers and dispersants. As such a grinding additive, mention may be made for example of the dispersant PPG-1-PEG-9 Lauryl Glycol Ether (Eumulgin® L, marketed by BASF), which was used to prepare the aqueous dispersion that was the subject of the final opinion SCCS/1594/18 of the Scientific Committee on Consumer Safety (SCCS). In this aqueous dispersion comprising between 45 and 55% by weight of water:

- phenylene bis-diphenyltriazine is between 40 and 50%,
- PPG-1-PEG-9 Lauryl Glycol Ether is present at about 4.5%,

the % being expressed by weight relative to the total weight of the dispersion.

In particular embodiments of the invention, the size D50 of the phenylene bis-diphenyltriazine particles contained in the composition according to the invention is between 100 and 1,000 nm, more particularly between 100 and 500 nm, even more particularly between 120 and 400 nm, in particular between 120 and 250 nm, in particular between 120 and 200 nm, typically between 150 and 200 nm.

By "size D50" or "median size", it should be understood the size for which the cumulative particle size distribution function is equal to 50%. The value of the size D50 may be determined using a Mastersizer 3000 liquid laser diffraction granulometer.

Phenylene bis-diphenyltriazine represents between 1% and 5% by weight relative to the total weight of the composition. In particular embodiments of the invention, it represents between 2% and 5%, in particular between 2% and 4%, preferably between 3% and 4%, by weight relative to the total weight of the composition.

It is understood that these mass percentages, as well as all those indicated here, are expressed as a percentage by mass of active material relative to the total mass of the composition.

In the composition according to the present invention, phenylene bis-diphenyltriazine may be associated with one or more additional sunscreen(s), to constitute a photoprotective system that allows, after application to a surface

(skin, hair, etc.), by mechanisms of absorption and/or reflection and/or scattering of the UVA and/or UVB radiation, to prevent, or at least limit, the contact of said radiation with said surface.

Such additional sunscreens are preferably selected, and introduced into the composition in an appropriate amount, so that the composition according to the invention has a sun protection factor (SPF) between 20 and 99, preferably between 30 and 80, and more preferably between 50 and 80.

The total SPF of the composition itself is evaluated in a conventional manner, for wavelengths between 290 and 400 nm. The value thereof may be determined according to the method recommended by the COLIPA (European Cosmetic, Toiletry and Perfumery Association), in the guidelines thereof published in March 2011.

In particular embodiments of the invention, the SPF of the composition is greater than or equal to 50, advantageously greater than or equal to 60.

In other particular embodiments, the SPF/UVA ratio is less than or equal to 3, in accordance with the regulations in force. The denominator of said quotient corresponds to the UVA portion (320 to 400 nm) of the total SPF, and can be calculated according to the method recommended by the COLIPA (European Cosmetic, Toiletry and Perfumery Association), in the guidelines thereof published in March 2011. Advantageously, the SPF/UVA ratio of the composition according to the invention is less than or equal to 2.5.

In particular embodiments of the invention, the total amount of additional sunscreens contained in the composition is between 3 and 19% by weight, preferably between 5 and 17% by weight, in particular between 7 and 15% by weight, and typically between 8 and 15% by weight, for example between 10 and 13% by weight, relative to the total weight of the composition.

In particular embodiments of the invention, the composition comprises at least one additional sunscreen.

At least one additional sunscreen may be selected from among those conventionally known, including organic sunscreens such as triazine derivatives, benzotriazole and phenyl benzotriazole derivatives, dibenzoylmethane derivatives, amino-substituted benzophenone and 2-hydroxybenzophenone derivatives, merocyanine derivatives, para-aminobenzoic acid derivatives,

salicylic derivatives, cinnamic derivatives, β,β'-diphenylacrylate derivatives, benzylidene camphor derivatives, phenylbenzimidazole derivatives, anthranyl derivatives, imidazoline derivatives, and benzylmalonate derivatives.

Preferably, at least one additional sunscreen is selected from among triazine derivatives, benzotriazole and phenyl benzotriazole derivatives, dibenzoylmethane derivatives, amino-substituted benzophenone and 2-hydroxybenzophenone derivatives, and merocyanine derivatives.

Nonetheless, in particular advantageous embodiments of the invention, the tinted cosmetic composition does not comprise ethylhexyl salicylate, octocrylene, ethylhexyl methoxycinnamate, isoamyl methoxylcinnamate, homosalate, para-aminobenzoic acid (PABA), octyl dimethyl PABA, 3-methylbenzylidene-camphor, 4-methylbenzylidene-camphor, benzophenone-3 and/or benzophenone-4. Both octocrylene and ethylhexyl salicylate are suspected of being potential endocrine disruptors. Other sunscreens present in many commercial products are also controversial due to the potentially harmful effects thereof on the user or on the environment. In particular, mention may be made of derivatives of cinnamate (ethylhexyl methoxycinnamate, isoamyl methoxylcinnamate), homosalate, para aminobenzoic acid (PABA, octyl dimethyl PABA), camphor (3-methylbenzylidene camphor, 4-methylbenzylidene camphor) or benzophenone (benzophenone-3, benzophenone-4). The use of such compounds is therefore not desirable.

Thus, in particular embodiments of the invention, the composition comprises at least one additional sunscreen, excluding ethylhexyl salicylate, octocrylene, ethylhexyl methoxycinnamate, isoamyl methoxylcinnamate, homosalate, para-aminobenzoic acid (PABA), octyl dimethyl PABA, 3-methylbenzylidene-camphor, 4-methylbenzylidene-camphor, benzophenone-3 and/or benzophenone-4.

The composition according to the invention preferably contains, as an additional sunscreen, at least one liposoluble organic sunscreen.

Thus, in preferred embodiments of the invention, the tinted cosmetic composition comprises the sunscreen/UV filter phenylene bis-diphenyltriazine and at least one additional sunscreen, in particular a liposoluble organic sunscreen, selected in particular from among:

- hexyl 2-[4-(diethylamino)-2-hydroxybenzoyl]benzoate (CAS No.: 302776-68-7), also called diethylamino hydroxybenzoyl hexyl benzoate or DHHB, in particular as marketed by BASF under the name Uvinul® A Plus, a liposoluble UVA filter with a maximum absorption wavelength λmax equal to 354 nm;

- 2,4-bis[4-(2-ethylhexyloxy)-2-hydroxyphenyl]-6-(4-methoxyphenyl)-1,3,5-triazine (CAS No.: 187393-00-6), also called bis-ethylhexyloxyphenol methoxyphenyl triazine or BEMT, in particular as marketed by BASF under the name Tinosorb® S, a liposoluble broad band filter, having two absorption peaks at 310 nm and 340 nm;

- diethylhexyl butamido triazone, or DBT (chemical name: 4,4'-[[6-[[4-[[(1,1-dimethylethyl)amino]carbonyl]phenyl]amino]-1,3,5-triazine-2,4-diyl]diimino]bis-, bis(2-ethylhexyl)benzoate; CAS No.: 154702-15-5), in particular as marketed by 3V Sigma under the name Uvasorb® HE, a liposoluble UVB filter, having a maximum absorption wavelength λmax equal to 310 nm;

- ethylhexyl triazone or EHT (chemical name: 4-[[4,6-bis[[4-(2-ethylhexoxy-oxomethyl)phenyl]amino]-1,3,5-triazin-2-yl]amino]benzoic acid 2-ethylhexyl ester; CAS No.: 88122-99-00), in particular as marketed by BASF under the name Uvinul® T 150, a liposoluble UVB filter, having a maximum absorption wavelength λmax equal to 314 nm;

- and butyl methoxydibenzoylmethane, or 4-tert-butyl-4-methoxydibenzoylmethane (chemical name: 1,4-(1,1-dimethylethyl)phenyl-3-(4-methoxyphenyl)-1,3-propanedione; CAS No.: 70356-09-1), also called avobenzone or BMDBM, in particular as marketed by DSM under the name Parsol® 1789, a liposoluble UVA filter, having a maximum absorption wavelength λmax equal to 357 nm;

- or any mixture thereof.

In preferred embodiments of the invention, the tinted cosmetic composition comprises the phenylene bis-diphenyltriazine UV filter and at least one liposoluble sunscreen selected from among:

- hexyl 2-[4-(diethylamino)-2-hydroxybenzoyl]benzoate;

- 2,4-bis[4-(2-ethylhexyloxy)-2-hydroxyphenyl]-6-(4-methoxyphenyl)-1,3,5-triazine;

- diethylhexyl butamido triazone;

- and ethylhexyl triazone;

or one of the mixtures thereof.

In particular, the cosmetic composition according to the invention comprises the following additional sunscreens, preferably excluding any other (except phenylene bis-diphenyltriazine, always present in the composition according to the invention):

- diethylamino hydroxybenzoyl hexyl benzoate,
- bis-ethylhexyloxyphenol methoxyphenyl triazine, and
- ethylhexyl triazone or diethylhexyl butamido triazone

A certain number of sunscreens are not sufficiently photostable, i.e. they tend to degrade with prolonged exposure to ultraviolet radiations, and therefore no longer provide sufficient protection to the user. In particular, it is well known that the molecule butyl methoxydibenzoylmethane, an UVA filter widely used in commercial sunscreen products, splits into different chemical constituents with no absorbing capacity when subjected to UV irradiation, if it is not combined with other compounds that improve its photostability. Consequently, preferably, the tinted cosmetic composition according to the invention is free of butyl methoxydibenzoylmethane.

In particular embodiments of the invention, the tinted cosmetic composition does not comprise any water-soluble sunscreen. Alternatively, it may contain at least one water-soluble organic sunscreen, such as phenylbenzimidazole sulfonic acid.

In particular embodiments of the invention, the tinted cosmetic composition further comprises at least one particulate organic sunscreen, in particular selected from among the following filters:

- methylene bis-benzotriazolyl tetramethylbutylphenol (chemical name: 2,2'-methylene-bis-(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol;
CAS No.: 103597-45-1), also called MBBT, in particular as marketed by BASF under the name Tinosorb® M;
- and 2,4,6-tris(biphenyl-4-yl)-1,3,5-triazine (CAS No.: 31274-51-8), also called trisbiphenyl triazine or TBPT, in particular as marketed by BASF under the name Tinosorb® A2B;

or it contains one of the mixtures thereof.

In other particular embodiments, the composition according to the invention is devoid of such particulate organic sunscreens.

At least one additional sunscreen may be selected from among those conventionally known, of which inorganic sunscreens such as metal oxides coated or uncoated, such as oxides of titanium, iron, zinc, zirconium, or cerium. These inorganic filters are insoluble and are in particulate form.

In other particular embodiments, the composition according to the invention is devoid of such inorganic sunscreens.

It is important to differentiate between titanium dioxide as used as a sunscreen/UV filter and titanium dioxide as a pigment. Titanium dioxide can indeed take several different forms, which have different properties. The main difference between the titanium dioxide UV filter and the titanium dioxide pigment is the size of the particles, with the size of the pigment being significantly larger than that of the UV filter.

Nano-sized titanium dioxide, having a size smaller than 200 nm, which should be considered synonymous with "titanium dioxide UV filter", is present in most physical sunscreens due to the strong UV-absorbing capabilities thereof and resistance thereof to discoloration under ultraviolet light. This advantage enhances the stability thereof and ability thereof to protect the skin from UV radiation. Nano-sized titanium dioxide particles are primarily used in sunscreen compositions since they scatter visible light much less than titanium dioxide pigments and can provide UV protection.

The titanium dioxide pigment, the size of which is more than 200 nm, is the most widely used white pigment due to the brightness thereof and very high refractive index thereof, in which it is only surpassed by a few other materials. The crystal size of the titanium dioxide pigment may even reach a micrometer scale, such as about 7000 nm (measured by electron microscopy) to optimize maximum reflection of visible light. The titanium dioxide pigment is also an effective opacifier in powder form, form in which it is used as a pigment to confer whiteness and opacity on products such as paints, plastics, food, medicines, and most toothpastes. Titanium dioxide pigment is able to diffuse light, making it very useful as pigment.

More generally, "pigments" in the present description means mineral or organic, natural or synthetic, coated or uncoated, insoluble and coloring particles. As indicated above, the definition of pigments includes titanium dioxide with a particle size greater than 200 nm. Pigments are generally in powder form or in a pre-dispersed form in an aqueous or oily solution.

The pigment(s) implemented in the composition according to the invention confer on the latter the shade thereof and contribute to the covering power thereof, i.e. the ability thereof to cover and mask the imperfections of the skin area on which it is applied.

This or these pigments are preferably, but not limited to, of the mineral type.

In preferred embodiments of the invention, the composition according to the invention contains one or more pigments, in particular mineral ones, which are preferably selected from among iron oxides and titanium dioxide, or any of the mixtures thereof. Preferably, the composition according to the invention contains a pigment mixture, this pigment mixture comprising, and, preferably consisting of, yellow, red and black iron oxides, and titanium dioxide. Such a mixture of pigments makes it possible on its own, quite advantageously, to adapt to a wide range of skin tones, by an appropriate choice of the respective proportions thereof.

In preferred embodiments, the composition according to the invention does not comprise any other pigment than iron oxides and titanium dioxide.
In particular, the composition according to the invention is preferably devoid of natural or synthetic mica (fluorophlogopite).

Pigments of mineral origin are referenced by a color index (CI, for the English Color Index) in the INCI nomenclature (International Nomenclature of Cosmetic Ingredients), the main pigments used in cosmetics / make-up being the following:

- CI 77891 White (Titanium Dioxide)
- CI 77491 Red (Iron Trioxide)
- CI 77492 Yellow (Iron Oxide)
- CI 77499 Black (Iron Tetraoxide)
- CI 77007 Blue (Lazurite)
- CI 77742 Violet (Manganese Violet)
- CI 77510 Prussian Blue (Ferric Ferrocyanide)

- CI 77163 White (Bismuth Oxychloride)
- CI 77288 Green (Dichromium Trioxide)
- CI 77000 White (Aluminum)
- CI 77289 Green (Green Chromium Hydroxide)
- CI 77400 Brown (Bronze)
- CI 77120 White (Barium Sulfate)
- CI 77820 White (Silver)
- CI 77002 White (Aluminum Hydroxide)
- CI 77947 White (Zinc Oxide)
- CI 77480 Yellow Brown (Gold)
- CI 77713 White (Magnesium Carbonate)
- CI 77489 Orange (Iron Oxide)
- CI 77019 (Mica White).

In preferred embodiments of the invention, the composition comprises at least one, preferably a plurality, and preferably all, of the four mineral pigments CI77491, CI77492, CI77499 and CI77891. Preferably, these four pigments are the only pigments contained in the composition according to the invention.

The total pigment content in the composition is between 1 and 5%, preferably between 2 and 5%, preferably between 2 and 4%, more preferably between 2 and 3%, and even more preferably about 2.5%, by weight relative to the total weight of the composition.

The amount of titanium dioxide pigment (or CI 77891) preferably represents at least 50%, preferably at least 75%, by weight of the total weight of the pigments contained in the composition.

Advantageously, the composition according to the invention has, at the end of the preparation method thereof, a fixed shade, which does not change when applied to the skin.

It is furthermore, as indicated above, in the form of a stable suspension of the particulate matters that enter into the composition thereof, this including when the total content of pigment(s) therein is as high as 2% by weight, and even up to 5% by weight relative to the total weight of the composition.

The term “stable suspension” means, in a manner conventional per se, that the particles contained therein do not settle or aggregate. Thus, virtually no settling

of the insoluble particles contained therein is observed in the composition according to the invention, including for long periods, in particular for a period as long as the general shelf-life of the composition, which is more than 6 months, preferably more than 12 months, more preferably more than 18 months and preferably 36 months. In particular, the stability and homogeneity of the composition can be ensured by visual observation of the composition or a centrifugation test.

The composition according to the invention also has a good viscosity, this even without the need to implement therein an additional ingredient having a thickening effect. In the present description, by "good viscosity", it should be understood a viscosity enabling the composition to be dispensed by different packagings, in particular tubes and pump vials, and not escape from the hands of the user when it is dispensed therein. Thus, the sunscreen cosmetic composition of the present invention is advantageously stable, with the desired viscosity, appearance, color, microscopy and pH range.

In particularly preferred embodiments of the invention, the cosmetic composition has a dynamic viscosity at 25°C +/- 2°C less than or equal to 10000 mPa.s, preferably between 700 and 10000 mPa.s, more preferably between 700 and 5000 mPa.s, and for example between 1500 and 4000 mPa.s. This viscosity may for example be measured by means of a Brookfield viscometer by applying the following parameters: spindle 5, speed 100 rpm, for 1 minute.

The composition according to the invention contains, as a suspension agent, one or several unmodified smectites. It preferably contains a single unmodified smectite.

Smectites are clays of the class of natural phyllosilicates primarily in the form of lamellar, foamy or spherical aggregates, characterized by a layer structure in which a central layer of octahedrally coordinated cations is sandwiched by two layers of $[(Si,Al)O_4]$ tetrahedra. There are many clay compounds/materials belonging to the smectite class. In this respect, mention may in particular be made, in the class of dioctahedric smectites, of beidelite and montmorillonite, and, in the class of trioctahedric smectites, of hectorite, saponite, etc. Bentonite, essentially consisting of montmorillonite, is also considered according to the present invention as belonging to the family of smectites.

As disclosed above, it was discovered by the present Inventors that, quite surprisingly, the presence, in a cosmetic composition in the form of an emulsion, of a smectite in a content by weight of 0.3 to 2%, allows keeping therein particulate pigments in stable suspension up to a content of 5% by weight relative to the total weight of the composition, and that being so even when the composition contains the particulate sunscreen phenylene bis-diphenyltriazine, at a content between 1 and 5% by weight, and, where appropriate, other particulate sunscreens which are not soluble in the vehicle of the composition. This advantageous result is advantageously not obtained to the detriment of the fluidity and sensory properties of the composition, or to the detriment of the sun protection effectiveness thereof. It further allows stably forming tinted sunscreen cosmetic compositions containing a sufficient amount of pigments to be able to cover a wide range of shades, adapting to all existing user skin tones.

Equally surprisingly, this advantageous result is not obtained when smectite is modified, for example so as to increase the lipophilic character thereof, by reaction with quaternary ammonia, such as stearalkonium chloride or quaternium-18.

Preferably, the unmodified smectite(s) substantially constitute the only suspension agents contained in the composition according to the invention.

Preferably, an unmodified smectite contained in the composition according to the invention as a suspension agent is hectorite or bentonite. For convenience, the terms "hectorite" and "bentonite", when used alone in the present description (i.e. without mention of any group modifying their formula), specifically mean, respectively, unmodified hectorite and unmodified bentonite.

In preferred embodiments of the invention, the composition comprises, as a suspension agent, either only unmodified hectorite, or only unmodified bentonite.

The total amount of suspension agent(s) selected from among unmodified smectites in the composition according to the invention is preferably between 0.3 and 1.5% by weight, preferably between 0.3 and 1% by weight, relative to the total weight of the composition.

When the composition according to the invention contains hectorite as a suspending agent, the hectorite concentration therein is preferably between 0.3

and 0.8% by weight, preferably between 0.3 and 0.5% by weight, relative to the total weight of the composition.

When the composition according to the invention contains bentonite as a suspension agent, the bentonite concentration therein is preferably between 0.5 and 1.5% by weight, preferably between 0.8 and 1.2% by weight, relative to the total weight of the composition.

In particular embodiments of the invention, the mass ratio between the suspension agent(s), and the pigment(s), contained in the composition, is between 0.08 and 0.6, preferably between 0.1 and 0.4.

The cosmetic composition according to the invention is preferably in the form of an oil-in-water type emulsion, i.e. it comprises an oily phase maintained homogeneously dispersed, in the form of fine droplets, in an aqueous phase, by the emulsifier(s) contained in the composition.

The cosmetic composition according to the invention comprises, by weight relative to the total weight of the composition, 30 to 50% of water, preferably 35 to 50% of water, or 30 to 45% of water, more preferably 35 to 45% of water, or else 40 to 50% of water, and more preferably 40 to 45% of water.

The composition according to the invention may contain a single oily emollient, or a plurality of oily emollients.

In the present description, the term “oily emollient” means an ingredient present in the oily phase, and ensuring that the composition according to the invention has a good sensoriality, and a good ability to soften the epidermis.

Preferably, the oily emollient(s) contained in the composition according to the invention are in liquid form, in particular at any temperature between 5°C and ambient temperature (between 20°C and 25°C).

The oily emollients typically comprise one or more polar chemical function(s) from among the functions ester (-CO_2-), alcohol (-OH), ether (-O-), carbonate (-OCO_2-) and carboxylic acid (-CO_2H), and one or more lipophilic group(s), i.e. one or more aliphatic and/or aromatic hydrocarbon group(s), in particular one or more saturated or unsaturated, linear or branched, hydrocarbon chain(s), comprising between 6 and 20 carbon atoms, for example between 7 and 18 carbon atoms, in particular between 8 and 16 carbon atoms, a phenyl group (-C_6H_5) and/or a phenylalkyl group.

Preferably, the composition according to the invention comprises at least one oily emollient selected from among C12-C15 alkyl benzoate, caprylic/capric triglycerides, dicaprylyl carbonate, coco-caprylate, coco-caprylate/caprate, diisopropyl sebacate, diethylhexyl succinate, isopropyl palmitate, isopropyl myristate, propylheptyl caprylate, phenethyl benzoate, dibutyl adipate, diisopropyl adipate, glyceryl tri-2-ethylhexanoate, pentaerythrityl tetra-2-ethylhexanoate, cetyl 2-ethylhexanoate, isononyl isonanoate, neopentyl glycol diheptanoate, diethylhexyl succinate, butylene glycol dicaprylate/dicaprate, octyldodecanol, propylene glycol dicaprylate/dicaprate and dicaprylyl ether, or any of the mixtures thereof.

In particular embodiments of the invention, the oily emollient(s) contained in the composition according to the invention are liquid lipophilic emollients, capable of totally solubilizing the liposoluble sunscreen(s) possibly present in the composition, and are preferably selected from among C12-C15 alkyl benzoate, dicaprylyl carbonate, diisopropyl adipate, coco-caprylate caprate, diisopropyl sebacate, neopentyl glycol diheptanoate, diethylhexyl succinate, glyceryl tri-2-ethylhexanoate, isononyl isononanoate and cetyl 2-ethylhexanoate.

In particular embodiments of the invention, the oily emollient(s) are present in the composition in a total content of between 10 and 40% by weight, preferably between 15 and 40% by weight, preferably between 15 and 35% by weight, or between 20 and 35% by weight, in particular between 20 and 30% by weight, for example between 20 and 25% by weight, relative to the total weight of the composition.

In particular embodiments of the invention, C12-C15 alkyl benzoate represents between 30 and 100% by weight of the total weight of the oily emollients contained in the composition.

In particular embodiments of the invention, dicaprylyl carbonate represents between 30 and 100% by weight of the total weight of the oily emollients contained in the composition.

In particular embodiments of the invention, diisopropyl adipate represents between 10 and 100%, preferably 10 and 50%, by weight of the total weight of the oily emollients contained in the composition.

In particular embodiments of the invention, the caprylic/capric triglycerides represent less than 5% by weight, preferably less than 1% by weight, of the total weight of the oily emollients contained in the composition.

The cosmetic composition according to the invention contains no humectant(s), or contains at most 5% by weight, for example between 0.01 and 5% by weight, preferably at most 4% by weight, for example between 0.01 and 4% by weight, in total of humectant(s), relative to the total weight of the composition.

For the purposes of the present description, humectant means a polyol. A "polyol" (otherwise referred to as polyalcohol) is herein defined, in a manner conventional per se, as a compound comprising a hydrocarbon chain with at least two carbon atoms and comprising at least two hydroxyl groups.

The polyol(s) that may be contained in the composition according to the invention may be natural or synthetic. They may have a linear, branched or cyclic molecular structure.

In particular embodiments wherein the composition according to the invention contains at least one humectant, the latter may be selected from among glycerin and derivatives thereof, and glycols and derivatives thereof. At least one humectant, preferably each of the humectants, contained in the composition according to the invention, is preferably selected from the group consisting of glycerin, diglycerin, polyglycerin, diethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, pentylene glycol, hexylene glycol, 1,3-propanediol, 1,5-pentanediol, 1,2-hexanediol, octane 1,2-diol, polyethylene glycols, in particular having from 5 to 50 ethylene oxide groups, but also erythritol, threitol, arabitol, xylitol, ribitol, mannitol, sorbitol, galactitol, fucitol, iditol, inositol, volemitol, isomalt, maltitol, lactitol, maltotriitol, maltotetrol, and polyglycitol.

In particular embodiments of the invention, the composition thus contains at least one humectant, preferably at least glycerin, preferably in an amount less than or equal to 5% by weight relative to the total weight of the composition.

Preferably, the cosmetic composition according to the invention contains less than 3% by weight in total of humectant(s), relative to the total weight of the composition. Preferably, the cosmetic composition according to the invention contains in total less than 2% by weight of humectant(s), even more preferably

less than 1.5% by weight of humectant(s), and even more preferably less than 1% by weight of humectant(s), relative to the total weight of the composition.

The cosmetic composition according to the invention may comprise one or more emulsifiers, advantageously selected from among emulsifiers capable of forming oil-in-water emulsions. For example, the emulsifier(s) may be selected from among ethoxylated fatty alcohols, the products marketed under the names Montanov® 68 (Cetearyl Alcohol (and) Cetearyl Glucoside) and Montanov® 82 (Cetearyl Alcohol (and) Coco-Glucoside), potassium cetyl phosphate, glucoside waxes, glyceryl stearate citrate, lauryl glucoside and polyglyceryl-2 dipolyhydroxystearate, in particular the product marketed under the name Eumulgin® VL75, lecithins, in particular hydrogenated soy lecithin, glycerol monostearate, sorbitan monostearate, sodium dilauramidoglutamide lysine, sodium stearoyl glutamate, in particular the product marketed under the name Eumulgin® SG, sodium stearoyl lactylate, sucrose stearate, etc.

In particular embodiments of the invention, the emulsifier(s) are present in the composition in a total content of 2 to 12% by weight, preferably 2 to 10% by weight, preferably 2 to 8% by weight, even more preferably 3 to 8% by weight, or even 2 to 6% by weight, in particular 2 to 5% by weight, for example 3 to 5% by weight, relative to the total weight of the composition. Advantageously, such contents allow obtaining a good stability of the emulsion and a good sensoriality of the composition.

The composition according to the invention may further contain one or more cosmetically active agents for skin care and/or hygiene, such as tocopheryl glucoside, zinc gluconate, *Lens esculenta* seed extracts.

The composition according to the invention may further comprise one or more cosmetically and/or dermatologically acceptable excipient(s).

In the present invention, "cosmetically and/or dermatologically acceptable" means what is useful in the preparation, preservation or administration of a cosmetic or dermatological composition, is generally safe, non-toxic and neither biologically nor otherwise undesirable, and which is acceptable for human cosmetic or dermatological use.

Thus, the composition according to the invention may comprise excipients selected in particular from among consistency factors, texture agents, water-

resistance agents, gelling agents, opacifiers, fragrances, essential oils, preservatives, sequestrants, bactericides, odor absorbers, alkalizing or acidifying agents, or any other ingredient commonly used for the manufacture of sunscreen compositions.

Thus, the composition according to the invention may comprise in particular one or more texture agent(s) which could also be qualified as mattifying agents or oil-absorbing agents, preferably in the form of powder(s). Such texture agents may be selected in particular from ingredients of the starch family, such as rice, corn, and tapioca starches, talcs and cellulose and derivatives thereof, in particular microcrystalline cellulose.

In particular embodiments of the invention, the texture agent(s) represent between 1 and 15% by weight, preferably between 1% and 10% by weight, more preferably between 2% and 6% by weight, relative to the total weight of the composition.

In particular embodiments of the invention, the composition does not comprise a texture agent selected from among nylon derivatives and polymethyl methacrylate (PMMA).

The composition according to the invention is preferably devoid of silica, silica being relatively controversial for an application in the cosmetic field, in particular due to the negative environmental impact linked to the production thereof.

The cosmetic composition according to the invention may also comprise one or more consistency factors.

This or these consistency factor(s) are preferably selected from fatty alcohols, fatty acids, fatty esters, hydrogenated vegetable oils, and other waxy bodies. Mention may be made, for example, of glyceryl behenate or glyceryl laurate.

Preferably, the composition according to the invention contains only one consistency factor, or no consistency factor.

The total content in consistency factor(s) in the composition is preferably less than or equal to 5% by weight, for example less than or equal to 4% by weight, in particular less than or equal to 3% by weight, relative to the total weight of the composition.

The cosmetic composition according to the invention does not contain any gelling agent, or contains a maximum of 1% by weight in total of gelling agent(s),

relative to the total weight of the composition. Thus, in particular embodiments of the invention, the composition is devoid of gelling agent, or it comprises 0.01 to 1% by weight, preferably 0.01 to 0.8% by weight, and preferably 0.01 to 0.5% by weight, of gelling agent(s), relative to the total weight of the composition.

At least one gelling agent, preferably each of the gelling agents, contained in the composition according to the invention, is preferably selected from among xanthan gum, scleroglucan gum, carrageenans, gellan gum, diutan gum, and *Caesalpinia spinosa* gum, or any of the mixtures thereof.

The composition according to the invention may also comprise one or more water-resistance agent(s), selected in particular from among a copolymer of N-vinylpyrrolidone (VP) and eicosene (INCI name: VP/eicosen copolymer), a crosspolymer of trimethylpentanediol, adipic acid, and glycerol (INCI name: trimethylpentanediol/adipic acid/glycerin crosspolymer), polyamide 3 (INCI), an acrylate and octylacrylamide copolymer (INCI name: acrylates/octylacrylamide copolymer), and triacontanyl PVP (INCI).

In particular embodiments of the invention, the water-resistance agent(s) represent in total between 0% and 2%, preferably between 0.01% and 1% by weight, relative to the total weight of the composition.

Preferably, the composition according to the invention comprises trimethylpentanediol/adipic acid/glycerin crosspolymer (INCI name) as a water-resistance agent.

In preferred embodiments of the invention, the composition is devoid of volatile silicones (also called volatile silicone oils).

Volatile silicones are short chain cyclic polymers of general formula $[Si\text{-}(CH_3)_2\text{-}O]_n$ with n=3-7. Commonly called cyclomethicone, regardless of the number of patterns, the most common are cyclotetrasiloxane (n=4) and cyclopentasiloxane (n=5), but mention may also be made of cyclotrisiloxane (n=3), cyclohexasiloxane (n=6) and cycloheptasiloxane (n=7). Volatile silicones are substances deemed to be environmentally accumulative and not biodegradable due to the high stability thereof. Studies have shown that cyclopentasiloxane, for example, has a potential for bioaccumulation in aquatic environments (Gobas et al., 2015, Environmental Toxicology and Chemistry, 34, 12:2703-2714).

More generally, the composition according to the invention is preferably devoid of volatile ingredients. By "volatile ingredients", it should be understood, within the meaning of the present invention, non-alcoholic organic or inorganic compounds such as esters, silicones or alkanes, characterized by a flash point of less than 60°C.

By “flash point” (denoted FP), it should be understood, in a conventional manner per se, the minimum temperature at which a combustible substance releases vapors in a sufficient concentration to form with the ambient air a gaseous mixture that ignites in contact with a flame or a hot point, but insufficient for combustion to propagate on its own in the absence of the so-called pilot flame. According to Regulation (EC) No. 1272/2008 on the classification, labeling and packaging of substances and mixtures, a substance with a FP such as 23°C ≤ FP < 60°C belongs to category 3 "lowly flammable".

Thus, the composition according to the present invention is in particular preferably devoid of volatile esters, such as isohexyl neopentanoate, and/or volatile alkanes, such as isohexadecane.

The composition according to the invention may also contain one or more monoalcohol(s). However, it is preferably free of monoalcohols.

In particular embodiments of the invention, the composition is devoid of essential oils. Indeed, most essential oils contain allergens, sources of irritation and skin intolerance. Dyes having the same characteristics are also preferably avoided for similar reasons.

In particular embodiments of the invention, the composition is devoid of ethylenediaminetetraacetic acid (EDTA). Alternatively, it may contain such an acid.

In particular embodiments of the invention, the tinted cosmetic composition is free of microplastics.

The term "microplastic", within the meaning of the present invention, designates synthetic polymer microparticles, and refers to the definition given in the draft amendment to Annex XVII of REACH Regulation (EC) No. 1907/2006, D083921/01 of September 5th, 2022 ("Commission Regulation (EU) …/… of XXX amending Annex XVII to Regulation (EC) No. 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation,

Authorisation and Restriction of Chemicals (REACH) as regards synthetic polymer microparticles" accessible in particular at the following URL: https://ec.europa.eu/transparency/comitology-register/screen/documents/083921/1/consult?lang=en). According to this document, microplastics, or microparticles of synthetic polymers, are defined as polymers that are solid and that either are contained in particles and constitute at least 1% by weight of these particles or form a continuous surface coating on particles, when at least 1% by weight of these particles meet one of the following conditions: (a) all particle dimensions are less than or equal to 5 mm; (b) the length of the particles is less than or equal to 15 mm and the length to diameter ratio thereof is greater than 3. The following polymers are excluded from this description:

(a) polymers resulting from a polymerization process that occurred in nature, which are not chemically modified substances;

(b) polymers that are degradable as proven in accordance with Annex [X] to the document;

(c) polymers that have a solubility greater than 2 g/L as proven in accordance with Annex [Y] of the document (solubility test in water at pH 7 under stirring for 24 h at 20 °C, with a polymer load of 10 g/1,000 mL, according to the protocol of Test No. 120 or Test No. 105 of the OECD Guidelines for Chemical Testing);

(d) polymers that do not contain carbon atoms in the chemical structure thereof.

Synthetic polymer microparticles subject to the derogation provided for in point 4a of the said draft amendment to Annex XVII are also excluded from this definition.

More generally, microplastics may be defined as particles all dimensions of which are less than 5 mm, formed or coated with water-insoluble and non-biodegradable synthetic solid organic polymer(s).

Thus, in particular, the cosmetic composition according to the invention is preferably devoid of microplastic polyquaterniums, ingredients used in many cosmetic compositions proposed by the prior art.

It is also preferably devoid of microplastic acrylates.

On the other hand, in particular embodiments of the invention, the cosmetic composition may comprise one or more non-microplastic acrylate(s), selected in

particular from the group consisting of (INCI names):

- Acrylates/C10-30 Alkyl Acrylate Crosspolymer,
- Acrylates/vinyl isodecanoate crosspolymer,
- Sodium Polyacrylate,
- Hydroxyethyl Acrylate/Sodium Acryloyldimethyl Taurate Copolymer,
- Acrylates copolymer,
- Polyacrylate-13,
- Acrylates/t-Butylacrylamide Copolymer,
- Octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer,
- Polyacrylamide,
- VP/Methacrylamide/Vinyl Imidazole Copolymer,

used alone or in any mixture thereof.

The composition according to the invention may be in any form conventional per se, this form being suitable for topical application on the skin and mucous membranes. In particular, yet without limitation, it may be in the form of a fluid emulsion, a rich emulsion, a cream, a milk, or a lotion.

Throughout the present description, the term skin encompasses both the skin strictly speaking and the mucous membranes, in particular the lips. The term "cutaneous" encompasses both the skin and the mucous membranes.

The composition according to the invention may be intended to be applied to the skin of the face and/or of the body, and/or on the hair. For example, it may be in the form of a cream or balm for protection, treatment or care of the face, of the hands and/or of the body, or in the form of a body milk for protection, treatment or care.

Another aspect of the invention relates to a method for preparing a composition according to the invention, as described previously, in particular in the form of an oil-in-water emulsion. This method comprises the following steps of:

- preparing the oily phase: prior solubilization and, where appropriate, of liposoluble filter(s) in the oily emollient(s) at a temperature between 70°C and 85°C, typically at 80°C, under stirring, preferably under mechanical stirring; then adding the other ingredients constituting the oily phase of the emulsion – such as the pigment(s) - to the mixture obtained before, at a temperature between 70°C and 85°C, typically at 80°C, under stirring, preferably under mechanical

stirring;

- preparing the aqueous phase: prior dispersion of the phenylene bis-diphenyltriazine and, where appropriate, of the other organic particulate filter(s) in water, at a temperature between 50°C and 75°C, typically at 60°C, under stirring, preferably under mechanical stirring; then adding the other ingredients constituting the aqueous phase of the emulsion to the mixture obtained before, at a temperature between 50°C and 75°C, typically at 60°C, under stirring, preferably under mechanical stirring;

- adding a suspension agent selected from unmodified smectites in at least one of said aqueous phase and said oily phase, and preferably in said aqueous phase;

- adding emulsifier(s) in at least one of said aqueous phase and said oily phase;

- introducing the previously obtained oily phase into the previously obtained aqueous phase, under stirring, preferably under mechanical stirring, until a homogeneous solution is obtained;

- cooling the emulsion thus obtained to room temperature; and

- optionally, adding fragrance, active agent(s) and/or texture agent(s) in powder form, under stirring, preferably under mechanical stirring.

The cosmetic composition according to the invention is in particular intended to be applied topically to any area of the skin of a subject likely to be exposed to solar radiation or to artificial ultraviolet radiation, in particular an area of the skin of the face or body of the subject.

Another aspect of the invention relates to the use of a composition according to the invention for sun protection of the skin and/or hair of a subject, this use comprising topically applying the composition to said skin and/or hair. The subject may be a mammal, in particular a human.

The composition according to the invention may for example be applied topically, to an area of the skin of the subject concerned, such as the skin of the face, including the lips, or of the body, in an effective amount, as often as necessary before or during exposure to sunlight.

The invention is also expressed in terms of a therapeutic method for protecting an area of the skin of a subject, in particular of a human, this method comprising

topically applying, on this skin area, an effective amount of a composition according to the invention.

This method may meet one or more of the features described above with reference to the use of the cosmetic composition according to the invention for sun protection of the skin and/or hair.

The present invention also relates to a method for non-therapeutic cosmetic treatment of an area of the skin and/or of the hair of a subject, in particular of a human, for the sun protection of this skin area and/or hair, by topical application, on this skin area and/or hair, of an effective amount of a composition according to the invention.

Here again, this method may meet one or more of the features described above with reference to the use of the cosmetic composition according to the invention for sun protection of the skin and/or hair.

Another object of the invention relates to the non-therapeutic cosmetic use of a composition according to the invention for sun protection of an area of the skin and/or of the hair of a subject, in particular of a human. This use comprises topically applying this composition to this skin area and/or hair. It may meet one or more of the features described above with reference to the use of the composition according to the invention for sun protection of the skin and/or hair.

The features and advantages of the invention will become more apparent in light of the following examples of implementation, provided merely by way of illustration and non-limiting example of the invention, with the support of Figure 1, which represents a graph showing the proportion of the total surface area (average in pixels) occupied by heterogeneous areas on an area of skin of interest of a subject, determined by a skin analysis imaging system coupled to a color-tracking image analysis module, respectively at an initial time (T0), then 10 to 30 minutes after application on the skin area of interest of a cosmetic composition according to the invention (Timm).

1/ <u>Example 1</u> - General formula of the compositions tested

The compositions tested, in the form of an oil-in-water emulsion, comprising phenylene bis-diphenyltriazine, meet the general formula presented in Table 1 below.

Ingredients	Amount (% w/w)
Water	30 - 50
Phenylene bis-diphenyltriazine as an aqueous dispersion:	
Phenylene bis-diphenyltriazine	3.5
PPG-1 PPG-9 Lauryl Glycol Ether	0.3
Additional UV filters:	8 - 15
Bis-ethylhexyloxyphenol methoxyphenyl Triazine	
Ethylhexyl Triazone	
Diethylamino Hydroxybenzoyl Hexyl Benzoate	
Oily emollients:	20 - 25
C12-C15 alkyl benzoate	
Dicaprylyl carbonate	
Diisopropyl adipate	
C9-C12 alkanes & Coco-caprylate caprate	
Emulsifiers:	2 - 8
Potassium cetyl phosphate	
Lauryl Glucoside	
Polyglyceryl-2 dipolyhydroxystearate	
Active agents:	
Tocopheryl glucoside	0.2
Zinc gluconate	0.1
Excipients:	
Trimethylpentanediol/Adipic Acid/Glycerin Crosspolymer	1
Starches	2 – 6
Preservative	qs
Suspension agent	X
Pigment(s):	Y
CI77491	
CI77492	
CI77499	
CI77891	

Table 1 - General formula of the compositions tested

2/ Example 2 - Objectification of the technical problem

Two compositions not in accordance with the invention are tested in order to evaluate the stability thereof by focusing on the visual aspect, a centrifugation test and a stability study. Viscosities are also measured. Finally, an analysis of the formulas under microscopy is performed.

The various protocols of the tests performed are as follows.

Fluidity

Viscosity measures the resistance of the fluid. This analysis makes it possible to understand how fluid or viscous the formula is, and how this property behaves throughout the stability study. Product viscosity impacts packaging selection, active ingredient release, spread and consumer experience. This analysis is carried out at a temperature of 25°C, using a Brookfield viscometer, with the following parameters: spindle 5, 100 rpm, for 1 minute.

Brookfield viscometers use the principle of rotational viscosity – the torque required to rotate an object, such as a spindle, in a fluid indicates the viscosity of the fluid. The torque is applied by means of a calibrated spring to a disk or shaft immersed in the fluid to be tested and the deflection of the spring measures the viscous drag of the fluid against the shaft.

Stability of the emulsion by centrifugation

The centrifugation test is carried out on a fresh sample of the compositions. This sample is subjected to high speed rotation for a certain time, here 4000 rpm for 20 minutes. The objective is to stress the formula and anticipate potential instabilities without having to wait too long for the end of the stability study. Indeed, the dispersed phase of an oil-in-water emulsion tends to separate and rise to the top of the emulsion forming a layer of oil droplets. This phenomenon is called creaming. This is one of the first signs of emulsion instability.

Homogeneity

The visual aspect makes it possible to appreciate the homogeneity of the composition. This test is performed by the same person trained in this type of exercise.

A microscopic evaluation of the microstructure of the composition is performed in order to verify the presence or not of signs of future instabilities. In general, a good emulsion profile is sought, i.e. fine round oil droplets of the same size,

homogeneously dispersed in the continuous phase, a cohesive edge, and therefore no sign of large undispersed particles should be present.

The compositions tested meet the general formula of Table 1, wherein X is 0 (absence of smectite). The values of Y are as follows:

- composition A: Y = 1.2

Composition B Y = 2.5.

The results obtained are shown in Table 2.

Composition	A	B
Viscosity (mPa.s)	2100	1809
Stability by centrifugation	OK	KO
Homogeneity: Visual Appearance Microscopy	 Compliant OK	 Not compliant Agglomerates

Table 2 - Evaluation of the stability of compositions not in accordance with the invention – OK means "satisfactory", KO means "unsatisfactory"

Composition A corresponds to a tinted sunscreen composition based on phenylene bis-diphenyltriazine, wherein the concentration of pigment mixture is relatively low, namely 1.2% by weight relative to the total weight of the composition. As shown in Table 2, all tests are positive with this composition A. It is stable, fluid and homogeneous.

Composition B is very close to composition A, only the concentration of the same pigment mixture is different, namely 2.5% by weight relative to the total weight of the composition. This higher concentration of pigments changes everything, since a non-homogeneous appearance is observed, the pigments and particles of the filter then form agglomerates when the composition is observed under the microscope.

Thus, when the concentration of pigments increases, and is higher than 1.2% by weight, the stability of the composition free of smectite is no longer ensured.

3/ Example 3 - Evaluation of different compositions

Two compositions according to the invention C1 and C2, as well as two comparative compositions not according to the invention D and E, all meeting the general formula of Table 1, are tested in this example. Comparative

compositions D and E contain, respectively, as a suspension agent, modified smectite or aluminum magnesium silicate (Mg Al Silicate).

The stability of these compositions is evaluated according to the protocols described in Example 2.

The results obtained, for each composition, are shown in Table 3.

Composition	C1	C2	D	E
Y	2.5	2.5	2.5	2.5
Suspension agent	Hectorite	Bentonite	Stearalkonium hectorite	Mg Al Silicate
X	0.3	1	0.3	0.3
Viscosity (mPa.s)	2752	2886	2786	3490
Stability by centrifugation	OK	OK	KO	KO
Homogeneity: Visual Appearance Microscopy	Compliant OK	Compliant OK	Not compliant Agglomerates	Not compliant Agglomerates

Table 3 - Evaluation of the stability of compositions in accordance with the invention C1 and C2 and compositions not in accordance with the invention D and E – OK means "satisfactory", KO means "unsatisfactory"

It is observed that when the composition contains 0.3% by weight of hectorite (composition C1) or 1% by weight of bentonite (composition C2), even with 2.5% by weight of the pigment mixture, the different stability criteria evaluated are in accordance with expectations. The compositions appear stable and are homogeneous on microscopic examination.

On the other hand, in the presence of other suspension agents such as stearalkonium hectorite (brought by the product Bentone Gel® TN V), which is a modified smectite, (composition D), the stability of this formula is altered, and agglomerates are formed.

Similarly, in the presence of another suspension agent other than smectites, aluminum and magnesium silicate, a lack of homogeneity and stability is observed even though the viscosity was in the expected range.

This demonstrates that the choice of the suspension agent is paramount, and only unmodified smectites are appropriate and enable to stabilize the tested compositions.

4/ Example 4 - Other comparative examples

Two comparative compositions not in accordance with the invention F and G, meeting the general formula of Table 1, and containing, respectively, a content of suspension agent selected from unmodified smectites higher than that recommended by the invention, or a content of pigments higher than that recommended by the invention,

The stability of these compositions is evaluated according to the protocols described in Example 2.

The results obtained, for each composition, are shown in Table 4.

Composition	F	G
Y	2.5	8
Suspension agent	Hectorite	Hectorite
X	2.5	0.5
Viscosity (mPa.s)	> 10,000	1470
Stability by centrifugation	NE	KO
Homogeneity: Visual Appearance Microscopy	 NE NE	 Not compliant Agglomerates

Table 4 - Evaluation of the stability of compositions not in accordance with the invention – OK means "satisfactory", KO means "unsatisfactory" and NE means "not evaluated"

It is interesting to note that an excessive amount of the suspension agent (2.5% by weight in composition F) is harmful, since a viscosity that is far too high (> 10,000 mPa.s) is then measured. Such a viscosity is not conceivable, as it affects the texture and sensoriality of the formulas.

Similarly, it is observed that with an excessive amount of pigments (8% by weight), even with hectorite as the suspension agent, at a concentration of 0.5% by weight (composition G), the various particles are not dispersed

homogeneously. The particulate fillers are probably too high and the suspension is not stable, even forming agglomerates.

Thus, the Inventors demonstrate that, in the context of a phenylene bis-diphenyltriazine-based tinted sunscreen composition comprising at least 2% by weight of a pigment mixture, only an unmodified smectite and in an adequate amount (i.e. between 0.3 and 2% by weight) is able to suspend this composition homogeneously and stably, without altering the desired fluidity.

5/ <u>Example 5</u> - Analysis of the coverage of a composition according to the invention

This analysis is performed using the VISIA®-CR device (skin analysis imaging system) from Canfield.

The tested composition, named C3, is described in Table 5.

Ingredients	Amount (% w/w)
Water	30 - 50
Phenylene bis-diphenyltriazine as an aqueous dispersion: Phenylene bis-diphenyltriazine PPG-1 PPG-9 Lauryl Glycol Ether	 3.5 0.3
Additional UV filters: Bis-ethylhexyloxyphenol methoxyphenyl Triazine Ethylhexyl Triazone Diethylamino Hydroxybenzoyl Hexyl Benzoate	8 - 15
Oily emollients: C12-C15 alkyl benzoate Dicaprylyl carbonate Diisopropyl adipate C9-C12 alkanes & Coco-caprylate caprate	20 - 25
Emulsifiers: Potassium cetyl phosphate Lauryl Glucoside Polyglyceryl-2 dipolyhydroxystearate	2 - 8
Active agents:	

Tocopheryl glucoside	0.2
Zinc gluconate	0.1
Lens Esculenta (p-Refinyl®) seed extract	1
Excipients: Trimethylpentanediol/Adipic Acid/Glycerin Crosspolymer	1
Rice starch and tapioca starch	2 – 6
Preservative	qs
Hectorite	0.3
Pigment(s): CI77491 CI77492 CI77499 CI77891	2.5

Table 5 - Composition C3 in accordance with the invention

Images of a skin area at the forehead of the subjects tested are acquired by means of the VISIA®-CR device, by a qualified technician trained in this analysis, at the following times:

- T0: before application of the composition on the skin area concerned,
- Timm: between 10 and 30 minutes after this application.

The selected skin area, known as the area of interest, is a heterogeneous pigmentation area (with the presence of dark spots).

An evaluation of the images taken by the device is performed in order to study the coverage of this composition C3, using the FrameScan® software. This software consists of two analysis modules, one colorimetric, used for color and brightness analysis, and the other morphological, used for analysis of spot morphology, wrinkle density and skin homogeneity.

To evaluate the potential coverage of the composition C3 according to the invention, the images obtained at T0 are compared to the images obtained immediately after application of the composition (Timm). For the coverage analysis, photos with a cross-polarized filter are used as well as a color tracking module of the FrameScan® software, wherein the total surface area parameter is used.

The software calculates the share of the total surface area of interest occupied by heterogeneous areas at T0 and Timm. The results obtained are shown in Figure 1.

It is observed that a statistically significant reduction (by 65%) of the parameter that is the share of the total surface area occupied by heterogeneous areas, is obtained after application of the composition according to the invention on the skin area concerned, reflecting a much more uniform appearance of the skin and therefore fewer heterogeneous areas.

The inventors therefore clearly highlight that a composition according to the invention is able to make the appearance of the skin more uniform.

CLAIMS

1. Tinted sunscreen cosmetic composition in the form of an emulsion, suitable for topical application on the skin, comprising, the percentages being expressed by weight relative to the total weight of the composition:

- 30 to 50% of water,
- 1 to 5% of the particulate sunscreen phenylene bis-diphenyltriazine,
- at least one emulsifier,
- at least one oily emollient,
- at least one pigment,

characterized in that the total content of pigment(s) in the composition is between 1 and 5% by weight relative to the total weight of the composition, and in that said composition further comprises a suspension agent selected from among unmodified smectites, the amount of suspension agent(s) selected from among unmodified smectites in the composition being between 0.3 and 2% by weight relative to the total weight of the composition.

2. Cosmetic composition according to claim 1, wherein said at least one pigment is selected from among iron oxides and titanium dioxide, and any of the mixtures thereof.

3. Cosmetic composition according to claim 2, comprising the four pigments CI 77491, CI 77492, CI 77499 and CI 77891.

4. Cosmetic composition according to any one of claims 1 to 3, wherein said suspension agent selected from among unmodified smectites is hectorite or bentonite.

5. Cosmetic composition according to any one of claims 1 to 4, wherein the total content of emulsifier(s) is between 2 and 12% by weight relative to the total weight of the composition.

6. Cosmetic composition according to any one of claims 1 to 5, wherein the total content of oily emollient(s) is between 10 and 40% by weight relative to the total weight of the composition.

7. Cosmetic composition according to any one of claims 1 to 6, wherein said at least one oily emollient is selected from among C12-C15 alkyl benzoate, caprylic/capric triglycerides, dicaprylyl carbonate, coco-caprylate, coco-caprylate/caprate, diisopropyl sebacate, diethylhexyl succinate, isopropyl

palmitate, isopropyl myristate, propylheptyl caprylate, phenethyl benzoate, dibutyl adipate, diisopropyl adipate, glyceryl tri-2-ethylhexanoate, pentaerythrityl tetra-2-ethylhexanoate, cetyl 2-ethylhexanoate, isononyl isonanoate, neopentyl glycol diheptanoate, diethylhexyl succinate, butylene glycol dicaprylate/dicaprate, octyldodecanol, propylene glycol dicaprylate/dicaprate, and dicaprylyl ether, and any of the mixtures thereof.

8. Cosmetic composition according to any one of claims 1 to 7, comprising at least one additional sunscreen, preferably at least one liposoluble organic sunscreen selected from among diethylamino hydroxybenzoyl hexyl benzoate, bis-ethylhexyloxyphenol methoxyphenyl triazine, diethylhexyl butamido triazone, ethylhexyl triazone, butyl methoxydibenzoylmethane, or any of the mixtures thereof.

9. Cosmetic composition according to claim 8, comprising the additional sunscreens:

- diethylamino hydroxybenzoyl hexyl benzoate,
- bis-ethylhexyloxyphenol methoxyphenyl triazine, and
- ethylhexyl triazone or diethylhexyl butamido triazone.

10. Cosmetic composition according to any one of claims 1 to 9, devoid of ethylhexyl salicylate, octocrylene, ethylhexyl methoxycinnamate, isoamyl methoxylcinnamate, homosalate, para-aminobenzoic acid (PABA), octyl dimethyl PABA, 3-methylbenzylidene-camphor, 4-methylbenzylidene-camphor, benzophenone-3 and/or benzophenone-4.

11. Cosmetic composition according to any one of claims 1 to 10, further comprising between 1 and 15% by weight of texture agent(s) relative to the total weight of the composition.

12. Cosmetic composition according to any one of claims 1 to 11, further comprising a *Lens esculenta* seed extract.

13. Cosmetic composition according to any one of claims 1 to 12, further comprising at least one humectant, preferably at least glycerin, preferably in an amount less than or equal to 5% by weight relative to the total weight of the composition.

14. Cosmetic composition according to any one of claims 1 to 13, devoid of gelling agent or comprising 0.01 to 1% by weight of gelling agent(s) relative to

the total weight of the composition.

15. Cosmetic composition according to any one of claims 1 to 14, in the form of an oil-in-water emulsion.

16. Cosmetic composition according to any one of claims 1 to 15, having a dynamic viscosity at 25°C between 700 and 10000 mPa.s.

17. Cosmetic composition according to any one of claims 1 to 16, for use thereof for sun protection of the skin and/or of the hair of a subject, wherein said composition is applied to said skin and/or hair topically.