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(54) Title: USE OF BENZOPHENONE-4 AND ITS SALTS TO QUENCH THE FLUORESCENCE OF DISODIUM PHENYL DIBENZIMIDAZOLE TETRASULFONATE

(57) Abstract: The present invention relates to cosmetic preparations for protection of the human skin and human hair against the harmful effects of ultraviolet solar radiation containing the water soluble UVA absorbing substance disodium phenyl dibenzimidazole tetrasulfonate [2,2'-(1,4-Phenylene)bis(1H-benzimidazole-4,6-disulfonic acid, monosodium salt); 1H-Benzimidazole-4,6-Disulfonic Acid, 2,2'-(1,4-Phenylene)Bis-, Disodium Salt] together with Benzophenone-4 (2-Hydroxy- 4-methoxybenzophenone-5-sulfonic acid) and its salts to quench the fluorescence of disodium phenyl dibenzimidazole tetrasulfonate.



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Use of Benzophenone-4 and its salts to quench the fluorescence of disodium phenyl dibenzimidazole tetrasulfonate

The present invention relates to cosmetic preparations for protection of the human skin and human hair against the harmful effects of ultraviolet solar radiation containing the water soluble UVA absorbing substance disodium phenyl dibenzimidazole tetrasulfonate [2,2'-(1,4-Phenylene)bis(1H-benzimidazole-4,6-disulfonic acid, monosodium salt); 1H-Benzimidazole-4,6-Disulfonic Acid, 2,2'-(1,4-Phenylene)Bis-, Disodium Salt] together with Benzophenone-4 (2-Hydroxy-4-methoxybenzophenone-5-sulfonic acid) and its salts to quench the fluorescence of disodium phenyl dibenzimidazole tetrasulfonate. In this description and claims, no differentiation is made between disodium phenyl dibenzimidazole tetrasulfonic acid and any salts thereof, unless otherwise indicated. Thus, the terms disodium phenyl dibenzimidazole tetrasulfonate, its salts and disodium phenyl dibenzimidazole tetrasulfonic acid and its salts are used interchangeably unless otherwise indicated.

UV absorbers are compounds which have a pronounced absorption capacity for ultraviolet radiation. They are used in particular as sunscreens in cosmetic and

pharmaceutical preparations, but also to improve the light fastness of industrial products, such as paints, varnishes, plastics, textiles, polymers such as, for example, polymers and copolymers of mono- and diolefins, polystyrenes, polyurethanes, polyamides, polyesters, polyureas and polycarbonates, packaging materials and rubbers.

UV rays are classified according to wavelength as UVA rays (320-400 nm, UVA-I: 340-400 nm, UVA-II: 320-340 nm) or UVB rays (280-320 nm). UV rays can cause acute and chronic damage to the skin, the type of damage depending on the wavelength of the radiation. For instance, UVB radiation can cause sunburn (erythema) extending to most severe burning of the skin; reduction in enzyme activities, weakening of the immune system, disturbances of the DNA structure and changes in the cell membrane are also known as harmful effects of UVB rays. UVA rays penetrate into deeper layers of the skin where they can accelerate the aging process of the skin. The shorter wave UVA-II radiation additionally contributes to the development of sunburn. Moreover, UVA radiation can trigger phototoxic or photoallergic skin reactions. Very frequent and unprotected irradiation of the skin by sunlight leads to a loss of skin elasticity and to increased development of wrinkles. In extreme cases, pathogenic changes in the skin extending to skin cancer are observed. To attenuate these negative effects of UV radiation, materials which absorb or reflect UV light, generally called UV absorbers, are used in cosmetic or pharmacological preparations. The UV absorbers are classified as UVA and UVB absorbers depending on the location of their absorption maxima; if a UV absorber absorbs both UVA and UVB, it is referred to as a UVA/B broadband absorber.

The number of suitable UVA absorbers is very limited and they have considerable deficiencies. Thus, the filter 4-tert.-butyl-4'-methoxy-dibenzoylmethane (Butyl methoxydibenzoylmethane; absorption maximum at 357 nm) that is frequently used in particular for protection against UVA I radiation is not photostable. Photoreactions are also observed in combination with the UVB filters 2-ethylhexyl and isoamyl p-methoxycinnamate. Moreover, it has only a limited solubility in cosmetic oils, which can lead to problems in the formulation of cos-

metic preparations. Furthermore, sunscreen products containing dibenzoyl-methane derivatives can leave marks on textiles that are extremely difficult to wash out.

5 A relatively novel UVA filter that does not have these disadvantages is disodium phenyl dibenzimidazole tetrasulfonate sold under the trade name of Neo Heliopan® AP (e.g. EP 669 323, WO 03/084496; Symrise GmbH & Co. KG, Germany). This very photostable UVA filter harmlessly dissipates its absorbed UV energy via fluorescence/phosphorescence which by a small number of consumers is regarded as a negative. There is therefore a need for agents to quench
10 this fluorescence for use in cosmetic and pharmaceutical preparations. It is known that quenching of fluorescence can occur by a number of mechanisms including self quenching when high concentrations of the substance are present; static quenching which occurs from a complex formed by the ground state of the
15 fluorescor and the quencher; and colour quenching in which coloured molecules absorb the emitted fluorescence energy. Typical quenchers include oxygen, but singlet oxygen is produced as a result and so is undesirable in cosmetics and pharmaceutical preparations; heavy metals such as thallium, or certain organic compounds such as alkyl bromide/fluoride/chlorides, tetrafluoroborates, anthra-
20 cene derivatives, could in principle be used but are toxic and so are of no use in cosmetics and pharmaceutical preparations; and colours, which will give an unacceptable colour to cosmetics and pharmaceutical preparations. Additional possible quenchers are water soluble plant extracts which contain UV and visible light absorbing chromophors such as but not restricted to Green Tea, Rooibos,
25 *Sophora japonica*, or the UV absorbing materials that are found in the plant extracts such as rutin, riboflavins, tannins, nictinamides, quercetin, ubiquinones, polyphenols etc, or their derivatives. However these materials are either unstable in cosmetic preparations on storage or can lead to unacceptable colouration of the preparations.

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The UV absorbing substance Benzophenone-4 (2-Hydroxy-4-methoxybenzophenone-5-sulfonic acid) and its salts absorbs strongly in the UVB wavelength with a lambda maximum of 286 nm and a molar extinction coefficient

of 13400. It also possesses a weak absorbance in the UVA region with a lambda max at 319 nm with a molar extinction coefficient of 8400. The absorbance tails off rapidly at wavelengths above 330 nm. It was therefore not expected that Benzophenone-4 and/or any of its salts, would efficiently quench the fluorescence of disodium phenyl dibenzimidazole tetrasulfonate since it does not absorb strongly in the long UVA and visible ranges of the spectrum. Contrary to this expectation we have surprisingly and unexpectedly found that cosmetic and dermatological preparations containing a mixture of Benzophenone-4 or its salts, and disodium phenyl dibenzimidazole tetrasulfonate does not fluoresce under UV irradiation. Particularly, the sodium salt "Benzophenone-5" of Benzophenone-4 is also effective to quench fluorescence of disodium phenyl dibenzimidazole sulfonic acid and its salts. Thus, the term "benzophenone-4 and its salts" also includes benzophenone-5.

According to the invention, there is thus provided a preparation comprising disodium phenyl dibenzimidazole tetrasulfonic acid and/or one or more salts thereof, further comprising benzophenone-4 and/or one or more salts thereof, in an amount sufficient to reduce the fluorescence of disodium phenyl dibenzimidazole tetrasulfonic acid and, if present, its respective salt(s). Preferably, the preparation is a cosmetic or pharmaceutical, especially dermatological, preparation.

Preferably, the molar ratio of the total of benzophenone-4 and its salts to the total amount of disodium phenyl dibenzimidazole tetrasulfonic acid and its salts is in the range from 0.1 : 5.0 to 5.0 : 0.1, more preferably in the range 0.3 : 3.0 to 3.0 : 0.3 and most preferably in the range 0.4 : 2.0 to 2.0 : 0.5.

In preferred embodiments of the invention, the preparation (particularly a cosmetic and/or pharmaceutical preparation) comprises Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonate and/or one or more salts thereof in combination with one or more further UV absorbers, such that the total fraction of UV absorbers is in the range from 0.1% to 40% by

weight, more preferably in the range from 0.2% to 30% by weight and more preferably in the range 0.5% to 20% by weight, based on the total weight of the preparation.

5 In a further preferred embodiment of the invention, a (cosmetic and/or dermatological/pharmaceutical) preparation comprises a total amount of UV filters and/or inorganic pigments such that the preparation of the invention has a sun protection factor of greater than or equal to 2 (preferably greater than or equal to 5). These sunscreens are suitable for protecting skin and hair.

10 Further suitable photoprotective agents (UV absorbers) are, for example, organic UV absorbers from the class of 4-aminobenzoic acid and derivatives, salicylic acid derivatives, benzophenone derivatives, dibenzoylmethane derivatives, diphenylacrylates, 3-imidazol-4-ylacrylic acid and its esters, benzofuran derivatives, benzylidenemalonate derivatives, polymeric UV absorbers containing one
15 or more organosilicon radicals, cinnamic acid derivatives, camphor derivatives, trianilino-s-triazine derivatives, 2-hydroxyphenylbenzotriazole derivatives, phenyl, menthyl anthranilate, benzotriazole derivatives, indole derivatives.

The UV absorbers specified below, which can be used additionally for the purposes of the present invention, are preferred, but of course are not limiting.

20 Such preferred UV filters are as follows:

UVB filters such as, for example:

- p-aminobenzoic acid
- ethyl p-aminobenzoate (25 mol) ethoxylated
- 2-ethylhexyl p-dimethylaminobenzoate
- 25 • ethyl p-aminobenzoate (2 mol) N-propoxylated

- glycerol p-aminobenzoate
- homomenthyl salicylate (homosalate) (Neo Heliopan[®]HMS)
- 2-ethylhexyl salicylate (Neo Heliopan[®]OS)
- triethanolamine salicylate (Neo Heliopan[®] TS)
- 5 • 4-isopropylbenzyl salicylate
- menthyl anthranilate (Neo Heliopan[®]MA)
- ethyl diisopropylcinnamate
- 2-ethylhexyl p-methoxycinnamate (Neo Heliopan[®]AV)
- methyl diisopropylcinnamate
- 10 • isoamyl p-methoxycinnamate (Neo Heliopan[®]E 1000)
- p-methoxycinnamic acid diethanolamine salt
- isopropyl p-methoxycinnamate
- 3-(4'-trimethylammonium)benzylidenebornan-2-one methyl sulphate
- β -imidazole-4(5)-acrylic acid (urocanic acid)
- 15 • 3-(4'-sulpho)benzylidenebornan-2-one and salts
- 3-(4'-methylbenzylidene)-d,l-camphor (Neo Heliopan[®]MBC)
- 3-benzylidene-d,l-camphor
- N-[(2 and 4)-[2-(oxoborn-3-ylidene)methyl]benzyl]acrylamide polymer
- 4,4'-[(6-[4-(1,1-dimethyl)aminocarbonyl]phenylamino)-1,3,5-triazine-2,4-
20 diyl]diimino]bis(benzoic acid 2-ethylhexyl ester) (Uvasorb[®]HEB)

- benzylidenemalonate-polysiloxane (Parsol[®]SLX)
- glyceryl ethylhexanoate dimethoxycinnamate
- dipropylene glycol salicylate
- tris(2-ethylhexyl) 4,4',4''-(1,3,5-triazine-2,4,6-triyltriimino)tribenzoate
5 (Uvinul[®]T150)
- Benzylidene butyrolactones described in EP 1008593
- Benzylidene- β -dicarbonyl compounds described in WO 2005/107692

Broadband filters such as, for example:

- 10 • 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (Neo Heliopan[®]303)
- ethyl 2-cyano-3,3'-diphenylacrylate
- hydroxy-4-methoxybenzophenone (Benzophenone-3, Oxybenzone) (Neo Heliopan[®] BB)
- disodium 2,2'-dihydroxy-4,4'-dimethoxy-5,5'-disulphobenzophenone
- 15 • phenol, -(2H-benzotriazol-2-yl)-4-methyl-6-(2-methyl-3-(1,3,3,3-tetramethyl-1-(trimethylsilyl)oxy)disiloxyanyl)propyl), (Mexoryl[®]XL)
- 2,2'-methylenebis(6-(2H-benzotriazol-2-yl)-4-1,1,3,3-tetramethylbutyl)-phenol), (Tinosorb[®]M)
- 2,4-bis[4-(2-ethylhexyloxy)-2-hydroxyphenyl]-1,3,5-triazine
- 20 • 2,4-bis[4-(2-ethylhexyloxy)-2-hydroxyphenyl]-6-(4-methoxyphenyl)-1,3,5-triazine, (Tinosorb[®]S)

- 2,4-bis[{{4-(3-sulphonato)-2-hydroxypropyloxy}-2-hydroxy}phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine sodium salt
- 2,4-bis[{{3-(2-propyloxy)-2-hydroxypropyloxy}-2-hydroxy}phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine
- 5 • 2,4-bis[{{4-(2-ethylhexyloxy)-2-hydroxy}phenyl]-6-[4-(2-methoxyethyl-carbonyl)phenylamino]-1,3,5-triazine
- 2,4-bis[{{4-(3-(2-propyloxy)-2-hydroxypropyloxy)-2-hydroxy}phenyl]-6-[4-(2-ethylcarboxyl)phenylamino]-1,3,5-triazine
- 2,4-bis[{{4-(2-ethylhexyloxy)-2-hydroxy}phenyl]-6-(1-methylpyrrol-2-yl)-
10 1,3,5-triazine
- 2,4-bis[{{4-tris(trimethylsiloxysilylpropyloxy)-2-hydroxy}phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine
- 2,4-bis[{{4-(2''-methylpropenyloxy)-2-hydroxy}phenyl]-6-(4-methoxyphenyl)-
1,3,5-triazine
- 15 • 2,4-bis[{{4-(1',1',1',3',5',5',5'-heptamethylsiloxy-2''-methylpropyloxy)-2-hydroxy}phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine.

UVA filters such as, for example:

- terephthalylidenedibornanesulphonic acid and salts (Mexoryl[®]SX)
- 20 • 4-t-butyl-4'-methoxydibenzoylmethane (avobenzone) (Neo Heliopan[®]357)
- hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate (Uvinul[®] A Plus)
- 4-isopropylidibenzoylmethane
- menthyl anthranilate (Neo Heliopan[®]MA)

- indanylidene compounds as described in DE 100 55 940 (= WO 02/38537).
- Benzoylcinnamyl nitriles described in WO 2006/015954

UV absorbers particularly suitable for combination are as follows:

- 5 • p-aminobenzoic acid
- 3-(4'-trimethylammonium)benzylidenebornan-2-one methyl sulphate
- homomenthyl salicylate (Neo Heliopan[®]HMS)
- terephthalylidenedibornanesulphonic acid and salts (Mexoryl[®]SX)
- 4-tert-butyl-4'-methoxydibenzoylmethane (Neo Heliopan[®]357)
- 10 • 3-(4'-sulpho)benzylidenebornan-2-one and salts
- 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (Neo Heliopan[®]303)
- N-[(2 and 4)-[2-(oxoborn-3-ylidene)methyl]benzyl]acrylamide polymer
- 2-ethylhexyl p-methoxycinnamate (Neo Heliopan[®]AV)
- ethyl p-aminobenzoate (25 mol) ethoxylated
- 15 • isoamyl p-methoxycinnamate (Neo Heliopan[®]E1000)
- 2,4,6-trianilino(p-carbo-2'-ethylhexyl-1'-oxy)-1,3,5-triazine (Uvinul[®]T150)
- phenol,2-(2H-benzotriazol-2-yl)-4-methyl-6-(2-methyl-3(1,3,3,3-tetramethyl-1-(trimethylsilyl)oxy)disiloxyanyl)propyl), (Mexoryl[®]XL)
- 4,4'-[(6-[4-(1,1-dimethyl)aminocarbonyl]phenylamino)-1,3,5-triazin-2,4-diyl]-
20 diimino]bis(benzoic acid 2-ethylhexyl ester), (Uvasorb[®] HEB)

- 3-(4'-methylbenzylidene)-d,l-camphor (Neo Helipan[®]MBC)
- 3-benzylidenecamphor
- 2-ethylhexyl salicylate (Neo Helipan[®]OS)
- 2-ethylhexyl 4-dimethylaminobenzoate (Padimate O)
- 5 • 2-hydroxy-4-methoxybenzophenone (Benzophenone-3, Oxybenzone) (Neo Heliopan[®] BB)
- 2,2'-methylenebis(6-(2H-benzotriazol-2-yl)-4-1,1,3,3-tetramethylbutyl)-phenol), (Tinosorb[®]M)
- 2,4-bis[4-(2-ethylhexyloxy)-2-hydroxyphenyl]-6-(4-methoxyphenyl)-1,3,5-
10 triazine, (Tinosorb[®]S)
- benzylidenemalonate-polysiloxane (Parsol[®]SLX)
- menthyl anthranilate (Neo Heliopan[®]MA)
- hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate (Uvinul[®] A Plus)
- indanylidene compounds as described in DE 100 55 940 (= WO 02/38537).
- 15 • Benzoylcinnamyl nitriles described in WO 2006/015954
- Benzylidene butyrolactones described in EP 1008593
- Benzylidene- β -dicarbonyl compounds described in WO 2005/107692

20 It is possible, furthermore, to use particulate UV filters or inorganic pigments, which if desired may have been rendered hydrophobic, such as the oxides of titanium (TiO₂), of zinc (ZnO), of iron (Fe₂O₃), of zirconium (ZrO₂), of silicon

(SiO₂), of manganese (z.B. MnO), of aluminium (Al₂O₃), of cerium (e.g. Ce₂O₃) and/or mixtures.

The total amount of all sulfonated water soluble UV filters in the cosmetic or dermatological formulation, for example but not limited to, phenylbenzimidazole sulfonic acid alone or in combination with Disodium Phenyl Dibenzimidazole Tetrasulphonic Acid and Benzophenone-4, and/or terephthalylidenedibornane-sulphonic and/or 3-(4'-trimethylammonium)benzylidenebornan-2-one methyl sulphate, and/or 3-(4'-sulpho)benzylidenebornan-2-one, and their salts are in the range of 0.1 to 15.0% and more particularly in the range from 0.5 to 10.0% and most particularly in the range of 1.0 to 8.0% of the total formulation.

The amount of Mexoryl[®] SX and its salts used in the cosmetic or dermatological formulation containing Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonate is in the range of 0.1 to 10.0%, preferably in the range from 0.3 to 8% and most preferably in the range from 0.5 to 5.0% of the total formulation.

The total amount of oil soluble UV filters that may be used in a cosmetic or dermatological formulation containing Benzophenone-4 or its salts, and disodium phenyl dibenzimidazole tetrasulfonate, for example but not limited to (2-ethylhexyl) 4,4',4''-(1,3,5-triazine-2,4,6-triyltriimino)tribenzoate and /or -tert-butyl-4'-methoxydibenzoylmethane, and / or 2-ethylhexyl 4-dimethylaminobenzoate, and / or Mexoryl[®]XL and/or Uvasorb[®]HEB and/or Tinosorb[®]S and/or Benzophenone-3 and/or Parsol[®]SLX and/or Neo Heliopan[®]MA, and /or isoamyl p-methoxycinnamate, and/or 2-ethylhexyl salicylate, and/or homosalate, and/or ethylhexyl methoxycinnamate, and/or octocrylene, and/or Uvinul[®] A Plus, and/or 3-(4'-methylbenzylidene)-d,l-camphor, is in the range of 0.1 to 30 wt.-%, particularly in the range of 0.5 to 25%, most particularly in the range of 1 to 20% of the total formulation.

The amount of Ethylhexyl methoxycinnamate used in the cosmetic or dermatological formulation Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonate is in the range of 0.1 to 20.0%, preferably in the range from 0.3 to 15% and most preferably in the range from 0.5 to 10.0% of the total formulation.

The amount of Isoamyl p-methoxycinnamate used in the cosmetic or dermatological formulation containing Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonate is in the range of 0.1 to 20.0%, preferably in the range from 0.3 to 15% and most preferably in the range from 0.5 to 10.0% of the total formulation.

The amount of Octocrylene used in the cosmetic or dermatological formulation containing Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonate is in the range of 0.1 to 20.0%, preferably in the range from 0.3 to 15% and most preferably in the range from 0.5 to 10.0% of the total formulation.

The amount of salicylate esters used in the cosmetic or dermatological formulation containing Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonate is in the range of 0.1 to 20.0%, preferably in the range from 0.3 to 15% and most preferably in the range from 0.5 to 10.0% of the total formulation. When Ethylhexyl salicylate is chosen as the UV filter, it is advantageous that its total amount ranges from 0.1 to 5.0% of the formulation and when Homosalate is chosen as the UV filter it is advantageous that its total amount ranges from 0.1 to 15.0% of the formulation

The amount of Butyl methoxydibenzoylmethane used in the cosmetic or dermatological formulation containing Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonate is in the range of 0.1 to 10.0%, preferably in the range from 0.3 to 7.0% and most preferably in the range from
5 0.5 to 5.0% of the total formulation.

The amount of Uvinul[®] A Plus used in the cosmetic or dermatological formulation containing Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonate is in the range of 0.1 to 10.0%, preferably in the range
10 from 0.3 to 7.0% and most preferably in the range from 0.5 to 5.0% of the total formulation.

The amount of Tinosorb[®] S used in the cosmetic or dermatological formulation containing Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonate is in the range of 0.1 to 10.0%, preferably in the range
15 from 0.3 to 7.0% and most preferably in the range from 0.5 to 5.0% of the total formulation.

The amount of Uvasorb[®] HEB used in the cosmetic or dermatological formulation containing Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonate is in the range of 0.1 to 10.0%, preferably in the range
20 from 0.3 to 7.0% and most preferably in the range from 0.5 to 5.0% of the total formulation.

The amount of Uvinul[®] T-150 used in the cosmetic or dermatological formulation containing Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonate is in the range of 0.1 to 10.0%, preferably in the range
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from 0.3 to 7.0% and most preferably in the range from 0.5 to 5.0% of the total formulation.

The total amount of oil microfine organic and/or inorganic pigments, for example
5 but not limited to triazine derivatives and/or Zinc Oxide (coated and un-coated),
and/or titanium dioxide (coated or un-coated) that may be used in a cosmetic or
dermatological formulation containing Benzophenone-4 and/or any of its salts
and disodium phenyl dibenzimidazole tetrasulfonate is in the range of 0.1 to
20.0%, preferably in the range from 0.3 to 15% and more preferably in the range
10 from 0.5 to 10.0% and most preferably in the range from 0.75% to 7.5%. When
titanium dioxide is chosen as the UV filter, it is advantageous that its total amount
ranges from 0.1% to 10.0% of the formulation. When Zinc Oxide is chosen as the
UV filter it is advantageous that its total amount ranges from 0.1% to 10.0% of
the formulation and when one or more triazine organic pigment(s) are chosen it is
15 advantageous that its total amount ranges from 0.1% to 10.0% of the formulation.

Combining Benzophenone-4 or its salts and disodium phenyl dibenzimidazole
tetrasulfonic acid or one or more of its salts with other UV filters, for example with
the UV filters listed above and particularly with the UV filters listed as "particularly
20 suitable for combination", but not limited to these, leads to synergistic effects in
the degree of protection offered against UVB and UVA radiation as determined
by measurements to determine sun protection factors against UVA and / or UVB
radiation.

The invention thus also provides the teaching that combining (a) Benzophenone-
25 4 or any of its salts and (b) disodium phenyl dibenzimidazole tetrasulfonic acid or
any of its salts with individual or any desired mixtures of any of the UV filters
listed above as well as any from the allowed UV filters for use in sun protection
products legislated in :

- USA: by the Food and Drug Administration (FDA).published in the Monograph for Sunscreen Drug Products for Over-The-Counter Human Use.
- 5 Europe: by the Cosmetics Directive 76/768 EEC of the Council of European Communities published in the in the Official Journal of the European Communities.
- 10 Japan: in the positive list of allowed UV filters in the publication of the cosmetic criteria by the Ministry of Health and Welfare (MHW).
- Australia: in the positive list of allowed UV filters published by the Australian Therapeutic Goods Administration in the Australian Register of Therapeutic Goods (ARTG).

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will lead to synergistic protective effects against UVA and/or UVB radiation.

Particularly in cosmetic and dermatological preparations, benzophenone-4 absorbs UV radiation, when it is used in combination with disodium phenyl dibenzimidazole tetrasulfonate it also leads to photostabilisation of UV absorbers of lower stability to UV such as derivatives of butyl methoxydibenzoylmethane. In particular, benzophenone-4 and its salts together with disodium phenyl dibenzimidazole tetrasulfonate or its acid form give rise to stabilisation of the UVA absorber 4-tert.-butyl-4'-methoxydibenzoylmethane, which is highly unstable to light.

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It is furthermore advantageous to add to this three-compound combination one or more highly photostable UV absorbers, such as, for example, methylbenzylidene-camphor, 2-ethylhexyl-2-cyano-3,3'-diphenylacrylate, octyltriazone, Uvasorb[®]HEB, Tinosorb[®]S, Tinosorb[®]M, ethylhexyl salicylate, homomenthyl salicylate, phenylenbenzimidazolesulphonic acid, Uvinul A Plus, Mexoryl[®]SX, Mexoryl[®]XL, Parsol[®]SLX or indanylidene compounds as described in DE 100 55 940 and/or WO 02/38537, or Benzoylcinnamyl nitriles as described in WO 2006/015954, or Benzylidene butyrolactones as described in EP 1008593, or Benzylidene- β -dicarbonyl compounds as described in WO 2005/107692.

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It is furthermore advantageous to add, alone or in addition to the UV filters listed above, the photostabilising emollient 2,6-Diethylhexyl Naphthalate sold under the trade name of Corapan[®] TQ by Symrise to improve the photostability of Butyl methoxydibenzoylmethane.

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The combination of Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonic acid and/or any of its salts together with UVA absorbers, especially UVA-I absorbers, provides comprehensive protection against UVA radiation (320-400 nm). A combination of Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonic acid and/or any of its salts together with butyl methoxydibenzoylmethane, or Tinosorb S or indanylidene derivatives or Benzoylcinnamyl nitriles (UVA-I absorbers) is to be mentioned in particular for broad UV protection. Further UVA filters that are preferred to be used in combination with both of Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonic acid and/or any of its salts, on their own or in combination, are Mexoryl SX, Mexoryl[®]XL, Tinosorb[®]M, Tinosorb[®]S, Benzophenone-3, Uvinul[®] A Plus, Neo Heliopan[®]357 and Neo Heliopan[®]MA.

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The abovementioned combinations can be combined with all UVB filters and mixtures of these filters (cf. the above mentioned particularly suitable UV (sic) absorbers) for optimum broadband protection against UVA and UVB radiation. Neo Heliopan[®]AV, Neo Heliopan[®]E1000, Neo Heliopan[®]Hydro, Neo Heliopan[®]MBC, Neo Heliopan[®]303, Neo Heliopan[®]OS, Neo Heliopan[®]HMS, Uvinul[®]T150, Uvasorb[®]HEB, Parsol[®]SLX are particularly suitable UVB filters.

Synergies of both of Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonate together with other constituents that do not absorb UV light, with regard to an improved protection against UV light, are to be expected.

Cosmetic and dermatological preparations in the sense of this invention contain one or more conventional UVA, UVB and/or broadband filters as single substances or in arbitrary mixtures with one another in the lipid phase and/or in the aqueous phase. They are satisfactory products in every respect which, surprisingly are distinguished by high UVA protection and a high UVB protection factor.

It is highly disadvantageous if UV absorbers leave marks on articles of clothing that can no longer be washed out. In particular, the UVA absorber tert.-butyl-methoxydibenzoylmethane is known to produce marks on textiles that can no longer be washed out. The use of a of Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonate according to the invention do not have this disadvantage since any marks formed on textiles can be washed out very readily.

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The (cosmetic and/or pharmaceutical/dermatological) preparations according to the invention can be formulated in the customary manner and serve as cosmetic

and/or dermatological sunscreens and also for the treatment, care and cleansing of the skin and/or the hair and as a make-up product in decorative cosmetics.

5 These cosmetic and pharmaceutical preparations serving for protection of skin and hair against UV radiation can be in the use forms conventionally used, i.e. in the form of oil-in-water, water-in-oil or mixed emulsion, in the form of milk, in the form of lotion or cream, aerosol, hydrodispersion gel or oil gel (emulsifier-free), spray, foam, solution, powder, pencil preparation or in the form of any other customary cosmetic or pharmaceutical formulation. Preparations such as sham-
10 poo, rinse, conditioner, gel, lotion, spray or cream are preferably used for protection of the hair against UV rays.

The (cosmetic and/or pharmaceutical/dermatological) preparations according to the present invention can have the customary composition and can be used for
15 cosmetic and/or dermatological sun protection, and also for the treatment, care and cleansing of the skin and/or of the hair and as a make-up product in decorative cosmetics. Accordingly, the preparations according to the present invention can, depending on their formulation, be used, for example, as skin protection cream, cleansing milk, sunscreen lotion, nourishing cream, day cream or night
20 cream. The preparations according to the present invention can, depending on their formulation, also be used for example, in hair care compositions such as shampoos, conditioners, 2 in 1 preparations, anti-dandruff shampoos, hair tonics, hair lotions, hair rinses, styling products, sprays, etc. In some instances, it is possible and advantageous to use the preparations according to the present
25 invention as bases for pharmaceutical preparations. Preference is given, in particular, to those cosmetic and dermatological preparations in the form of a skin care, hair care or make-up product. Typical embodiments are creams, gels e.g. but not limited to hydrogels, hydrodispersion gels, oil gels; lotions, alcoholic and aqueous/alcoholic solutions, emulsions in their various forms for example but not
30 limited to oil in water (O/W), water in oil (W/O), mixed emulsions, PIT emulsions,

Pickering emulsions, microemulsions, nano-emulsions; aerosol foams, non-aerosol foams, aerosols sprays, non-aerosol sprays, pump sprays, serums, roll-ons, pastes, balsams, or stick preparations. These compositions may also comprise, as further auxiliaries and additives, mild surfactants, co-emulsifiers, super-
5 fattening agents, pearlescent waxes, bodying agents, thickeners, polymers, silicone compounds, fats, waxes, stabilizers, biogenic active ingredients, deodorant active ingredients, antidandruff agents, film formers, swelling agents, hydrotropic agents, preservatives, insect repellants, tanning agents, artificial self-tanning agents (e.g. dihydroxyacetone), stabilizers, perfume oils, dyes, antimicrobial
10 agents, aqueous and non-aqueous plant extracts and the like.

For use, the cosmetic and dermatological preparations according to the present invention are applied to the skin and/or the hair in a sufficient amount in the manner customary for cosmetics or pharmacological and dermatological preparations.

15 More preference is given to those cosmetic and dermatological preparations in the form of a cosmetic composition for the protection of the skin and hair. Advantageously, in addition to Benzophenone-4 and/or any of its salts and disodium phenyl dibenzimidazole tetrasulfonate used according to the present invention, these can contain at least one inorganic pigment, preferably an inorganic mi-
20 cropigment. Those cosmetic and dermatological preparations that are in the form of a skin care or make-up product are particularly preferred.

The cosmetic and dermatological preparations according to the present invention can comprise cosmetic auxiliaries, as are customarily used in such preparations,
25 e.g. preservatives, bactericides, perfumes, antifoams, dyes, pigments which have a coloring action, thickeners, moisturizers and/or humectants, fats, oils, waxes or other customary constituents of a cosmetic or dermatological formulation, such as alcohols, polyols, polymers, foam stabilizers, electrolytes, organic solvents or silicone derivatives. The amounts of cosmetic or dermatological auxiliaries and
30 carrier substances and perfume which can be used in each case can be deter-

mined easily by the person skilled in the art by simple trial and error, depending on the nature of the product in question.

Preferred embodiments of the cosmetic and/or pharmaceutical, especially dermatological preparations of the invention may also comprise anionic, cationic, 5 nonionic and/or amphoteric surfactants. Surfactants are amphiphilic substances which can dissolve organic, nonpolar substances in water. In this context, the hydrophilic components of a surfactant molecule are usually polar functional groups, for example $-\text{COO}^-$, $-\text{OSO}_3^{2-}$, $-\text{SO}_3^-$, while the hydrophobic parts as a rule are nonpolar hydrocarbon radicals. Surfactants are in general classified according to the nature and charge of the hydrophilic molecular moiety. A distinction 10 can be made between four groups here:

- anionic surfactants,
- cationic surfactants,
- amphoteric surfactants and
- 15 • nonionic surfactants.

Anionic surfactants as a rule contain carboxylate, sulphate or sulphonate groups as functional groups. In aqueous solution, they form negatively charged organic ions in an acid or neutral medium. Cationic surfactants are almost exclusively characterized by the presence of a quaternary ammonium group. In aqueous 20 solution, they form positively charged organic ions in an acid or neutral medium. Amphoteric surfactants contain both anionic and cationic groups and accordingly behave like anionic or cationic surfactants in aqueous solution, depending on the pH. In a strongly acid medium they have a positive charge, and in an alkaline medium a negative charge. On the other hand, they are zwitterionic in the neutral 25 pH range. Polyether chains are typical of nonionic surfactants. Nonionic surfactants do not form ions in an aqueous medium.

A. Anionic surfactants

Anionic surfactants which are advantageously used are acylamino acids (and salts thereof), such as:

- acyl glutamates, for example sodium acyl glutamate, di-TEA-palmitoyl aspartate and sodium caprylic/capric glutamate,
- 5 - acyl peptides, for example palmitoyl hydrolysed milk protein, sodium cocoyl hydrolysed soya protein and sodium/potassium cocoyl hydrolysed collagen,
- sarcosinates, for example myristoyl sarcosine, TEA-lauroyl sarcosinate, sodium lauroyl sarcosinate and sodium cocoyl sarcosinate,
- taurates, for example sodium lauroyl taurate and sodium methylcocoyl
10 taurate,
- acyl lactylates, lauroyl lactylate, caproyl lactylate
- alaninates

carboxylic acids and derivatives, such as for example:

- TEA stearate, Glyceryl stearates, PEG glyceryl stearates
- 15 lauric acid, aluminium stearate, magnesium alkanolate and zinc undecylate,

ester-carboxylic acids, for example calcium stearoyl lactylate, laureth-6 citrate and sodium PEG-4 lauramide carboxylate, glyceryl stearates, glyceryl-oleylstearates, glyceryl citrates, glyceryl oleyl citrates,
- 20 - ether-carboxylic acids, for example sodium laureth-13 carboxylate and sodium PEG-6 cocamide carboxylate,

Glucoside esters, such as for example

- cetearyl glucoside, lauryl glucoside

phosphoric acid esters and salts, such as, for example :

- cetyl phosphate (mono, di cetyl and their mixtures), Potassium cetyl phosphate, (mono, di cetyl and their mixtures), DEA cetyl phosphate (mono, di cetyl and their mixtures), DEA -oleth-10 phosphate and dilaureth-4 phosphate,

5 sulphonic acids and salts, such as

- acyl isethionates, e.g. sodium/ammonium cocoyl isethionate,
 - alkylarylsulphonates,
 - alkylsulphonates, for example sodium coco-monoglyceride sulphate, sodium C12-14 olefinsulphonate, sodium lauryl sulphoacetate and magnesium PEG-3 cocamide sulphate,
- 10
- sulphosuccinates, for example dioctyl sodium sulphosuccinate, disodium laureth-sulphosuccinate, disodium laurylsulphosuccinate and disodium undecylenamido-MEA-sulphosuccinate

15 and

sulphuric acid esters, such as:

- alkyl ether sulphate, for example sodium, ammonium, magnesium, MIPA, TIPA laureth sulphate, sodium myreth sulphate and sodium C12-13 pareth sulphate,
- 20
- alkyl sulphates, for example sodium, ammonium and TEA lauryl sulphate.

B. Cationic surfactants

Cationic surfactants which are advantageously used are

- alkylamines,

- alkylimidazoles,
- ethoxylated amines,
- quaternary surfactants,
- $\text{RNH}_2\text{CH}_2\text{CH}_2\text{COO}^-$ (at pH=7)
- 5 - $\text{RNHCH}_2\text{CH}_2\text{COO}^- \text{B}^+$ (at pH=12) B^+ = any desired cation, e.g. Na^+ and
- ester quats.

Quaternary surfactants contain at least one N atom which is covalently bonded to 4 alkyl or aryl groups. This leads to a positive charge, independently of the pH. Alkylbetaine, alkylamidopropylbetaine and alkylamidopropylhydroxysulphaine are advantageous. The cationic surfactants used can further preferably be chosen from the group consisting of quaternary ammonium compounds, in particular benzyltrialkylammonium chlorides or bromides, such as, for example, benzyltrimethylstearyl ammonium chloride, and also alkyltrialkylammonium salts, for example cetyltrimethylammonium chloride or bromide, alkyldimethylhydroxyethylammonium chlorides or bromides, dialkyldimethylammonium chlorides or bromides, alkylamideethyltrimethylammonium ether sulphates, alkylpyridinium salts, for example lauryl- or cetylpyridinium chloride, imidazoline derivatives and compounds having a cationic character, such as amine oxides, for example alkyldimethylamine oxides or alkylaminoethyldimethylamine oxides.

20 Cetyltrimethyl-ammonium salts in particular are advantageously used.

C. Amphoteric surfactants

Amphoteric surfactants which are advantageously to be used are

- acyl/dialkylethylenediamine, for example sodium acylamphoacetate, disodium acylamphodipropionate, disodium alkylamphodiacetate, sodium acylamphohydroxypropylsulphonate, disodium acylamphodiacetate and sodium acylamphopropionate,
- 25

- N-alkylamino acids, for example aminopropyl alkylglutamide, alkylaminopropionic acid, sodium alkylimidodipropionate and lauroamphocarboxyglycinate.
- acylamphohydroxypropylsulphonate, disodium acylamphodiacetate and sodium acylamphopropionate,
- N-alkylamino acids, for example aminopropyl alkylglutamide, alkylaminopropionic acid, sodium alkylimidodipropionate and lauroamphocarboxyglycinate.

10 D. Nonionic surfactants

Nonionic surfactants which are advantageously used are

- alcohols,
- alkanolamides, such as cocamides MEA/DEA/MIPA,
- amine oxides, such as cocoamidopropylamine oxide,
- ethers, for example ethoxylated/propoxylated alcohols, ethoxylated/propoxylated esters, ethoxylated/propoxylated glycerol esters, ethoxylated/propoxylated cholesterols, ethoxylated/propoxylated triglyceride esters, ethoxylated/propoxylated lanolin, ethoxylated/propoxylated polysiloxanes, propoxylated POE ethers and alkyl polyglycosides, such as lauryl glucoside, decyl glucoside and coco-glycoside.
- sucrose esters, sucrose ethers
- polyglycerol esters, diglycerol esters, monoglycerol esters polyglyceryl-2 dipolyhydroxystearate (Dehymuls[®]PGPH), polyglyceryl-3 diisostearate (Lameform[®]TGI), polyglyceryl-4 isostearate (Isolan[®]GI 34), polyglyceryl-3 oleate, diisostearyl polyglyceryl-3 diisostearate (Isolan[®]PDI), polyglyceryl-3 methylglucose distearate (Tego Carey[®]450), polyglyceryl-3 beeswax (Cera Bellina[®]), polyglyceryl-4 caprate (polyglycerol caprate T2010/90), polyglyceryl-3 cetyl ether (Chimexane[®]NL), polyglyceryl-3 distearate (Cremo-

phor[®]GS 32), polyglyceryl-2 stearate (Hostacerin[®]DGMS) and polyglyceryl polyricineoleate (Admul[®]WOL 1403), and mixtures thereof.

- methylglucose esters, esters of hydroxy acids

- 5 The use of a combination of anionic and/or amphoteric surfactants with one or more nonionic surfactants is further advantageous.

In addition, cosmetic and dermatological preparations according to the present invention advantageously, but not obligatorily, comprise inorganic pigments based on finely disperse metal oxides and/or other metal compounds which are
10 insoluble or sparingly soluble in water, in particular the oxides of titanium (TiO₂), zinc (ZnO), iron (e.g. Fe₂O₃), zirconium (ZrO₂), silicon (SiO₂), manganese (e.g. MnO), aluminum (Al₂O₃), cerium (e.g. Ce₂O₃), mixed oxides of the corresponding metals, and mixtures of such oxides. These pigments are X-ray-amorphous or non-X-ray-amorphous. More preference is given to pigments based on TiO₂.
15 X-ray-amorphous oxide pigments are metal oxides or semi-metal oxides which reveal no or no recognizable crystalline structure in X-ray diffraction experiments. Such pigments are often obtainable by flame reaction, for example by reacting a metal or semi-metal halide with hydrogen and air (or pure oxygen) in a flame.

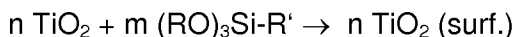
In cosmetic, dermatological or pharmaceutical preparations, X-ray-amorphous
20 oxide pigments are used as thickeners and thixotropic agents, flow auxiliaries for emulsion and dispersion stabilization and as carrier substance (for example for increasing the volume of finely divided powders). X-ray-amorphous oxide pigments which are known and often used in cosmetic or dermatological galenics are, for example, high-purity silicon oxide. Preference is given to high-purity, X-
25 ray-amorphous silicon dioxide pigments with a particle size in the range from 5 to 40 nm and an active surface area (BET) in the range from 50 to 400 m²/g, preferably 150 to 300 m²/g, where the particles are to be regarded as spherical particles of very uniform dimension. Macroscopically, the silicon dioxide pigments are recognizable as loose, white powders. Silicon dioxide pigments are sold com-

mercially under the name Aerosil® (CAS-No. 7631-85-9) or Carb-O-Sil

Advantageous Aerosil® grades are, for example, Aerosil®0X50, Aerosil®130, Aerosil®150, Aerosil®200, Aerosil®300, Aerosil®380, Aerosil®MQX 80, Aerosil®MOX 170, Aerosil®COK 84, Aerosil® R 202, Aerosil®R 805, Aerosil®R 812,
5 Aerosil®R 972, Aerosil®R 974, Aerosil®R976.

According to the present invention, cosmetic or dermatological light protection preparations comprise 0.1 to 20% by weight, advantageously 0.5 to 10% by weight, more preferably 1 to 5% by weight, of X-ray-amorphous oxide pigments.

The non-X-ray-amorphous inorganic pigments are, according to the present
10 invention, advantageously in hydrophobic form, i.e. have been surface-treated to repel water. This surface treatment may involve providing the pigments with a thin hydrophobic layer by processes known per se. Such a process involves, for example, producing the hydrophobic surface layer by a reaction according to



15 where n and m are stoichiometric parameters to be used as desired, and R and R' are the desired organic radicals. Hydrophobicized pigments prepared analogously to DE-A 33 14 742, for example, are advantageous.

For example, mention may be made of TiO₂ pigments, as are sold under the trade name T805 from Degussa. Preference is also given to TiO₂/Fe₂O₃ mixed
20 oxides, as are supplied, for example, under the trade name T817, also from Degussa.

The total amount of inorganic pigments, in particular hydrophobic inorganic micro-pigments, in the finished cosmetic or dermatological preparations is advantageously chosen from the range from 0.1 to 30% by weight, preferably 0.1 to
25 10.0% by weight, preferably 0.5 to 6.0% by weight, based on the total weight of the preparations.

An additional content of skin lightening ingredients in the cosmetic or dermatological preparation is optional. Such skin lightening ingredients which can be used are for example but not limited to the following : kojic acid (5-hydroxy-2-hydroxymethyl-4-pyranone), kojic acid derivatives such as for example kojic dipalmitate, arbutin, ascorbic acid, ascorbic acid derivatives, hydroquinone, hydroquinone derivatives, styryl resorcinol derivatives (e.g. 4-(1-phenylethyl)1,3-benzenediol), molecules containing sulphur, such as glutathione or cysteine for example, alpha-hydroxy acids (e.g. citric acid, lactic acid, malic acid) and their derivatives, N-acetyltirosine and derivatives, undecenoylphenylalanine, gluconic acid, chromone derivatives such as aloesin, flavonoids, thymol derivatives, 1-aminoethylphosphinic acid, thiourea derivatives, ellagic acid, nicotinamide, zinc salts such as zinc chloride or zinc gluconate for example, thujaplicin and derivatives, triterpenes such as maslic acid, sterols such as ergosterol, benzofuranones such as senkyunolide, vinyl- and ethylguaiacol, dionic acids such as octodecenedionic acid and azelaic acid, nitrogen oxide synthesis inhibitors such as L-nitroarginine and its derivatives, 2,7-dinitroindazole or thiocitrulline, metal chelators (e.g. alpha-hydroxy fatty acids, palmitic acid, phytic acid, lactoferrin, humic acid, gallic acid, bile extracts, bilirubin, biliverdin), retinoids, soja milk, soya extract, serine protease inhibitors or lipoic acid or other synthetic or natural active compounds for skin and hair lightening, these compounds also being used in the form of an extract from plants, such as bearberry extract, rice extract, papaya extract, liquorice root extract or constituents concentrated from these, such as glabridin or licochalcone A, Artocarpus extract, extract from Rumex and Ramulus species, extracts from pine species (Pinus) and extracts from Vitis species or stilbene derivatives concentrated from these, extract from saxifraga, mulberry, Scutellaria and/or grapes.

An additional content of antioxidants in the cosmetic or dermatological preparation is generally preferred. According to the present invention, favorable antioxidants which can be used are all antioxidants customary or suitable for cosmetic and/or dermatological applications.

The antioxidants are advantageously chosen from the group of amino acids (e.g.

glycine, histidine, tyrosine, tryptophan) and derivatives thereof, imidazoles (e.g. urocanic acid) and derivatives thereof, peptides, such as D,L-carnosine, D-carnosine, L-carnosine and derivatives thereof (e.g. anserine), carotenoids, carotenes (e.g. α -carotene, β -carotene, lycopene) and derivatives thereof, 5 chlorogenic acid and derivatives thereof, lipoic acid and derivatives thereof (e.g. dihydrolipoic acid), aurothioglucose, propylthiouracil and other thiols (e.g. thioredoxin, glutathione, cysteine, cystine, cystamine and the glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl and lauryl, palmitoyl, oleyl, γ -linoleyl, cholesteryl and glyceryl esters thereof) and salts thereof, dilauryl thiodipropionate, distearyl 10 thiodipropionate, thiodipropionic acid and derivatives thereof (esters, ethers, peptides, lipids, nucleotides, nucleosides and salts), and sulfoximine compounds (e.g. buthionine sulfoximines, homocysteine sulfoximine, buthionine sulfones, penta-, hexa-, heptathionine sulfoximine) in very low tolerated doses (e.g. pmol to μ mol/kg), and also (metal) chelating agents (e.g. α -hydroxy fatty acids, palmitic 15 acid, phytic acid, lactoferrin), α -hydroxy acids (e.g. citric acid, lactic acid, maleic acid), humic acid, bile acid, bile extracts, bilirubin, biliverdin, EDTA, EGTA and derivatives thereof, unsaturated fatty acids and derivatives thereof (e.g. γ -linolenic acid, linoleic acid, oleic acid), folic acid and derivatives thereof, ubiquinone and ubiquinol and derivatives thereof, vitamin C and derivatives (e.g. 20 ascorbyl palmitate, Mg ascorbyl phosphate, ascorbyl acetate), tocopherols and derivatives (e.g. vitamin E acetate), vitamin A and derivatives (vitamin A palmitate), and coniferyl benzoate of benzoin resin, rutinic acid and derivatives thereof, α -glycosylrutin, ferulic acid, furfurylidene-glucitol, carnosine, butylhydroxy-toluene, butylhydroxyanisol, nordihydroguaiacic acid, nordihydroguaiaretic acid, trihydroxybutyrophenone, uric acid and derivatives thereof, mannose and derivatives 25 thereof, zinc and derivatives thereof (e.g. ZnO, ZnSO₄), selenium and derivatives thereof (e.g. selenomethionine), stilbenes and derivatives thereof (e.g. stilbene oxide, trans-stilbene oxide) and the derivatives (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids) of the active ingredients suitable 30 according to the present invention.

The amount of the above-mentioned antioxidants (one or more compounds) in the preparations is preferably 0.001 to 30% by weight, more preferably 0.05 to

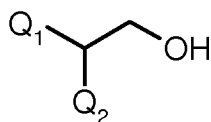
20% by weight, and most preferably 1 to 10% by weight, based on the total weight of the preparation.

Preferred embodiments of the cosmetic and/or pharmaceutical, especially dermatologically active preparations of the invention may advantageously also comprise vitamins and vitamin precursors, it being possible for all the vitamins and vitamin precursors which are suitable or usual for cosmetic and/or dermatological applications to be used. Those worth mentioning here are, in particular, vitamins and vitamin precursors, such as tocopherols, vitamin A, niacin acid and niacinamide, further vitamins of the B complex, in particular biotin, and vitamin C and panthenol and derivatives thereof, in particular the esters and ethers of panthenol, and cationically derivatized panthenols, such as panthenol triacetate, panthenol monoethyl ether and the monoacetate thereof and cationic panthenol derivatives. If vitamin E and/or derivatives thereof represent the antioxidant(s), it is advantageous to choose their respective concentrations from the range from 0.001 to 10% by weight, based on the total weight of the formulation. If vitamin A or vitamin A derivatives, or carotenes or derivatives thereof represent the antioxidant(s), it is advantageous to choose their respective concentrations from the range from 0.001 to 10% by weight, based on the total weight of the formulation.

Preferred embodiments of the cosmetic and/or pharmaceutical, especially dermatological preparations of the invention may also comprise lipids chosen from the following group of substances:

- (i) linear or branched saturated paraffins (mineral oils) having 15 or more C atoms, in particular having 18 to 45 C atoms;
- (ii) esters having 12 or more C atoms of linear or branched fatty acids having 6 to 30 C atoms and linear or branched, saturated or unsaturated mono-, di- or triols having 3 to 30 C atoms, these esters having no free hydroxyl groups;

- (iii) esters of benzoic acid and linear or branched, saturated or unsaturated monoalkanols having 8 to 20 C atoms;
- (iv) monoesters or diesters of alcohols having 3 to 30 C atoms and naphthalene-monocarboxylic or -dicarboxylic acids; especially naphthalenemonocarboxylic acid C₆-C₁₈ esters and naphthalenedicarboxylic acid di-C₆-C₁₈ esters;
- (v) linear or branched, saturated or unsaturated di-C₆-C₁₈-alkyl ethers;
- (vi) silicone oils;
- (vii) 2-alkyl-1-alkanols of the formula (III)



(III)

where

Q₁ is a linear or branched alkyl radical having 6 to 24 C atoms and

Q₂ is a linear or branched alkyl radical having 4 to 16 C atoms.

An oil phase or oil component in the narrower (and preferred) sense of the present invention, i.e. of the inventively limited substances or substances present only in a minor fraction, encompasses the following groups of substances:

- (i) linear or branched, saturated paraffins having 20 to 32 C atoms;
- (ii) esters having at least 14 C atoms of linear or branched, saturated fatty acids having 8 to 24 C atoms and linear or branched, saturated or unsatu-

rated mono-, di- or triols having 3 to 24 C atoms, these esters containing no free hydroxyl groups;

- (iii) esters of benzoic acid and linear or branched, saturated monoalkanols having 10 to 18 C atoms;
- 5 (iv) 2,6-naphthalenedicarboxylic acid di-C6-C12 esters;
- (v) linear or branched, saturated di-C6-C18-alkyl ethers, especially (straight-chain) di-C6-C12-alkyl ethers;
- (vi) silicone oils from the group of the cyclotrisiloxanes, cyclopentasiloxanes, dimethylpolysiloxanes, diethylpolysiloxanes, methylphenylpolysiloxanes,
10 diphenylpolysiloxanes and hybrid forms thereof;
- (vii) 2-alkyl-1-alkanols having 12 to 32 C atoms of the formula (III)

where

Q₁ is a (preferably linear) alkyl radical having 6 to 18 C atoms and

Q₂ is a (preferably linear) alkyl radical having 4 to 16 C atoms.

15 An oil phase in the narrowest (and most preferred) sense of the present invention encompasses the following groups of substances:

- (i) linear or branched, saturated paraffins having 20 to 32 C atoms such as isoeicosane or squalane;
- (ii) esters having at least 16 C atoms of linear or branched, saturated fatty
20 acids having 8 to 18 C atoms and linear or branched, saturated mono-, di- or triols having 3 to 18 C atoms, these esters containing no free hydroxyl groups;

- (iii) esters of benzoic acid and linear or branched, saturated monoalkanols having 12 to 15 C atoms, especially C₁₂₋₁₅-alkyl benzoates;
- (iv) 2,6-naphthalenedicarboxylic acid di-C₆-C₁₀ esters, especially diethylhexyl 2,6-naphthalenedicarboxylate;
- 5 (v) straight-chain di-C₆-C₁₀-alkyl ethers; especially di-n-octyl ether (dicaprylyl ether);
- (vi) silicone oils from the group undecamethylcyclotrisiloxane, cyclomethicone, decamethylcyclopentasiloxane, dimethylpolysiloxanes, diethylpolysiloxanes, methylphenylpolysiloxanes and diphenylpolysiloxanes;
- 10 (vii) 2-alkyl-1-alkanols having 12 to 32 C atoms of the formula (III)

where

Q₁ is a (preferably linear) alkyl radical having 6 to 18 C atoms and

Q₂ is a (preferably linear) alkyl radical having 4 to 16 C atoms.

Particularly preferred components of type (i) in the oil phase are as follows: iso-
15 propyl myristate, isopropyl palmitate, isopropyl stearate, isopropyl oleate, n-butyl
stearate, n-hexyl laurate, n-decyl oleate, isooctyl stearate, isononyl stearate,
isononyl isononanoate, 2-ethylhexyl palmitate, 2-ethylhexyl laurate, 2-hexyldecyl
stearate, 2-octyldecyl palmitate, oleyl oleate, oleyl erucate, erucyl oleate,
erucyl erucate, 2-ethylhexyl isostearate, isotridecyl isononanoate, 2-ethylhexyl
20 cocoate, caprylic/capric triglyceride, and also synthetic, semisynthetic and natural
mixtures of such esters, e.g. jojoba oil.

Fatty acid triglycerides (oil components of type (i) in the oil phase) may also be in the form of, or in the form of a constituent of, synthetic, semisynthetic and/or

natural oils, examples being olive oil, sunflower oil, soya oil, peanut oil, rapeseed oil, almond oil, palm oil, coconut oil, palm kernel oil and mixtures thereof.

Particularly preferred oil components of type (vii) in the oil phase are as follows:
2-butyl-1-octanol, 2-hexyl-1-decanol, 2-octyl-1-dodecanol, 2-decyltetradecanol,
5 2-dodecyl-1-hexadecanol and 2-tetradecyl-1-octadecanol.

Particularly preferred oil components in the oil phase are mixtures comprising
C₁₂-C₁₅-alkyl benzoate and 2-ethylhexyl isostearate, mixtures comprising C₁₂-C₁₅-
alkyl benzoate and isotridecyl isononanoate, mixtures comprising C₁₂-C₁₅-alkyl
benzoate, 2-ethylhexyl isostearate and isotridecyl isononanoate, mixtures com-
10 prising cyclomethicone and isotridecyl isononanoate, and mixtures comprising
cyclomethicone and 2-ethylhexyl isostearate.

Preferred embodiments of the cosmetic and/or pharmaceutical, especially der-
matologically active preparations of the invention may advantageously also com-
prise the use of polymers to improve the spreadability of the formulation upon the
15 skin or hair, or improve the water and or sweat and or rub-off resistancy of the
formula and to improve the protection factor of the formulation. Examples of such
polymers are : VP/Eicosene copolymers sold under the trade name of Antaron
V-220 by International Speciality Products, VP/Hexadecene copolymer sold
under the trade names Antaron V-216 and Antaron V-516 by International Speci-
20 ality Products, Tricontanyl PVP sold under the trade name of Antaron WP-660 by
International Speciality Products, Isohexadecane and Ethyl-
ene/Propylene/Styrene copolymer and Butylene/Styrene copolymer sold under
the trade names of Versagel MC and MD by Penreco, Hydrogenated polyisobu-
tene and and Ethylene/Propylene/Styrene copolymer and Butylene/Styrene
25 copolymer sold under the trade mane of Versagel ME by Penreco, Acry-
lates/Octylacrylamide Coploymers sold under the trade name of Dermacryl 79,
Dermacryl AQF and Dermacryl LT by National Starch, Polyurethanes such as
PPG-17/IPDI/DMPA copolymer sold under the trade name of Avalure UR 450 &
525 sold by Noveon, Polyurethanes-2 and -4 sold under the trade names Avalure
30 UR-405, -410, - 425, -430 and – 445 525 sold by Noveon, Polyurethane 5 and

Butyl Acetate and isopropyl alcohol sold under the trade name Avalure UR - 510 and - 525 sold by Noveon, Polyurethanes -1 and - 6 sold under the trade name of Luviset PUR by BASF, Hydrogenated Dimer Dilinoleyl/Dimethylcarbonate Copolymer sold under the trade name of Cosmedia DC by Cognis.

5 Of course, as one well versed in the art of cosmetic and dermatological formulation knows, this is not an exhaustive list and other suitable polymers not listed here may be used. Examples of such polymers may be found in the latest edition of the CTFA's International Cosmetic Ingredient Dictionary

The amount of polymers used to obtain the desired effect in the formulation
10 range from 0.10% to 5.0% by weight of the formulation and especially in the range from 0.25% to 3.0% by weight of the formulation.

Preferred embodiments of the cosmetic and/or pharmaceutical, especially dermatologically active preparations of the invention comprise, if desired, further ingredients having care properties, such as, for example, fatty alcohols having
15 to 30 C atoms. The fatty alcohols here can be saturated or unsaturated and linear or branched. Furthermore, these fatty alcohols can in some cases be part of the oil phase (III) if they correspond to the definition given there. Alcohols which can be employed are, for example, decanol, decenol, octanol, octenol, dodecanol, dodecenol, octadienol, decadienol, dodecadienol, oleyl alcohol, ricinoleyl alcohol, erucyl alcohol, stearyl alcohol, isostearyl alcohol, cetyl alcohol,
20 lauryl alcohol, myristyl alcohol, arachidyl alcohol, caprylyl alcohol, capryl alcohol, linoleyl alcohol, linolenyl alcohol and behenyl alcohol, and also Guerbet alcohols thereof, such as, for example, 2-octyl-1-dodecanol, it being possible for the list to be extended virtually as desired by further alcohols of related structural chemistry. The fatty alcohols preferably originate from natural fatty acids, being conventionally prepared from the corresponding esters of the fatty acids by reduction.
25 Fatty alcohol fractions which are formed by reduction from naturally occurring fats and fatty oils, such as beef tallow, peanut oil, colza oil, cottonseed oil, soya oil, sunflower oil, palm kernel oil, linseed oil, maize oil, castor oil, rapeseed oil, sesame oil, cacao butter and coconut fat, can further be employed.
30

Substances having care properties which advantageously can be employed in the cosmetic and/or dermatologically active preparations can further include

- ceramides, where ceramides are understood as meaning N-acylsphingosins (fatty acid amides of sphingosin) or synthetic analogues of such lipids (so-called pseudo-ceramides), which significantly improve the water retention capacity of the stratum corneum.
- phospholipids, for example soya lecithin, egg lecithin and cephalins
- fatty acids
- phytosterols and phytosterol-containing fats or waxes
- vaseline, paraffin oils and silicone oils; the latter include, inter alia, dialkyl- and alkylarylsiloxanes, such as dimethylpolysiloxane and methylphenyl-polysiloxane, and also alkoxyated and quaternised derivatives thereof.

Animal and/or plant protein hydrolysates can advantageously also be added to preferred embodiments of cosmetic and/or pharmaceutical, especially dermatologically active, preparations of the invention. Substances which are advantageous in this respect are, in particular, elastin, collagen, keratin, milk protein, soya protein, oat protein, pea protein, almond protein and wheat protein fractions or corresponding protein hydrolysates, and also condensation products thereof with fatty acids, and quaternised protein hydrolysates, the use of plant protein hydrolysates being preferred.

The aqueous phase of the preparations according to the present invention optionally advantageously comprises alcohols, diols or polyols (lower alkyl), and ethers thereof, preferably ethanol, isopropanol, propylene glycol, 1,2-hexanediol, 1,2-octanediol, 1,2-decanediol, a mixture of 1,2-hexanediol and 1,2-octanediol, a mixture of 1,2-hexanediol and 1,2-decanediol, a mixture of 1,2-octanediol and 1,2-decanediol, a mixture of 1,2-hexanediol, 1,2-octanediol and 1,2-decanediol, glycerol, ethylene glycol-monoethyl or monobutyl ether, propylene glycol mono-

methyl, -monoethyl or monobutyl ether, diethylene glycol monomethyl or -
monoethyl ether and analogous products, and also alcohols (lower alkyl), e.g.
ethanol, 1,2-propanediol, glycerol, and, in particular, one or more thickeners
5 which can advantageously be chosen from the group of silicon dioxide, aluminum
silicates, polysaccharides and derivatives thereof, e.g. hyaluronic acid, xanthan
gum, hydroxypropylmethylcellulose, particularly advantageously from the group
of polyacrylates, preferably a polyacrylate from the group of so-called Carbopols,
for example, Carbopol grades 980, 981, 1382, 2984, 5984, in each case indi-
vidually or in combination.

10 Preferred embodiments of the cosmetic and/or pharmaceutical, especially der-
matologically active preparations of the invention may also comprise active anti-
inflammatory and/or redness- and/or itching-alleviating compounds (anti-irritants).
All the active anti-inflammatory or redness- and/or itching-alleviating compounds
which are suitable or usual for cosmetic and/or dermatological applications can
15 be used here. Active anti-inflammatory and redness- and/or itching-alleviating
compounds which are advantageously employed are steroidal anti-inflammatory
substances of the corticosteroid type, such as hydrocortisone, dexamethasone,
dexamethasone phosphate, methylprednisolone or cortisone, it being possible for
the list to be extended by addition of further steroidal anti-inflammatories. Non-
20 steroidal anti-inflammatories can also be employed. Those to be mentioned here
by way of example are oxicams, such as piroxicam or tenoxicam; salicylates,
such as aspirin, Disalcid, Solprin or fendosal; acetic acid derivatives, such as
diclofenac, fenclofenac, indomethacin, sulindac, tolmetin, or clindanac; fena-
mates, such as mefenamic, meclofenamic, flufenamic or niflumic; propionic acid
25 derivatives, such as ibuprofen, naproxen, benoxaprofen or pyrazoles, such as
phenylbutazone, oxyphenylbutazone, febrazone or azapropazone.

Alternatively, natural anti-inflammatory or redness- and/or itching-alleviating
substances can be employed. Plant extracts, specific highly active plant extract
fractions and highly pure active substances isolated from plant extracts can be
30 employed. Extracts, fractions and active substances from camomile, aloe vera,
Commiphora species, Rubia species, willow, rose-bay willow-herb, oats, and also

pure substances, such as, inter alia, bisabolol, apigenin 7-glucoside, boswellic acid, phytosterols, glycyrrhizic acid, glabridin or licochalcone A, are particularly preferred. The preparations of the present invention can also comprise mixtures of two or more active anti-inflammatory compounds. Bisabolol, boswellic acid,
5 and also extracts and isolated highly pure active compounds from oats and Echinacea are particularly preferred for use in the context of the invention as anti-inflammatory and redness- and/or itching-alleviating substances, and alpha-bisabolol and extracts and isolated highly pure active compounds from oats are especially preferred.

10 The amount of anti-irritants (one or more compounds) in the preparations is preferably 0.0001% to 20% by weight, with particular preference 0.0001% to 10% by weight, in particular 0.001% to 5% by weight, based on the total weight of the preparation.

Preferred embodiments of the cosmetic and/or pharmaceutical, especially der-
15 matologically active preparations of the invention may advantageously also comprise moisture retention regulators. The following substances for example are used as moisture retention regulators (moisturizers): sodium lactate, urea, alcohols, sorbitol, glycerol, propylene glycol, aliphatic 1,2-diols with a C number of 5-10, collagen, elastin or hyaluronic acid, diacyl adipates, petrolatum, ectoin, uro-
20 canic acid, lecithin, pantheol, phytantriol, lycopene, algae extract, ceramides, cholesterol, glycolipids, chitosan, chondroitin sulphate, polyamino acids and polyamino sugars, lanolin, lanolin esters, amino acids, alpha-hydroxy acids (e.g. citric acid, lactic acid, malic acid) and derivatives thereof, sugars (e.g. inositol), alpha-hydroxy fatty acids, phytosterols, triterpene acids, such as betulinic acid or
25 ursolic acid, algae extracts.

Preferred embodiments of the cosmetic and/or pharmaceutical, especially der-
matologically active preparations of the invention may advantageously also com-
prise mono-, di- and oligosaccharides, such as, for example, glucose, galactose,
fructose, mannose, fruit sugars and lactose.

Preferred embodiments of the cosmetic and/or pharmaceutical, especially dermatologically active preparations of the invention may advantageously also comprise plant extracts, which are conventionally prepared by extraction of the whole plant, but also in individual cases exclusively from blossom and/or leaves, wood, bark or roots of the plant. In respect of the plant extracts which can be used, reference is made in particular to the extracts which are listed in the table starting on page 44 of the 3rd edition of the Leitfaden zur Inhaltsstoffdeklaration kosmetischer Mittel [Manual of Declaration of the Constituents of Cosmetic Compositions], published by Industrieverband Körperpflegemittel und Waschmittel e.V. (IKW), Frankfurt. Extracts which are advantageous in particular are those from aloe, witch hazel, algae, oak bark, rose-bay willow-herb, stinging nettle, dead nettle, hops, camomile, yarrow, arnica, calendula, burdock root, horsetail, hawthorn, linden blossom, almond, pine needle, horse chestnut, sandalwood, juniper, coconut, mango, apricot, orange, lemon, lime, grapefruit, apple, green tea, grapefruit pip, wheat, oats, barley, sage, thyme, wild thyme, rosemary, birch, mallow, lady's smock, willow bark, restharrow, coltsfoot, hibiscus, ginseng and ginger root.

In this context, the extracts from aloe vera, camomile, algae, rosemary, calendula, ginseng, cucumber, sage, stinging nettle, linden blossom, arnica and witch hazel are particularly preferred. Mixtures of two or more plant extracts can also be employed. Extraction agents which can be used for the preparation of plant extracts mentioned are, inter alia, water, alcohols and mixtures thereof. In this context, among the alcohols lower alcohols, such as ethanol and isopropanol, but also polyhydric alcohols, such as ethylene glycol, propylene glycol and butylene glycol, are preferred, and in particular both as the sole extraction agent and in mixtures with water. The plant extracts can be employed both in pure and in diluted form.

Preferred embodiments of the cosmetic and/or pharmaceutical, especially dermatologically active preparations of the invention may in numerous cases advantageously comprise the following preservatives:

Preservatives which are preferably chosen here are those such as benzoic acid, its esters and salts, propionic acid and its salts, salicylic acid and its salts, 2,4-hexadienoic acid (sorbic acid) and its salts, formaldehyde and paraformaldehyde, 2-hydroxybiphenyl ether and its salts, 2-zincsulphidopyridine N-oxide, inorganic sulphites and bisulphites, sodium iodate, chlorobutanolum, 4-ethylmercuryl(II)-5-amino-1,3-bis(2-hydroxybenzoic acid), its salts and esters, dehydracetic acid, formic acid, 1,6-bis(4-amidino-2-bromophenoxy)-n-hexane and its salts, the sodium salt of ethylmercury(II)-thiosalicylic acid, phenylmercury and its salts, 10-undecylenic acid and its salts, 5-amino-1,3-bis(2-ethylhexyl)-5-methyl-hexahydropyrimidine, 5-bromo-5-nitro-1,3-dioxane, 2-bromo-2-nitro-1,3-propanediol, 2,4-dichlorobenzyl alcohol, N-(4-chlorophenyl)-N'-(3,4-dichlorophenyl)urea, 4-chloro-m-cresol, 2,4,4'-trichloro-2'-hydroxydiphenyl ether, 4-chloro-3,5-dimethylphenol, 1,1'-methylene-bis(3-(1-hydroxymethyl-2,4-dioximidazolidin-5-yl)urea), poly(hexamethylene diguanide) hydrochloride, 2-phenoxyethanol, hexamethylenetetramine, 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride, 1-(4-chlorophenoxy)-1-(1H-imidazol-1-yl)-3,3-dimethyl-2-butanone, 1,3-bis-(hydroxymethyl)-5,5-dimethyl-2,4-imidazolidinedione, benzyl alcohol, octopirox, 1,2-dibromo-2,4-dicyanobutane, 2,2'-methylenebis(6-bromo-4-chlorophenol), bromochlorophene, mixture of 5-chloro-2-methyl-3(2H)-isothiazolinone and 2-methyl-3(2H)isothiazolinone with magnesium chloride and magnesium nitrate, 2-benzyl-4-chlorophenol, 2-chloroacetamide, chlorhexidine, chlorhexidine acetate, chlorhexidine gluconate, chlorhexidine hydrochloride, 1-phenoxypropan-2-ol, N-alkyl(C₁₂-C₂₂)trimethylammonium bromide and chloride, 4,4-dimethyl-1,3-oxazolidine, N-hydroxymethyl-N-(1,3-di(hydroxymethyl)-2,5-dioximidazolidin-4-yl)-N'-hydroxymethylurea, 1,6-bis(4-amidinophenoxy)-n-hexane and its salts, glutaraldehyde, 5-ethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane, 3-(4-chlorophenoxy)-1,2-propanediol, hyamines, alkyl-(C₈-C₁₈)-dimethylbenzylammonium chloride, alkyl-(C₈-C₁₈)-dimethylbenzylammonium bromide, alkyl-(C₈-C₁₈)-dimethylbenzylammonium saccharinate, benzyl hemiformal, 3-iodo-2-propynyl butylcarbamate, sodium hydroxymethylaminoacetate or sodium hydroxymethylaminoacetate.

In various cases it may also be advantageous to employ substances which are chiefly employed for inhibition of the growth of undesirable microorganisms on or in animal organisms in cosmetic and/or pharmaceutical, especially dermatologically active, preparations of the invention. In this respect, in addition to conventional preservatives, further active compounds which are worth mentioning, in addition to the large group of conventional antibiotics, are, in particular, the products relevant for cosmetics, such as triclosan, climbazol, octoxyglycerol, octopirox (1-hydroxy-4-methyl-6-(2,4,4-trimethylpentyl)-2(1H)-pyridone, 2-aminoethanol), chitosan, farnesol, glycerol monolaurate or combinations of the substances mentioned, which are employed, inter alia, against underarm odour, foot odour or dandruff formation.

Furthermore, cosmetic and/or pharmaceutical, especially dermatologically active preparations of the invention may also comprise substances having a cooling action. Individual active cooling compounds which are preferred for use in the context of the present invention are listed below. The skilled person is able to supplement the following list with a large number of further active cooling compounds; the active cooling compounds listed can also be employed in combination with one another: l-menthol, d-menthol, racemic menthol, menthone glycerol acetal (trade name: Frescolat[®]MGA), menthyl lactate (trade name: Frescolat[®]ML, menthyl lactate is preferably l-menthyl lactate, in particular l-menthyl l-lactate), substituted menthyl-3-carboxylic acid amides (e.g. menthyl-3-carboxylic acid N-ethylamide), 2-isopropyl-N-2,3-trimethylbutanamide, substituted cyclohexane-carboxylic acid amides, 3-menthoxypropane-1,2-diol, 2-hydroxyethyl menthyl carbonate, 2-hydroxypropyl menthyl carbonate, N-acetylglycine menthyl ester, isopulegol, menthyl hydroxycarboxylic acid esters (e.g. menthyl 3-hydroxybutyrate), monomethyl succinate, 2-mercaptocyclodecanone, menthyl 2-pyrrolidin-5-onecarboxylate, 2,3-dihydroxy-p-menthane, 3,3,5-trimethylcyclohexanone glycerol ketal, 3-menthyl 3,6-di- and -trioxaalkanoates, 3-menthyl methoxyacetate, icilin.

Preferred active cooling compounds are: l-menthol, d-menthol, racemic menthol, menthone glycerol acetal (trade name: Frescolat[®]MGA), menthyl lactate (pref-

erably l-menthyl lactate, in particular l-menthyl l-lactate, trade name: Frescolat[®]ML), substituted menthyl-3-carboxylic acid amides (e.g. menthyl-3-carboxylic acid N-ethylamide), 2-isopropyl-N-2,3-trimethylbutanamide, substituted cyclohexanecarboxylic acid amides, 3-menthoxypropane-1,2-diol, 2-hydroxyethyl menthyl carbonate, 2-hydroxypropyl menthyl carbonate, isopulegol.

Particularly preferred active cooling compounds are: l-menthol, racemic menthol, menthone glycerol acetal (trade name: Frescolat[®]MGA), menthyl lactate (preferably l-menthyl lactate, in particular l-menthyl l-lactate, trade name: Frescolat[®]ML), 3-menthoxypropane-1,2-diol, 2-hydroxyethyl menthyl carbonate, 2-hydroxypropyl menthyl carbonate.

Very particularly preferred active cooling compounds are: l-menthol, menthone glycerol acetal (trade name: Frescolat[®]MGA), menthyl lactate (preferably l-menthyl lactate, in particular l-menthyl l-lactate, trade name: Frescolat[®]ML).

The use concentration of the active cooling compounds to be employed is, depending on the substance, preferably in the concentration range from 0.01% to 20% by weight, and more preferably in the concentration range from 0.1% to 5% by weight, based on the total weight of the completed (ready-to-use) cosmetic or pharmaceutical preparation.

The following examples are intended to illustrate the present invention without restricting it. All amounts quoted, proportions and percentages are, unless indicated otherwise, based on the weight and the total amount or on the total weight of the preparations. When these preparations are irradiated with UV radiation they do not fluoresce whereas the preparations without the fluorescent quencher fluoresce strongly.

The invention is further described by the accompanying examples, without limiting the scope of the claims.

Examples

Fluorescence.

By way of example, comparative observations between preparations containing disodium phenyl dibenzimidazole tetrasulfonic acid and preparations containing mixtures of disodium phenyl dibenzimidazole tetrasulfonic acid and Benzophenone-4 are listed below:

Example 1

Part	Raw materials	INCI name	A % (w/w)	B% (w/w)
A	Emulsiphos	Potassium Cetyl Phosphate (and Hydrogenated Palm Glycerides)	1.50	1.50
	Lanette O	Cetearyl Alcohol	1.50	1,50
	Copherol 1250	Tocopherylacetate (sic)	0.50	0.50
	Dow Corning 246 Fluid	Cyclohexasiloxane	2.00	2.00
	Tegosoft TN	C 12-15 Alkyl Benzoate	5.00	5.00
	Neo Heliopan [®] AV	Ethyl Methoxycinnamate	7.50	7.50
	Neo Heliopan [®] E1000	Isoamyl p-Methoxycinnamate	10.50	10.50
	Carbopol ETD 2050	Carbomer	0.20	0.20
	Keltrol T	Xanthan Gum	0.20	0.20
	EDETA B fl.	Tetrasodium EDTA	0.10	0.10
		Titanium Dioxide	3.00	3.00
B	Distilled Water	Water (Aqua)	Ad 100	Ad 100

Part	Raw materials	INCI name	A % (w/w)	B% (w/w)
	Neo Heliopan [®] AP	Disodium Phenyl Dibenzimidazole Tetrasulfonate	2.00	2.00
	Benzophenone-4	Benzophenone-4	0.00	2.00
	Triethanolamine	Triethanolamine	qs	Qs
C	Fragrance	Parfum	0.40	0.40

Formula A when applied to human skin fluoresces strongly under UVA irradiation,
Sample B does not fluoresce under the same conditions.

5 Example 2

Part	Raw materials	INCI name	A % (w/w)	B% (w/w)
A	Emulsiphos	Potassium Cetyl Phosphate (and Hydrogenated Palm Glycerides)	1.50	1.50
	Lanette O	Cetearyl Alcohol	1.50	1,50
	Copherol 1250	Tocopherylacetate (sic)	0.50	0.50
	Dow Corning 246 Fluid	Cyclohexasiloxane	2.00	2.00
	Tegosoft TN	C 12-15 Alkyl Benzoate	5.00	5.00
	Neo Heliopan [®] AV	Ethyl Methoxycinnamate	7.50	7.50
	Neo Heliopan [®] E1000	Isoamyl p-Methoxycinnamate	10.50	10.50
	Carbopol ETD 2050	Carbomer	0.20	0.20
	Keltrol T	Xanthan Gum	0.20	0.20

Part	Raw materials	INCI name	A % (w/w)	B% (w/w)
	EDETA B fl.	Tetrasodium EDTA	0.10	0.10
		Titanium Dioxide	3.00	3.00
B	Distilled Water	Water (Aqua)	Ad 100	Ad 100
	Neo Heliopan [®] AP	Disodium Phenyl Dibenzimidazole Tetrasulfonate	2.00	2.00
	Benzophenone-4	Benzophenone-4	0.00	2.00
	Sodium Hydroxide	Sodium Hydroxide	qs	Qs
C	Fragrance	Parfum	0.40	0.40

Formula A when applied to human skin fluoresces strongly under UVA irradiation, Sample B does not fluoresce under the same conditions.

- 5 Note that Benzophenone-4 in this example has been neutralised with sodium hydroxide. The sodium salt of Benzophenone-4 is also called Benzophenone-5 and the same quenching effect is observed whether Benzophenone 4 neutralised in-situ or when Benzophenone-5 is used.

10 Example 3

Part	Raw materials	INCI name	A % (w/w)	B% (w/w)
A	Emulsiphos	Potassium Cetyl Phosphate (and Hydrogenated Palm Glycerides)	1.50	1.50

Part	Raw materials	INCI name	A % (w/w)	B% (w/w)
	Lanette O	Cetearyl Alcohol	1.50	1,50
	Copherol 1250	Tocopherylacetate (sic)	0.50	0.50
	Dow Corning 246 Fluid	Cyclohexasiloxane	2.00	2.00
	Tegosoft TN	C 12-15 Alkyl Benzoate	5.00	5.00
	Neo Heliopan [®] AV	Ethyl Methoxycinnamate	7.50	7.50
	Neo Heliopan [®] E1000	Isoamyl p-Methoxycinnamate	7.50	7.50
	Carbopol ETD 2050	Carbomer	0.20	0.20
	Keltrol T	Xanthan Gum	0.20	0.20
	EDETA B fl.	Tetrasodium EDTA	0.10	0.10
B	Distilled Water	Water (Aqua)	Ad 100	Ad 100
	Glycerin	Glyceri	4.70	4.70
	Phenonip	Phenoxyethanol, Methylparaben, Ethylparaben, Butylparaben, Propylparaben, Isobutylparaben	0.80	0.80
	Neo Heliopan [®] AP	Disodium Phenyl Dibenzimidazole Tetrasulfonate	2.00	2.00
	Benzophenone-4	Benzophenone-4	0.00	0.5
	Triethanolamine	Triethanolamine	qs	Qs
C	Fragrance	Parfum	0.40	0.40

Formula A when applied to human skin fluoresces strongly under UVA irradiation, Sample B does not fluoresce under the same conditions.

Manufacturing procedure for examples 1-3.

5

Part A. Mix all ingredients except Keltrol and Carbopol and heat up to 85°C until all ingredients are completely dissolved. Add Keltrol and Carbopol and homogenise.

10 Part B. Mix all ingredients together and heat to 85°C, then add to Part A. with stirring. Homogenise and cool to ambient temperature.

Part C. Add to parts A and B at 30°C with stirring. Homogenise.

15 Formulation Examples.

Formulation Example 1 Sunscreen soft cream (O/W), in-vitro SPF 5, water resistant

Part	Raw Materials	INCI Name	% (wt.)
A	Emulsiphos	Potassium Cetyl Phosphate, Hydrogenated Palm Glycerides	1.50
	Cutina GMS / V	Glyceryl Stearate	2.00
	Copherol 1250	Tocopheryl Acetate	0.50
	Lanette 16	Cetyl Alcohol	1.00
	Tegosoft TN	C 12-15 Alkyl Benzoate	24.00
	Prisorine 3505	Isostearic Acid	1.00
	Heo Heliopan® 357	Butyl Methoxydibenzolymethane	3.00
	Neo Heliopan® 303	Octocrylene	6.00

B	Water, dist.	Water (Aqua)	Ad 100
	Neo Heliopan® AP	Disodium Phenyl Dibenzimidazole Tetrasulfonate	2.0
	Benzophenone-4	Benzophenone-4	0.5
	Sodium Hydroxide	Sodium Hydroxide	qs
	EDETA B liq.	Tetrasodium EDTA	0.20
	Glycerol, 99%	Glycerin	3.00
	Phenoxyethanol	Phenoxyethanol	0.70
	Solbrol M	Methylparaben	0.20
	Solbrol P	Propylparaben	0.10
	Carbopol ETD 2050	Carbomer	0.20
C	Perfume oil	Parfum (Fragrance)	0.30

Manufacturing procedure.

Part A: Heat to about 85 °C.

5

Part B: Weigh in raw materials without Carbopol. Disperse Carbopol therein using Ultra Turrax. Heat to about 85 °C. Add B to A. and then homogenise while hot (Ultra Turrax). Leave to cool with stirring.

10 Part C: Add to A/B at 30 °C or less with stirring

Formulation Example 2 Sunscreen lotion (O/W), in-vitro SPF 20

Part	Raw Materials	INCI Name	% (wt.)
<u>A</u>	Emulsiphos	Potassium Cetyl Phosphate, Hydrogenated Palm Glycerides	1.50

Part	Raw Materials	INCI Name	% (wt.)
	Cutina GMS / V	Glyceryl Stearate	2.00
	Copherol 1250	Tocopheryl Acetate	0.50
	Lanette 16	Cetyl Alcohol	1.00
	Tegosoft TN	C 12-15 Alkyl Benzoate	10.60
	Prisorine 3505	Isostearic Acid	1.00
	Neo Heliopan 357	Butyl Methoxydibenzolymethane	2.00
	Neo Heliopan® AV	Ethylhexyl Methoxycinnamate	5.00
	EDETA BD	Disodium EDTA	0.10
	Carbopol ETD 2050	Carbomer	0.20
B	Water, dist.	Water (Aqua)	qs
	Glycerol, 99%	Glycerin	3.00
	Dragocid Liquid	Phenoxyethanol, Methylparaben, Ethylparaben, Butylparaben, Propylparaben, Isobutylparaben	0.80
C	Triethanolamine	Triethanolamine	qs
	Neo Heliopan® AP 22% strength solution neutralised with Triethanolamine	Disodium Phenyl Dibenzimidazole Tetrasulfonate	9.1
	Neo Heliopan® Hydro, 30% strength solution neutralised with Triethanolamine	Phenylbenzimidazole Sulfonic Acid	3.34
	Benzophenone-4	Benzophenone-4	0.5
D	Perfume oil	Parfum (Fragrance)	0.30

Manufacturing procedure.

Part A: Heat to about 85 °C.

Part B: Weigh in raw materials without Carbopol. Disperse Carbopol therein using Ultra Turrax. Heat to about 85°C. Add B to A.

Part C: Immediately add to A/B and then homogenise while hot (Ultra Tur-
5 rax). Leave to cool with stirring.

Part D: Add and stir in.

Formulation Example 3 Low oil content Sunscreen milk (O/W), in-vitro SPF 25

10

Part	Raw Materials	INCI Name	% (wt.)
A	Tegin M	Glyceryl Stearate	2.50
	Tagat S	PEG-30 Glyceryl Stearate	1.95
	Lanette O	Cetearyl Alcohol	2.20
	Copherol 1250	Tocopheryl Acetate	0.50
	Phenonip	Phenoxyethanol (and) methylparaben (and) Butylparaben (and) ethyl-paraben (and) Propylparaben	0.15
	Neo Heliopan® AV	Ethylhexyl Methoxycinnamate	5.00
	Neo Heliopan® 303	Octocrylene	5.00
	Neo Heliopan® 357	Butyl Methoxydibenzolymethane	2.00
	EDETA BD	Disodium EDETA	0.10
B	Water, dist.	Water (Aqua)	Ad 100
	Neo Heliopan® Hydro	Phenylbenzimidazole Sulfonic Acid,	3.3
	Neo Heliopan® AP,	Disodium Phenyl Dibenzimidazole Tetrasul- fonate	2.20
	Benzophenone-4	Benzophenone-4	0.5
	1,2-Propylene glycol	Propylene Glycol	2.00

Part	Raw Materials	INCI Name	% (wt.)
	Phenonip	Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	0.30
	NaOH, 10% strength	Sodium Hydroxide	2.2
C	Water, dist.	Water (Aqua)	19.00
	Carbopol 2050	Carbomer	0.40
	NaOH, 10% strength	Sodium Hydroxide	qs
D	Perfume oil	Parfum (Fragrance)	0.30

Manufacturing procedure.

Part A: Heat to 80-85°C.

5

Part B: Heat to 80-85°C, Add part B to part A with stirring.

Part C: Disperse Carbopol into the water and neutralise with NaOH, with stirring. Add part C at about 60°C with stirring. Allow to cool to RT (room temperature).

10

Part D: Add and stir.

Formulation Example 4 Sunscreen lotion (O/W), in-vitro SPF 18

15

Part	Raw Materials	INCI Name	% (wt.)
A	Eumulgin VL 75	Lauryl Glucoside (and) Polyglyceryl-2-Dipolyhydroxystearate (and) Glycerin	3.00
	Tegosoft TN	C12-25 Alkyl Benzoate	20.00
	Copherol 1250	Tocopheryl Acetate	0.50

	Perfume oil	Parfum (Fragrance)	0.20
	Neo Heliopan® 357	Butyl Methoxydibenzolymethane	2.00
	Neo Heliopan® E1000	Isoamyl p-Methoxycinnamate	5.00
	Neo Heliopan® 303	Octocrylene	5.00
	Carbopol 2050 ETD	Carbomer	0.35
	Pemulen TR-1	Acrylates/C10-30 Alkyl Acrylate Cross-polymer	0.15
	EDETA BD	Disodium EDTA	0.10
B	Water, dist.	Water (Aqua)	Ad 100
	Glycerol, 99%	Glycerin	5.00
	Dragocid Liquid	Phenoxyethanol, Methylparaben, Ethylparaben, Butylparaben, Propylparaben, Isobutylparaben	0.80
	Neo Heliopan® Hydro	Phenylbenzimidazole Sulfonic Acid	2.00
	Neo Heliopan® AP	Disodium Phenyl Dibenzimidazole Tetrasulfonate	1.10
	Benzophenone-4	Benzophenone-4	0.3
	Amino Methyl Propanol	Amino Methyl Propanol	4.30
C	Perfume oil	Parfum (Fragrance)	0.30

Manufacturing procedure.

5 Part A: Dissolve the solids in the oils and liquid UV filters (heating to about 70°C). Allow to cool to about 30°C, add the remaining constituents apart from Carbopol and Pemulen and mix at room temperature (stir for about 5 minutes). Stir in Carbopol and Pemulen.

Part B: Add water and glycerin, then disperse Neo Heliopan® Hydro with

vigorous stirring and heating to 70°C, add Amino Methyl Propanol until all of the Neo Heliopan® Hydro, Neo Heliopan® AP and Benzophenone-4 has been dissolved and add all of part B to part A with stirring. Stir for about 60 minutes with cooling and homogenise using the Ultra Turrax.

5

Part C: Stir in at ambient temperature.

10 Formulation Example 5 Sunscreen cream (W/O), in-vitro SPF 10, water resistant

Part	Raw Materials	INCI Name	% (wt.)
A	Dehymuls PGPH	Polyglyceryl-2 Dipolyhydroxystearate	5.00
	Copherol 1250	Tocopheryl Acetate	0.50
	Permulgin 3220	Ozokerite	0.50
	Aluminium stearate	Aluminium Stearate	0.50
	Tegosoft TN	C12-15 Alkyl Benzoate	25.00
	Neo Heliopan® 357	Butyl Methoxydibenzolymethane	2.00
	EDETA BD	Disodium EDTA	0.10
B	Water, dist.	Water (Aqua)	Ad 100
	Glycerol, 99%	Glycerin	4.00
	Dragocid Liquid	Phenoxyethanol, Methylparaben, Ethylparaben, Butylparaben, Propylparaben, Isobutylparaben	1.00
	Neo Heliopan® Hydro, 22% strength solution neutralised with Triethanolamine	Phenylbenzimidazole Sulfonic Acid	22.3

	Neo Heliopan® AP 22% strength solution neutralised with Triethanolamine	Disodium Phenyl Dibenzimidazole Tetrasulfonate	6.0
	Benzophenone-4	Benzophenone-4	0.3
	Triethanolamine	Triethanolamine	qs
	Magnesium sulfate	Magnesium Sulfate	0.50
C	Perfume oil	Parfum (Fragrance)	0.30

Manufacturing procedure.

Part A: Heat to about 85 °C.

5

Part B: Heat to about 85 °C. Add B to A. Allow to cool with stirring then homogenise.

Part C: Stir in at ambient temperature.

10

Formulation Example 6 Sunscreen softcream (W/O), in-vitro SPF 50

Part	Raw Materials	INCI Name	% (wt.)
A	Dehymuls PGPH	Polyglyceryl-2 Dipolyhydroxystearate	5.00
	Copherol 1250	Tocopheryl Acetate	0.50
	Permulgin 3220	Ozokerite	0.50
	Zinc stearate	Zinc Stearate	0.50
	Tegosoft TN	C12-15 Alkyl Benzoate	10.00
	Neo Heliopan®BB	Benzophenone 3	3.00
	Neo Heliopan® HMS	Homosalate	5.00
	Neo Heliopan® 303	Octocrylene	5.00

Part	Raw Materials	INCI Name	% (wt.)
	Neo Heliopan® OS	Ethylhexyl Salicylate	5.00
	Uvinul T-150	Ethylhexyl Triazone	3.00
	Zinc oxide neutral	Zinc Oxide	5.00
B	Water, dist.	Water (Aqua)	Ad 100
	EDETA BD	Disodium EDTA	0.10
	Glycerol, 99%	Glycerin	4.00
	Dragocid Liquid	Phenoxyethanol, Methylparaben, Ethylparaben, Butylparaben, Propylparaben, Isobutylparaben	1.00
	Neo Heliopan® Hydro, 15% strength solution neutralised with Sodium Hydroxide	Phenylbenzimidazole Sulfonic Acid	10.00
	Neo Heliopan® AP 10% strength solution neutralised with Sodium Hydroxide	Disodium Phenyl Dibenzimidazole Tetrasulfonate	12.0
	Benzophenone-4	Benzophenone-4	0.5
	Sodium Hydroxide	Sodium Hydroxide	qs
	Magnesium sulfate	Magnesium Sulfate	0.50
C	Parfume oil	Parfum (Fragrance)	0.20

Manufacturing procedure.

Part A: Heat to about 85 °C.

5

Part B: Heat to about 85 °C (without zinc oxide; disperse zinc oxide therein using the Ultra Turrax). Add B to A. Allow to cool with stirring.

Part C: Add and then homogenise.

10

Formulation Example 7 Day care cream with broad spectrum UV protection

Part	Raw Materials	INCI Name	% (wt.)
A	Emulgade PL 68/50	Cetearyl Glycoside (and) Cetearyl Alcohol	4.50
	Cetiol PGL	Hexyldecanol (and) Hexyldecyl Laurate	8.00
	Myritol 331	Cocoglycerides	8.00
	Copherol 1250	Tocopheryl Acetate	0.50
	Neo Heliopan® 303	Octocrylene	3.00
	Neo Heliopan® OS	Ethylhexyl Salicylate	5.00
B	Water, dist.	Water (Aqua)	qs
	Aqueous mixture of 30% Neo Heliopan® Hydro and 22% Neo Heliopan® AP neutralised with Triethanolamine	Phenylbenzimidazole Sulfonic Acid, Disodium Phenyl Dibenzimidazole Tetrasulfonate	11.00
	Benzophenone-4	Benzophenone-4	0.3
	Triethanolamine	Triethanolamine	qs
	Glycerol	Glycerin	3.00
	Dragocide Liquid	Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	0.50
C	Water, dist.	Water (Aqua)	25.00
	Carbopol ETD 2050	Carbomer	0.20
	Triethanolamine	Triethanolamine	qs
D	Perfume oil	Parfum (Fragrance)	0.30

Manufacturing procedure.

- 5 Part A: Heat to 80 °C.

Part B: Heat to 80 °C Add to part A with stirring.

Part C: Disperse Carbopol in water and neutralise with sodium hydroxide solution. Add to part A/B at about 55 °C.

5

Part D: Stir in at ambient temperature.

Formulation Example 8 Sunscreen spray in-vitro SPF 20

Part	Raw Materials	INCI Name	% (wt.)
A	Water, demin.	Water (Aqua)	62.1
	Glycerol, 99%	Glycerin	4.00
	Hydrolite 5	1,2-Pentylene Glycol	5.00
	D-Panthenol	Panthenol	0.50
	Lara Care A-200	Galactoarabinan	0.25
B	Baysilone oil M 10	Dimethicone	1.00
	Edeta BD	Disodium EDTA	0.10
	Copherol 1250	Tocopheryl Acetate	0.50
	Cetiol OE	Dicaprylyl Ether	3.00
	Neo Heliopan® HMS	Homosalate	5.00
	Neo Heliopan® AV	Ethylhexyl Methoxycinnamate	6.00
	Neo Heliopan® 357	Butyl Methoxydibenzoylmethane	1.00
	Tinosorb® S	Bis Ethylhexyloxyphenol Methoxyphenyl Triazine	2.00
	Alpha-Bisabolol	Bisabolol	0.10
	Pemulen TR-2	Acrylates/C10-30 Alkyl Acrylate Crosspolymer	0.25

Part	Raw Materials	INCI Name	% (wt.)
C	Phenoxyethanol	Phenoxyethanol	0.70
	Solbrol M	Methylparaben	0.20
	Solbrol P	Propylparaben	0.10
	Neo Heliopan® Hydro	Phenylbenzimidazole Sulfonic Acid	2.00
	Neo Heliopan® AP	Disodium Phenyl Dibenzimidazole Tetrasulfonate	1.50
	Benzophenone-4	Benzophenone-4	0.5
	Sodium Hydroxide	Sodium Hydroxide	qs
D	Perfume oil	Fragrance (Parfum)	0.20

Manufacturing procedure.

5 Part A: Dissolve Lara Care A-200 into the other constituents of part A with stirring.

10 Part B: Weigh in all raw materials (without Pemulen) and dissolve the crystalline substances with heating. Disperse Pemulen therein. Add part B to part A then homogenise for 1 minute.

Part C: Stir in the ingredients until all have dissolved and add part C+D then homogenise again for 1-2 minutes using the Ultra Turrax.

Formulation Example 9 Sunscreen hydrodispersion gel (balm)

15

Part	Raw Materials	INCI Name	% (wt.)
A	Water, dist.	Water (Aqua)	Ad 100
	Carbopol Ultrez 21	Acrylates/C10-30 Alkyl Acrylate Crosspol-	1.00

		ymer	
	Triethanolamine	Triethanolamine	1.20
B	Neo Heliopan® AP, 22% strength solution neutralised with Triethanolamine	Disodium Phenyl Dibenzimidazole Tetrasulfonate	10.0
	Benzophenone-4	Benzophenone-4	0.5
	Triethanolamine	Triethanolamine	qs
C	Neo Heliopan® E 1000	Isoamyl p-I Methoxycinnamate	3.00
	Neo Heliopan® 357	Butyl Methoxydibenzoylmethane	2.00
	Isopropyl myristate	Isopropyl Myristate	4.00
	Baysilone oil PK 20	Phenyl Trimethicone	3.00
	Dragocide Liquid	Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	0.50
	Perfume oil	Parfum (Fragrance)	0.30
	Edeta BD	Disodium EDTA	0.10
	Alpha Bisabolol	Alpha Bisabolol	0.10

Manufacturing procedure.

Part A: Disperse Carbopol in water and neutralise with triethanolamine solution.

5

Part B: Add to part A with stirring.

Part C: Dissolve crystalline constituents in the other raw materials of part C with warming (max.40°C) and add to part A/B. Stir well and then ho-

10

mogenise. (Homozenta).

Formulation Example 10 Hair Conditioner with UV filters

Part	Raw Materials	INCI Name	% (wt.)
A	Renex PEG 6000	PEG-150	2.5
	Hair Conditioner Base	Cetyl Alcohol, Behentrimonium Chloride, Triticum Vulgare (Wheat) Bran Extract, Linoleic Acid	3.0
	PCL-Solid	Stearyl Heptanoate, Stearyl Caprylate	0.50
	Dow Corning 5200	Laurylmethicone Copolyol	0.50
B	Natrosol 250 HR	Hydroxyethylcellulose	0.10
	Water, dist.	Water (Aqua)	87.07
	Neo Heliopan® AP	Disodium Phenyl Dibenzimidazole Tetrasulfonate	0.50
	Benzophenone-4	Benzophenone-4	0.50
	Amino Methyl propanol	Amino Methyl propanol	qs
	Nipagin M	Methylparaben	0.30
C	Dow Corning 949 Cationic Emulsion	Amodimethicone, Cetrimonium Chloride, Trideceth-12	2.00
	Perfume oil	Parfum (Fragrance)	0.80

5

Manufacturing procedure.

Part A: Heat to 80°C.

- 10 Part B: Swell Natrosol in water, Neo Heliopan® AP, Benzophenone-4 and Amino Methyl propanol, add Nipagin M and heat to 80°C. Add to part A with stirring and emulsify. Cool down with stirring.

Part C: Add at 35 °C and cool to RT with stirring.

Formulation Example 11 Broad Spectrum Aqueous Gel in-vitro SPF 14.0

5

Part	Ingredients	INCI-Name	% (wt.)
A	Demineralised Water	Water (Aqua)	59.20
	Amaze XT	Dehydroxanthan Gum	1.00
B	Demineralised Water	Water (Aqua)	15.00
	Neo Heliopan® Hydro	Phenylbenzimidazole Sulfonic Acid	3.00
	Neo Heliopan® AP	Disodium Phenyl Dibenzimidazole Tetrasulfonate	3.00
	Benzophenone-4	Benzophenone-4	0.75
	Triethanolamine	Triethanolamine	qs
C	Symdiol 68	1,2-Hexanediol and 1,2-Octanediol	0.50
	Hydrolite 5	Pentylene Glycol	2.00
	Dragoderm	Glycerin, Triticum Vulgare (Wheat) Gluten, Water (Aqua)	2.00
D	Dow Corning 193	PEG -12 Dimethicone	1.00
	Ethanol 96%	SD-Alcohol 39-C	10.00
	Perfume oil	Fragrance	0.10

Manufacturing procedure.

Part A: Stir Amaze XT into the water with stirring until it is swollen and a gel has formed

10

Part B: Stir the ingredients together and add to Part A and then add Parts C

with stirring until uniform and then add Part D with gentle stirring.

Formulation Examples 12 Water resistant Broad Spectrum O/W emulsions in-vitro SPF 50+

5

Part	Ingredients	INCI	A % (wt.)	B % (wt.)	C % (wt.)
A	Emulsiphos	Potassium Cetyl Phosphate, Hydrogenated Palm Glycerides	3.50	3.50	3.50
	Lanette O	Cetearylalcohol	1.00	1.00	1.00
	Neo Heliopan® HMS	Homosalate	5.00	5.00	5.00
	Neo Heliopan® 303	Octocrylene	10.00	10.00	10.00
	Neo Heliopan® OS	Ethylhexyl Salicylate	5.00	5.00	5.00
	Neo Heliopan® 357	Butyl Methoxydibenzoylmethane	5.00	4.50	5.00
	Eusolex T2000	Titanium Dioxide, Alumina, Simethicone	5.00	5.00	5.00
	Tinosorb S	Bis Ethylhexyloxyphenol Methoxyphenyl Triazine	0.00	4.50	3.00
	Abil Wax 9801	Cetyl Dimethicone	1.00	1.00	1.00
	Silcare Silicone 41M65	Stearyl Dimethicone	1.00	1.00	1.00
	Baysilone oil PK 20	Phenyl Trimethicone	2.00	2.00	2.00
	Isodipat	Diisopropyladipate	2.00	2.00	2.00
	Tocopherylacetat	Tocopheryl Acetate	0.50	0.50	0.50
	Antaron V216	VP/Hexadecene Copolymer	0.50	0.50	0.50
	EDTA BD	Disodium EDTA	0.10	0.10	0.10
	Keltrol T	Xanthan Gum	0.50	0.50	0.50
B	Water dem	Water (Aqua)	Ad 100	Ad 100	Ad 100

	Benzophenone-4	Benzophenone-4	1.0	1.0	1.00
	Neo Heliopan® AP	Disodium Phenyl Dibenzimidazole Tetrasulfonate	2.00	1.50	1.00
	Phenonip	Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	0.70	0.70	0.70
	Arginine	Arginine	2.20	1.23	1.72
	Lara Care A-200	Galactoarabinan	0.25	0.25	0.25
	Hydrolite 5	Pentylene Glycol	3.00	3.00	3.00
C	Fragrance	Fragrance (parfum)	0.30	0.30	0.30

Manufacturing procedure.

Part A: Heat all components except for the Xanthan Gum and TiO₂ to 85 °C.
 5 Then add Xanthan Gum and TiO₂ and homogenise.

Part B: Heat all components to 85 °C and add to Part A with stirring, stir to room temperature.

10 Part C: Add Part C to Parts A & B and homogenise.

Formulation Examples 13 Sunspray O/W exp. SPF 20

Part	Ingredients	INCI	% (wt.)
A	Dracorin GOC	Glyceryl Oleate Citrate, Caprylic/Capric Triglyceride	2.00
	Neo Heliopan HMS	Homosalate	7.00
	Neo Heliopan 357	Butyl Methoxydibenzoylmethane	4.00

	Neo Heliopan OS	Ethylhexyl Salicylate	5.00
	Isodipat	Diisopropyl Adipate	6.00
	Corapan TQ	Diethylhexyl 2,6 Naphthalate	3.00
	Edeta BD	Disodium EDTA	0.10
	Vitamin E Acetat	Tocopheryl Acetate	0.50
	Baysilone Oil M 10	Dimethicone	1.00
	Alpha-Bisabolol	Bisabolol	0.10
	Pemulen TR 2	Acrylates/ C10-30 Acrylates Copolymer	0.25
	Perfume	Fragrance (parfum)	0.25
B	Deion. Wasser	Water (Aqua)	Ad 100
	Glycerin 99%	Glycerin	4.00
	Butylenglycol	Butylene Glycol	5.00
	Dragocid Liquid	Phenoxyethanol, Methylparaben, Ethylparaben, Butylparaben, Propylparaben, Isobutylparaben	0.80
	Neo Heliopan® Hydro	Phenylbenzimidazole Sulfonic Acid	2.00
	Benzophenone-4	Benzophenone-4	1.0
	Neo Heliopan® AP	Disodium Phenyl Dibenzimidazole Tetrasulfonate	2.00
	Tris-Hydroxyaminomethane	Tris-Hydroxyaminomethane	0.47
C	Fragrance	Fragrance (parfum)	0.30

Manufacturing procedure.

Part A: Dissolve the Neo Heliopan 357 in the other components of phase A (except for Pemulen and EDTA) by heating up to 50 °C. Then add Xanthan Gum and TiO₂ and homogenise.

5 Part B: Add to Part A without stirring, then start emulsifying.

Part C: Add Part C to Parts A & B while homogenising.

Formulation Example 14 Clear Hair Shampoo with UV-Protection

10

Part	Ingredients	INCI-Name	% (wt.)
A	Demineralised Water	Water (Aqua)	Ad 100
	Merquat 550	Polyquaterium-7	0.50
B	Neo Heliopan® AP	Disodium Phenyl Dibenzimidazole Tetrasulfonate	1.00
	Benzophenone-4	Benzophenone-4	1.0
	Amino Methyl Propanol	Amino Methyl Propanol	0.6
C	Genapol LRO Liquid	Sodium Laureth Sulfate	30.00
	Tego Betain F 50	Cocoamidopropyl Betaine	5.00
	Antil 141	Propylene Glycol, PEG-55 Propylene Glycol Dioleate	0.80
	Dragocide Liquid	Phenoxyethanol, Methylparaben, Ethylparaben, Butylparaben, Propylparaben, Isobutylparaben	0.80
	D-Panthenol 75 L	Panthenol	1.00
	Extrapone® Lime	Propylene Glycol, Water (Aqua), Citrus Aurantifolia (Lime) Juice	1.00
	Sodium Chloride	Sodium Chloride	0.70
	Perfume	Fragrance	0.40

Manufacturing procedure.

- Part A: Dissolve Merquat in water with stirring
- 5 Part B: Add Neo Heliopan Hydro and neutralise with Amino Methyl Propanol, dissolve until a clear solution has formed.
- Part C: Add the ingredients to part AB as listed and stir until a uniform solution has formed. The viscosity can be adjusted by the amount of sodium chloride.
- 10

The pH of the resulting formulation was in the range of 5.2 - 5.5

15 Other Formulation Examples:

1. O/W Emulsions:, SPF > 20

RAW MATERIAL NAME (MANUFACTURER)	INCI	1	2	3	4	5	6	7	8	9	10	11
<u>Emulsifier</u>												
Emulsiphos (Symrise)	Potassium Cetyl Phosphate, Hydrogenated Palm Glycerides				2.0							
Dracorin CE	Glyceryl Stearate Citrate	1.0	1.0									
Dracorin GOC (Symrise)	Glyceryl Oleyl Citrate					4.0						
	Polyglyceryl 2-Dipolyhydroxystearate	0.25	0.25									
	Cetearyl Alcohol, Peg-40 Castor Oil, Sodium Cetearyl Sulfate							3.75				
	PEG-30 Dipolyhydroxystearate							1.0				

RAW MATERIAL NAME (MANUFACTURER)	INCI	1	2	3	4	5	6	7	8	9	10	11
			Polyglyceryl-3 Methylglucose Distearate								2.0	
	Sorbitan Stearate				0.5				1.0			
	Glyceryl Stearate SE							1.5				
	Glyceryl Stearate			2.5	1.0		4.0				4.0	
	Isostearic Acid						1.0					
	Stearic Acid				1.0					4.0		0.5
	PEG 40 Stearate			1.0						1.0		
	PEG 100 Stearate										2.0	0.5
	Potassium Cetyl Phosphate						2.0				0.5	2.0
Lanette E® (Cognis)	Sodium Cetearyl Sulphate									0.5		
Emulgin B2® (Cognis)	Ceteareth-20							0.7			1.0	
	<u>Oil Soluble UV Filters</u>											
Neo Heliopan® AV (Symrise)	Ethylhexyl Methoxycinnamate	8.0	8.0				4.0			5.0		
Neo Heliopan® 303 (Symrise)	Octocrylene				5.0	5.0			5.0		2.4	10.0
Neo Heliopan® 357 (Symrise)	Butyl Methoxydibenzoylmethane	4.5	4.5		2.5	0.5	3.0	0.5	2.0	2.0	3.0	3.0
Neo Heliopan® E 1000 (Symrise)	Isoamyl p-Methoxycinnamate				5.0		4.0					
Neo Heliopan® HMS (Symrise)	Homosalate				5.0	5.0				3.0	10.0	
Neo Heliopan® OS (Symrise)	Ethylhexyl Salicylate				2.0	5.0				5.0	5.0	3.0
Neo Heliopan® MBC (Symrise)	4-Methylbenzylidene-camphor				1.0							
Neo Heliopan® MA (Symrise)	Menthyl Anthranilate					1.0						
Neo Heliopan® BB (Symrise)	Benzophenone-3				0.5		1.0	0.5	0.5	4.0	5.0	

RAW MATERIAL NAME (MANUFACTURER)	INCI	1	2	3	4	5	6	7	8	9	10	11
		Mexoryl® XL	Drometrizole Trisiloxane				1.0					
Tinosorb® S	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	0.5	0.5		0.5							
Uvinul® T-150	Ethylhexyl Triazone	1.0	1.0	1.0	0.5							0.5
	-Bis[5- 1(dimethylpropyl)benzoxazo l-2-yl- 1.5 5 3 (4- phenyl)imino]-6-(2- ethylhexyl)imino-1,3,5- triazine						1.0					
Uvinul® A Plus	Diethylamino Hydroxyben- zoyl Hexyl Benzoate	1.0	1.0	2.0	0.5	2.0						
Indanylidene derivatives accord- ing to DE 10055940					0.5	0.5						
Benzoylcinnamyltri- nitrile derivatives according to WO 2006/015954				2.0	0.5	0.5						
Parsol® SLX	Polysiloxane-15				2.0							
Uvasorb® HEB	Diethylhexyl Butamido Triazone				0.5		2.0					
Benzylidene butyrolactones according to EP 1008593					1.0	2.0						
Benzylidene- dicarbonyl com- pounds described in WO/2005/107692					0.5							
Water Soluble UV Filters												
Neo Heliopan® AP (Symrise),	Disodium Phenyl- dibenzimidazoletetra- sulphonate	0.5	0.75	1.0	0.2	1.5	0.5	1.0	0.5	0.3	2.0	0.5

RAW MATERIAL NAME (MANUFACTURER)	INCI	1	2	3	4	5	6	7	8	9	10	11
		Neo Heliopan® Hydro (Symrise)	Phenylbenzimidazole- sulphonic Acid	1.0	1.0	2.0	1.0	2.0	1.5	2.0	2.0	2.0
Mexoryl® SX	Terephthalylidene Dicam- phor Sulfonic Acid				0.5		1.0					0.5
Sulisobenzone	Benzophenone-4	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Neutralisation base		qs	qs	qs	qs	qs	qs	qs	qs	qs	qs	qs
Microfine UV attenuating Pigments												
	Titanium Dioxide	3.0	3.0	3.0	0.5			6.0	1.0			3.0
	Zinc Oxide						3.0	6.0				
Tinosorb® M	Methylene Bis- Benzotriazolyl Tetramethyl- butylphenol			5.0	0.2					2.0		
Other oil soluble components												
PCL Liquid 100	Cetearyl Octanoate					3.0	3.0					
Corapan TQ® (Symrise)	Diethylhexyl 1,6- Naphthalate							3.0			3.0	
Dragoxat 89 (Symrise)	Ethylhexyl Isononoate				1.0	3.0						
Isoadipate	Diisopropyl Adipate			3.0	1.0	3.0						
Isopropyl myristate (Symrise)	Isopropyl Myristate						2.0			4.0		
Neutral oil (Sym- rise)	Caprylic/Capric Triglyceride					2.0		5.0		4.0		
Isodragol (Symrise)	Triisononanoin						1.0		6.0			
Cetiol OE (Cognis)	Dicaprylyl Ether	2.0	2.0				2.0	1.0	3.0			
	Dicaprylyl Carbonate			2.0			2.0					
	Isohexadecane											3.0
Paraffin oil	Mineral Oil									4.0		

RAW MATERIAL NAME (MANUFACTURER)	INCI	1	2	3	4	5	6	7	8	9	10	11
		Tegosoft TN® (Goldschmidt)	C12-15 Alkyl Benzoate	5.0	5.0	3.0	4.0	2.0			1.0	4.0
Abil 100® (Gold- schmidt)	Dimethicone				1.0				2.0		2.0	0.5
Dow Corning® 193 Fluid(Dow corning)	Peg-12 Dimethicone					1.0						
	Cyclopentasiloxane											5.0
	Cetyl Dimethicone										1.0	
	Hydrogenated Coco- Glycerides	1.0	1.0				1.0	0.5				
	Butylene Glycol Dicapryla- te/Dicaprate	1.0	1.0	4.0			1.0	7.5				
	Dibutyl Adipate				2.0							
	Trimethoxycaprylylsilane						1.0					
Lanette O® (Cognis)	Cetearyl Alcohol				1.5							
Lanette 16® (Cognis)	Cetyl Alcohol					1.0		1.0		0.5	1.0	
Lanette 18 ® (Cognis)	Stearyl Alcohol	1.0	1.0	2.0			1.0		4.5			
alpha-Bisabolol (Symrise)	Bisabolol				0.2	0.1						
Copherol 1250® (Cognis)	Tocopheryl Acetate	0.5	0.5	0.5	0.5	0.5	0.5	0.5		0.5		0.5
D-Panthenol (BASF)	Panthenol			0.5				0.5		0.5		
	Retinyl- Palmitate						0.5					
Frescolat® ML	Menthyl Lactate				0.5				0.5			
Fragrance	Fragrance/Parfum	qs	qs	qs	qs	qs	qs	qs	qs	qs		
	Creatinine	0.05	0.05									
EDTA BD® (BASF)	Disodium-EDTA	0.2	0.2	0.15	0.15	0.15	0.2	0.15	0.15	0.15	0.2	0.2

RAW MATERIAL NAME (MANUFACTURER)	INCI											
		1	2	3	4	5	6	7	8	9	10	11
1,3-Butylene glycol	1,3-Butylene Glycol					1.0						
Ethanol (96 %)	Ethyl Alcohol	3.0	3.0				3.0	3.0	2.0			
Glycerin 99 %	Glycerin	5.0	5.0	4.5		0	5.0	3.0	5.0	3.0	3.0	4.0
Hydrolite-5 (Symrise)	Pentylene Glycol	5.0	5.0	3.0	3.0	2.0	5.0	4.0	3.0			
Symdiol 68	1,2-hexylenediol and 1,2-Caprylyldiol				0.5							
1,2-Propylene glycol	Propylene Glycol					1.0				5.0		5.0
Soja extract	Glycine soja (soybean) germ extract				0.5					1.0	2.0	0.5
	Sodium Ascorbyl Phosphate				0.2							
DHA	Dihydroxyacetone					3.0			5.0			
Water soluble dyestuff		Qs	qs	qs	qs	qs	qs	qs	qs	qs	qs	qs
Plant Extract(s)		qs	qs	5.00	qs	qs	qs	qs	qs	5.0	qs	qs

2. W/O Emulsions:, SPF > 20

RAW MATERIAL NAME (MANUFACTURER)	INCI											
		1	2	3	4	5	6	7	8	9	10	
<u>Emulsifier</u>												
	Polyglyceryl 2-Dipolyhydroxystearate	4.0	5.0								3.0	2.5
	PEG-45/Dodecyl Glycol Copolymer					1.0						
	Polyglyceryl 3-Polyricinoleate										3.0	3.5
	Cetyl PEG/PPG-10/1-Dimethicone					1.5						
	Lauryl PEG/PPG-18/18 Methicone						3.0					

RAW MATERIAL NAME (MANUFACTURER)	INCI										
		1	2	3	4	5	6	7	8	9	10
	Cetearyl Alcohol, Peg-40 Castor Oil, Sodium Cetearyl Sulfate							3.75			
	PEG-30 Dipolyhydroxys- tearate			3.5	3.5		3.5	1.0			
	Polyglyceryl-3 Methylglu- cose Distearate					2.0			2.0		
	Sorbitan Stearate								1.0		
<u>Oil Soluble UV Filters</u>											
Neo Heliopan® AV (Symrise)	Ethylhexyl Methoxy- cinnamate	8.0	2.0		2.0	3.0					5.0
Neo Heliopan® 303 (Symrise)	Octocrylene	5.0	2.0	3.0	3.0	3.0	8.0		5.0	10.0	3.0
Neo Heliopan® 357 (Symrise)	Butyl Methoxydibenzoyl- methane	4.5	1.0		2.0	2.0	3.0	0.5	2.0	3.0	3.0
Neo Heliopan® E 1000 (Symrise)	Isoamyl p-Methoxy- cinnamate		1.0		1.0	3.0					5.0
Neo Heliopan® HMS (Symrise)	Homosalate		1.0		1.0	3.0	2.0			3.0	3.0
Neo Heliopan® OS (Symrise)	Ethylhexyl Salicylate		1.0		1.0	3.0	3.0			5.0	5.0
Neo Heliopan® MBC (Symrise)	4-Methylbenzylidene- camphor		0.5		0.5						1.0
Neo Heliopan® MA (Symrise)	Menthyl Anthranilate		1.0		0.5						
Neo Heliopan® BB (Symrise)	Benzophenone-3		1.0		1.0			0.5	0.5		
Mexoryl® XL	Drometrizole Trisiloxane		2.0		3.0		3.0				
Tinosorb® S	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	1.0	0.5	2.5	0.5	3.0				1.5	1.5
Uvinul® T-150	Ethylhexyl Triazone		0.5	2.0	0.5	3.0	1.0			1.0	1.0

RAW MATERIAL NAME (MANUFACTURER)	INCI	1	2	3	4	5	6	7	8	9	10
	-Bis[5- 1(dimethylpropyl)benzoxazo l-2-yl- 1.5 5 3 (4- phenyl)imino]-6-(2- ethylhexyl)imino-1,3,5- triazine	0.5	0.5		0.5						
Uvinul® A Plus	Diethylamino Hydroxyben- zoyl Hexylbenzoate	1.0	0.5	2.0	0.5	0.5				1.0	1.0
Indanylidene derivatives accord- ing to DE 10055940			0.5		0.5						
Benzoylcinnamyltri- nitride derivatives according to WO 2006/015954			0.5		0.5						
Parsol® SLX	Polysiloxane-15		1.0		1.0						3.0
Uvasorb® HEB	Diethylhexyl Butamido Triazone	0.5	0.5		0.5						
Benzylidene butyrolactones according to EP 1008593			0.5		0.5						
Benzylidene- dicarbonyl com- pounds described in WO/2005/107692			0.5		0.5						
Water Soluble UV Filters											
Neo Heliopan® AP (Symrise)	Disodium Phenyl- dibenzimidazoletetra- sulphonate	1.0	0.5	1.0	0.5	0.5	0.75	0.5	0.5	1.5	1.0
Neo Heliopan® Hydro (Symrise)	Phenylbenzimidazole- sulphonic Acid	0.75	1.3	2.0	1.0	1.25	1.5	2.0	2.0	1.0	1.0
Mexoryl® SX	Terephthalylidene Dicam- phor Sulfonic Acid		0.5		0.5		1.0				

RAW MATERIAL NAME (MANUFACTURER)	INCI	1	2	3	4	5	6	7	8	9	10
		Sulisobenzone	Benzophenone-4	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Neutralization base		qs	qs	qs	qs	qs	qs	qs	qs	qs	qs
Microfine UV attenuating Pigments											
	Titanium Dioxide	3.0	3.0	3.0	3.0	3.0		6.0	1.0	3.0	3.0
	Zinc Oxide							6.0			
Tinosorb M	Methylene Bis- Benzotriazolyl Tetramethyl- butylphenol		1.0		1.0						3.0
Other oil soluble components											
PCL Liquid 100	Cetearyl Octanoate										
Corapan TQ® (Symrise)	Diethylhexyl 1,6- Naphthalate							3.0			
Dragoxat 89 (Symrise)	Ethylhexyl Isononoate				1.0						
Isoadipate	Diisopropyl Adipate			3.0	5.0	5.0					
Isopropyl myristate (Symrise)	Isopropyl Myristate	3.0					2.0			4.0	
Neutral oil (Sym- rise)	Caprylic/Capric Triglyceride		5.0		3.0			5.0		4.0	4.0
Isodragol (Symrise)	Triisononanoïn								6.0		
	Isohexadecane						6.0				
	Dicaprylyl Carbonate			5.0			8.0				
Cetiol OE (Cognis)	Dicaprylyl Ether		5.0		5.0			1.0	3.0		
Paraffin oil	Mineral Oil										
Tegosoft TN® (Goldschmidt)	C12-15 Alkyl Benzoate	10.0	10.0	10.0	4.0	9.0			1.0	5.0	5.0
Abil 100® (Gold- schmidt)	Dimethicone		1.0		1.0				2.0		

RAW MATERIAL NAME (MANUFACTURER)	INCI	1	2	3	4	5	6	7	8	9	10
		Dow Corning® 193 Fluid (Dow corning)	PEG-12 Dimethicone						1.0		
	Cetyl Dimethicone				2.0					2.0	2.0
	Cyclomethicone					15					
	Cyclohexasiloxane						5.0				
	Cyclopentasiloxane						5.0				
	Simethicone									2.0	2.0
	Hydrogenated Coco- Glycerides				1.0			0.5			
	Butylene Glycol Dicapryla- te/Dicaprate	7.5	3.0		3.0	8.0		7.5			
	Trimethoxycaprylylsilane					0.2					
Lanette 16® (Cognis)	Cetyl Alcohol							1.0		0.5	0.5
Lanette 18 ® (Cognis)	Stearyl Alcohol								3.0		
alpha-Bisabolol (Symrise)	Bisabolol		0.2		0.2	0.2				0.1	0.1
Copherol 1250® (Cognis)	Tocopheryl Acetate	0.5	0.5	0.5	0.5	0.5	0.5	0.5		0.5	0.5
D-Panthenol (BASF)	Panthenol	0.5	0.5	0.5	0.5	0.5	0.5	0.5		0.5	0.5
	Retinyl Palmitate			0.5			0.5				
Fragrance	Fragrance/Parfum	qs	qs	qs	qs	qs	qs	qs	qs	qs	qs
	Creatinine	0.05	0.05	0.05							
	Taurine			1.0							
EDTA BD® (BASF)	Disodium-EDTA	0.2	0.2	0.15	0.15	0.15	0.2	0.15	0.15	0.15	0.15
Viscosity modifi- ers/stability aids											
Bentone Gel® M IO V (Elementis Specialties)	Mineral Oil and Distear- dimonium Hectorite and Propylene Carbonate								0.5		

RAW MATERIAL NAME (MANUFACTURER)	INCI	1	2	3	4	5	6	7	8	9	10
			Microcrystalline Wax								
	Beeswax				0.3						
	Tricontanyl PVP									2.0	2.0
Keltrol T® (Calgon)	Xanthan Gum							0.2			
Pemulen TR 2 (Novion)	Acrylates/C10-30 Alkyl Acrylate Crosspolymer				0.3				0.1		
	Sodium Starch Octenylsuc- cinate	0.5	0.5	0.4							
Aerosil® 200	Silica										
	Magnesium Sulfate	0.3	0.3	0.3							
	Sodium Chloride					0.5	0.5				
Other water soluble compo- nents											
Water	Water (Aqua)	qs	qs	qs	qs	qs	qs	qs	qs	qs	qs
Neutralisation base for acidic compo- nents such as carbomers, and/or stearic acid etc		qs	qs	qs	qs		qs		qs	qs	qs
Preservation agents		qs	qs	qs	qs	qs	qs	qs	qs	qs	qs
1,3-Butylene glycol	1,3-Butylene Glycol	5.0	5.0	3.0	3.0						
Ethanol (96 %)	Ethyl Alcohol	2.0	2.0	2.0	3.0	3.0	10.0	3.0	2.0	4.0	4.0
Glycerin 99 %	Glycerin	5.0	5.0	2.0	2.0	4.0	5.0	3.0	5.0	3.0	3.0
Hydrolite-5 (Sym- rise)	Pentylene Glycol	1.0	1.0	3.0	3.0	2.0	2.0	4.0	3.0		
Symdiol 68	1,2-hexylenediol and 1,2- Caprylyldiol			0.5	0.5	0.5					
1,2-Propylene glycol	Propylene Glycol						3.0			5.0	5.0
Soja extract	Glycine soja (soybean) germ extract			0.5	0.5						

RAW MATERIAL NAME (MANUFACTURER)	INCI	1	2	3	4	5	6	7	8	9	10
		Sodium Ascorbyl Phosphate				0.5	0.2	0.2			
Water soluble dyestuff		qs	qs	qs	qs	qs	qs	qs	qs	qs	qs
Plant Extract(s)		qs	qs	qs	qs	qs	qs	qs	qs	5.0	5.0

3. Spray / Mousse Emulsions:, SPF > 20

RAW MATERIAL NAME (MANUFACTURER)	INCI										
		1	2	3	4	5	6	7	8	9	10
<u>Emulsifier</u>											
	Polyglycery 2-Dipolyhydroxystearate	3.0									
	Disodium PEG-5 Lauryl Citrate Sulfosuccinate	2.5									
	Capryl/Capramidopropyl Betaine	0.7									
	Sodium Laureth Sulfate	0.3									
Emulgin B2® (Cognis)	Ceteareth-20		1.5	1.5							2.0
	Polyester-5				2.5						
	Sorbitan Laurate						2.5				
	Polyglycery I- 10 Laurate						2.0				
	PPG-15 Stearyl Ether							4.0			
	Polyacrylate-3				1.0						
	Stearyl Phosphate								2.5		
	Sorbitan Stearate										0.5
	Stearic Acid						1.0				1.0
	PEG 40 Stearate										1.0
<u>Oil Soluble UV Filters</u>											
Neo Heliopan® AV (Symrise)	Ethylhexyl Methoxy-cinnamate		6.0							5.0	6.0
Neo Heliopan® 303 (Symrise)	Octocrylene	5.0		8.0	10.0	10.0	5.0	4.0		4.0	
Neo Heliopan® 357 (Symrise)	Butyl Methoxydibenzoyl-methane	3.0	4.0	4.0	2.0	2.5	3.0	5.0		2.0	3.0
Neo Heliopan® E 1000 (Symrise)	Isoamyl p-Methoxy-cinnamate									5.0	
Neo Heliopan® HMS (Symrise)	Homosalate			3.0	3.0	5.0	5.0				3.0

RAW MATERIAL NAME (MANUFACTURER)	INCI										
		1	2	3	4	5	6	7	8	9	10
Benzylidene- dicarbonyl com- pounds described in WO 2005/107692										1.0	
Water Soluble UV Filters											
Neo Heliopan® AP (Symrise)	Disodium Phenyl- dibenzimidazole-tetra- sulphonate	0.5	15	1.5	0.75	0.5	1.0	2.2	2.0	1.0	0.75
Neo Heliopan® Hydro (Symrise)	Phenylbenzimidazole- sulphonic Acid	2.0	2.75	2.50	2.25	2.0	2.0	1.5	1.0	0.5	2.0
Mexoryl® SX	Terephthalylidene Dicam- phor Sulfonic Acid				1.0	0.5				0.5	
Sulisobenzone	Benzophenone-4	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Neutralisation base		qs	qs	qs	qs	qs	qs	qs	qs	qs	qs
Microfine UV attenuating Pigments											
	Titanium Dioxide				3.0					1.5	
	Zinc Oxide						3.0			1.5	
Tinosorb® M	Methylene Bis- Benzotriazolyl Tetramethyl- butylphenol		3.0	3.0						1.0	
Other oil soluble components											
PCL Liquid 100	Cetearyl Octanoate						10.0				
Corapan TQ® (Symrise)	Diethylhexyl 1,6- Naphthalate								3.0		
	C18-36 Acid Triglyceride		1.0	2.0						2.0	
Neutral oil (Sym- rise)	Caprylic/Capric Triglyceride	10							5.0		
Isodragol (Symrise)	Triisononanoin						2.0				
Cetiol OE (Cognis)	Dicaprylyl Ether						3.0		1.0		

RAW MATERIAL NAME (MANUFACTURER)	INCI										
		1	2	3	4	5	6	7	8	9	10
	Dicaprylyl Carbonate			5.0	2.0		2.0		5.0	10.0	
	Isohexadecane							3.0			
	Ethylhexylglycerin										0.5
	Cetyl Ricinoleate										0.1
Tegosoft TN® (Goldschmidt)	C12-15 Alkyl Benzoate	5.0			10.0	8.0	5.0		7.0		
Abil 100® (Gold- schmidt)	Dimethicone										4.0
Dow Corning® 193 Fluid (Dow corning)	PEG-12 Dimethiconel						1.0				
	Cyclohexasiloxane					10.0					
	Cyclopentasiloxane							2.0			
	Phenyl Trimethicone					3.0		2.0			
	Cyclomethicone							1.0	0.5		
	Butylene Glycol Dicapryla- te/Dicaprate		8.0	8.0					7.5	8.0	10.0
Lanette 16® (Cognis)	Cetyl Alcohol								1.0		0.5
alpha-Bisabolol (Symrise)	Bisabolol		0.3	0.3		0.2	0.1			0.3	
Copherol 1250® (Cognis)	Tocopheryl Acetate		0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	
D-Panthenol (BASF)	Panthenol		0.5	0.5	0.5		0.5		0.5	0.5	
	Retinyl- Palmitate							0.5			
Frescolat® ML	Menthyl Lactate						0.5				
Fragrance	Fragrance/Parfum	qs	qs	qs	qs	Qs	Qs	Qs	Qs	qs	Qs
	Taurine		1.0	1.0						1.0	0.5
	Creatinine		0.05	0.05						0.05	0.05
EDTA BD® (BASF)	Disodium-EDTA	0.2	0.2	0.2	0.15	0.15	0.15	0.2	0.15	0.2	0.15

RAW MATERIAL NAME (MANUFACTURER)	INCI										
		1	2	3	4	5	6	7	8	9	10
Viscosity modifiers/stability aids											
	Sodium Chloride	0.5									
Avicel PC 611 (FMC Corporation)	Microcrystalline Cellulose and Cellulose Gum					0.80					
Keltrol T® (Calgon)	Xanthan Gum						0.3		0.2		
Pemulen TR 2 (Novion)	Acrylates/C10-30 Alkyl Acrylate Crosspolymer		0.2	0.2		0.25			0.2	0.2	
<u>Film Forming Polymers</u>											
Antaron V-216/516	VP/Hexadecene Copolymer		0.5	0.5			2.0			0.5	
Dermacryl 79	Acrylates/Octylacrylamide Copolymer							1.0			
	Trimethylpentanediol adiopic acid glycerine copolymer							1.0			
Avalure UR 450/ 525	PPG-17/IPDI/DMPA copolymer			0.5						0.5	
Other water soluble compo- nents											
Water	Water (Aqua)	qs	qs	qs	qs	qs	Qs	Qs	Qs	Qs	Qs
Neutralisation base for acidic compo- nents such as carbomers, and/or stearic acid etc		qs	qs	qs	qs	qs	Qs	Qs		Qs	Qs
Preservation agents		qs	qs	qs	qs	qs	Qs	Qs	Qs	Qs	Qs
1,3-Butylene glycol	1,3-Butylene Glycol					3.0					
Ethanol (96 %)	Ethyl Alcohol	5.0	3.0	3.0	4.0	12.0		10.0		5.0	5.0
Glycerin 99 %	Glycerin	3.0	5.0	5.0	4.5		5.0		5.0	3.0	3.0
Hydrolite-5 (Sym- rise)	Pentylene Glycol		5.0	5.0	3.0					3.0	

4. Daily Protection Preparations:

RAW MATERIAL NAME (MANUFACTURER)	INCI	1	2	3	4	5	6	7	8	9
<u>Emulsifier</u>										
Emulsiphos (Symrise)	Potassium Cetyl Phosphate, Hydrogenated Palm Glyce- rides	1.5	1.5	1.5						
Dracorin CE	Glyceryl Stearate Citrate						2.5			
	PPG-1 Trideceth-6						0.5			
	Sorbitan Oleate						0.5			
	Sucrose stearate								0.8	
Hostaceron AMPS	Ammonium Polyacrylamido tauramide									2.0
	Polyglyceryl-3 Methylglu- cose Distearate							3.5		
	Sorbitan Stearate								2.0	
	Glyceryl Stearate									
	Isostearic Acid	1.0	1.0	1.0						
	Stearic Acid					2.0			1.0	4.0
	PEG 40 Stearate									1.0
	PEG 100 Stearate				0.2	2.0				
	PEG-4 Laurate								0.3	
Lanette E® (Cognis)	Sodium Cetearyl Sulphate									0.5
	Steareth-2				0.2					
	Steareth -21				1.0					
	Laureth-7				0.75					
<u>Oil Soluble UV Filters</u>										
Neo Heliopan® AV (Symrise)	Ethylhexyl Methoxy- cinnamate	8.0					4.0	3.0	5.5	5.0
Neo Heliopan® 303 (Symrise)	Octocrylene		3.0	3.0	1.0	2.0				

RAW MATERIAL NAME (MANUFACTURER)	INCI	1	2	3	4	5	6	7	8	9
		Neo Heliopan® 357 (Symrise)	Butyl Methoxydibenzoyl- methane	2.0	2.0	2.0	2.0	2.0	2.0	1.5
Neo Heliopan® HMS (Symrise)	Homosalate		3.0	3.0		5.0				
Neo Heliopan® OS (Symrise)	Ethylhexyl Salicylate		3.0	3.0	4.0	5.0			3.0	
Water Soluble UV Filters										
Neo Heliopan® AP (Symrise)	Disodium Phenyl- dibenzimidazole-tetra- sulphonate	0.25	0.5	0.5	1.0	1.25	1.0	1.5	2.0	0.5
Neo Heliopan® Hydro (Symrise)	Phenylbenzimidazole- sulphonic Acid	2.8	2.8	2.8	1.8	2.64	1.8	1.3	2.9	1.3
Mexoryl® SX	Terephthalylidene Dicam- phor Sulphonic Acid									0.5
Sulisobenzone	Benzophenone-4	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Neutralizing base		qs	qs	qs	qs	qs	qs	qs	qs	qs
Microfine UV attenuating Pigments										
	Titanium Dioxide				1.0	1.0				
Other oil soluble components										
Shea Butter	Butyrospermum Parkii									2.0
Corapan TQ® (Symrise)	Diethylhexyl 1,6- Naphthalate									
Dragoxat 89 (Symrise)	Ethylhexyl Isononoate	3.0	3.0	3.0		3.0				
Isoadipate	Diisopropyl Adipate					3.0				
Isopropyl myristate (Symrise)	Isopropyl Myristate				5.0	5.0				
	Tridecyl Trimellitate						2.0			
	Myristyl Myristate							5.0		

RAW MATERIAL NAME (MANUFACTURER)	INCI	1	2	3	4	5	6	7	8	9
		Neutral oil (Symrise)	Caprylic/Capric Triglyceride						3.0	
Cetiol OE (Cognis)	Dicaprylyl Ether						2.0			
	Dicaprylyl Carbonate	2.0	2.0	2.0				3.0		
	Isohexadecane								8.0	
	Ethylhexylglycerin						0.5			
Paraffin oil	Mineral Oil				2.0		0.5			
Tegosoft TN® (Goldschmidt)	C12-15 Alkyl Benzoate							3.0		
Abil 100® (Goldschmidt)	Dimethicone				1.0			2.0		1.0
Dow Corning® 193 Fluid (Dow corning)	PEG-12 Dimethicone				1.0	1.0				
	Hydrogenated Coco-Glycerides						1.0	0.5		
	Butylene Glycol Dicaprylate/Dicaprate							7.5		
	Dibutyl Adipate				2.0					
Lanette O® (Cognis)	Cetearyl Alcohol				1.5					
Lanette 16® (Cognis)	Cetyl Alcohol	0.5	0.5	0.5	0.5	0.5	0.5	2.0	0.2	
Lanette 18® (Cognis)	Stearyl Alcohol				0.5	0.5			4.5	
	Myristyl Alcohol								1.0	
Ceramide(s)									0.5	
alpha-Bisabolol (Symrise)	Bisabolol				0.2	0.1	0.2	0.1		
Copherol 1250® (Cognis)	Tocopheryl Acetate	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
D-Panthenol (BASF)	Panthenol	1.0	1.0	1.0	0.5	0.5	0.5		0.5	0.5

Claims

1. Use of benzophenone-4 (2-Hydroxy-4-methoxybenzophenone-5-sulfonic acid) to quench the fluorescence of disodium phenyl dibenzimidazole tetrasulfonic acid or its salts.
5
2. Use according to claim 1 in a cosmetic and/or dermatological preparation.
3. Use according to any of claims 1 or 2, wherein the molar ratio of benzophenone-4 to disodium phenyl dibenzimidazole tetrasulfonic acid or its salts is in the range from 0.1 : 5.0 to 5.0 : 0.1.
10
4. Use of a mixture comprising benzophenone-4 and disodium phenyl dibenzimidazole tetrasulfonic acid or a salt thereof for synergistically enhancing UV absorption properties of a further UV filter.
15
5. Method for quenching the fluorescence of disodium phenyl dibenzimidazole tetrasulfonic acid or any of its salts, preferably in a cosmetic and dermatological preparation, comprising the step of combining disodium phenyl dibenzimidazole tetrasulfonic acid or a salt thereof with benzophenone-4, wherein benzophenone-4 is provided in an amount sufficient to quench the fluorescence of disodium phenyl dibenzimidazole tetrasulfonic acid or its respective salt.
20
6. Method according to claim 4, wherein the disodium phenyl dibenzimidazole tetrasulfonic acid or its salt is provided in a cosmetically or pharmaceutically acceptable carrier.
25
7. Preparation comprising disodium phenyl dibenzimidazole tetrasulfonic acid and/or one or more salts thereof, further comprising benzophenone-4 and/or one or more salts thereof, in an amount sufficient to reduce the fluorescence of disodium phenyl dibenzimidazole tetrasulfonic acid and, if present, its respective salt(s).
30

8. Preparation according to claim 7, wherein the molar ratio of the total amount of benzophenone-4 and its salts to the total amount of disodium phenyl dibenzimidazole tetrasulfonic acid and its salts is in the range from 0.1 : 5.0 to 5.0 : 0.1.

5

9. Preparation according to any of claims 7 or 8, wherein the preparation is a cosmetic or pharmaceutical preparation.

10. Preparation according to any of claims 7, 8 and 9, comprising a further UV filter, wherein the total amount of benzophenone-4 and its salts and of disodium phenyl dibenzimidazole tetrasulfonic acid and its salts is sufficient for synergistically enhancing the UV absorption properties of said further UV filter.

11. Preparation according to any of claims 7, 8, 9 and 10, having a sun protection factor of at least 2.

12. Preparation according to any of claims 7 to 11, further comprising at least one additional UV absorbing substance selected from the group consisting of

- p-aminobenzoic acid
- 20 - 3-(4'-trimethylammonium)benzylidenebornan-2-one methyl sulphate
- homomenthyl salicylate
- terephthalylidenedibornanesulphonic acid and salts
- 4-tert-butyl-4'-methoxydibenzoylmethane
- 3-(4'-sulpho)benzylidenebornan-2-one and salts
- 25 - 2-ethylhexyl 2-cyano-3,3-diphenylacrylate
- N-[(2 and 4)-[2-(oxoborn-3-ylidene)methyl]benzyl]acrylamide polymer
- 2-ethylhexyl p-methoxycinnamate
- ethyl p-aminobenzoate (25 mol) ethoxylated
- isoamyl p-methoxycinnamate

- 2,4,6-trianilino(p-carbo-2'-ethylhexyl-1'-oxy)-1,3,5-triazine
- phenol, 2-(2H-benzotriazol-2-yl)-4-methyl-6-(2-methyl-3(1,3,3,3-tetramethyl-1-(trimethylsilyl)oxy)disiloxyanyl)propyl)
- 5 - 4,4'-[(6-[4-(1,1-dimethyl)aminocarbonyl]phenylamino)-1,3,5-triazin-2,4-diyl]-diimino]bis(benzoic - acid 2-ethylhexyl ester)
- 3-(4'-methylbenzylidene)-d,l-camphor
- 3-benzylidenecamphor
- 2-ethylhexyl salicylate
- 2-ethylhexyl 4-dimethylaminobenzoate
- 10 - hydroxy-4-methoxybenzophenone (Benzophenone-3, Oxybenzone)
- 2,2'-methylenebis(6-(2H-benzotriazol-2-yl)-4-1,1,3,3-tetramethylbutyl)-phenol)
- 2,4-bis[{{(4-(2-ethylhexyloxy)-2-hydroxy}phenyl)]-6-(4-methoxyphenyl)-1,3,5-triazine
- 15 - benzylidenemalonate-polysiloxane
- menthyl anthranilate
- hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate
- indanylidene compounds as per DE 100 55 940
- Benzoylcinnamyl nitriles described in WO 2006/015954
- 20 - Benzylidene butyrolactones described in EP 1008593
- Benzylidene- β -dicarbonyl compounds described in WO 2005/107692
- microfine titanium dioxide
- Zinc oxide
- Microfine zinc oxide.