

US 20030124075A1

(19) United States

Patent Application Publication (10) Pub. No.: US 2003/0124075 A1 Biatry et al. (43) Pub. Date: Jul. 3, 2003

(54) USE OF A COMPOSITION CONTAINING AT LEAST ONE OXIDATION-SENSITIVE HYDROPHILIC ACTIVE PRINCIPLE AND AT LEAST ONE N-VINYLIMIDAZOLE POLYMER OR COPOLYMER

(75) Inventors: **Bruno Biatry**, Vincennes (FR); **Eric Lheureux**, Montgeron (FR)

Correspondence Address:
OBLON, SPIVAK, MCCLELLAND, MAIER &
NEUSTADT, P.C.
1940 DUKE STREET
ALEXANDRIA, VA 22314 (US)

(73) Assignee: L'OREAL, Paris (FR)

(21) Appl. No.: 10/304,861

(22) Filed: Nov. 27, 2002

(30) Foreign Application Priority Data

Publication Classification

(57) ABSTRACT

The invention relates to the use of a composition contains at least one oxidation-sensitive hydrophilic active principle selected from the group consisting of ascorbic acid and its derivatives and at least one non-crosslinked N-vinylimidazole polymer or copolymer, the active principle and the said polymer or copolymer both being in the aqueous phase, for lightening and/or depigmenting the skin and/or hair, including body hair.

USE OF A COMPOSITION CONTAINING AT LEAST ONE OXIDATION-SENSITIVE HYDROPHILIC ACTIVE PRINCIPLE AND AT LEAST ONE N-VINYLIMIDAZOLE POLYMER OR COPOLYMER

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to the use of a composition comprising at least one oxidation-sensitive hydrophilic active principle and at least one N-vinylimidazole polymer or copolymer, preferably in a physiologically acceptable medium comprising an aqueous phase. Preferably the use is a cosmetic and/or dermatological use related to lightening or depigmenting the skin and/or the hair, and is thus preferably targeted to skin and/or hair to be lightened.

[0003] 2. Background of the Invention

[0004] It is known to introduce, into cosmetic compositions, various active principles intended to contribute specific treatments to the skin and/or hair. However, some of these active principles exhibit the disadvantage of being unstable in an aqueous medium and of easily decomposing on contact with water, in particular because of oxidation phenomena. They thus rapidly lose their activity over time and this instability conflicts with the desired effectiveness.

[0005] Attempts have thus been made for a long time to formulate ascorbic acid or vitamin C because of its numerous beneficial properties. In particular, ascorbic acid stimulates the synthesis of the connective tissue and in particular of collagen, strengthens the defences of the cutaneous tissue against external attacks, such as ultraviolet radiation and pollution, compensates for vitamin E deficiency of the skin, depigments the skin and has a role in combatting free radicals. These last two properties make it an excellent candidate as cosmetic or dermatological active principle for combatting ageing of the skin or for preventing ageing of the skin. Unfortunately, because of its chemical structure (of α-ketolactone), ascorbic acid is highly sensitive to certain environmental parameters and in particular to oxidation phenomena. There thus ensues rapid decomposition of formulated ascorbic acid in the presence of these parameters and in particular in the presence of oxygen, light or metal ions, as a function of the temperature or under certain pH conditions (Pharm. Acta. Helv., 1969, 44, 611-667; STP Pharma, 1985, 4, 281-286).

[0006] Several solutions have thus been envisaged in the prior art for reducing and/or slowing down the decomposition of ascorbic acid.

[0007] Provision has thus been made to use ascorbic acid in the form of a chemical derivative (magnesium ascorbyl phosphate or esters of fatty acids and ascorbic acid), but the bioavailability of these derivatives is very low (J. Am. Acad. Dermatol., 1996, 34, 29-33).

[0008] The instability of ascorbic acid with respect to oxygen can be improved by using specific packagings, such as twin compartments under an inert atmosphere, as disclosed in U.S. Pat. No. 5,935,584, or alternatively by the use of two-phase emulsions, one phase of which is composed of a dry powder comprising ascorbic acid and the second phase of which is a liquid phase. The mixing of the two phases has

to be carried out at the time of use (WO 98/43598). These solutions have disadvantages with regard to the cost and the complexity of the manufacturing operations and significant restrictions with regard to use.

[0009] Another solution provided in the prior art consists in using a high concentration of glycols or polyols in order to reduce the solubility of oxygen in the formulation, thus protecting the ascorbic acid (WO 96/24325, EP 0 755 674, U.S. Pat. No. 5,981,578). The polyols can optionally be incorporated in liposomes, as disclosed in U.S. Pat No. 6,020,367. However, these solutions exhibit the disadvantage of resulting in sticky formulations, the cosmetic quality of which is difficult to improve. Furthermore, the presence of a high concentration of these compounds can lead to phenomena of irritation.

[0010] Ascorbic acid can also be formulated in anhydrous media, such as silicones (U.S. Pat. No. 6,194,452), which are capable of creating an anhydrous barrier around ascorbic acid. A major disadvantage of such solutions results from the lack of freshness on application.

[0011] The need thus remains for a composition employable in particular in the cosmetics field, in which a hydrophilic active principle which is unstable in an oxidizing medium is stabilized, which is comfortable on application, which does not lead to any skin irritation after application and which is compatible with the constraints of an industrial implementation of its manufacturing process.

[0012] The activity of ascorbic acid or of its derivatives on pigmentation has been known for many years. Various mechanisms have been described to explain their effect on the reduction of melanogenesis. The inhibiting effect on tyrosinase has been demonstrated for ascorbic acid (J. Soc. Cosmet. Chem., 42, 1991, p. 361-368). Some of its esters have been used for some years in depigmenting treatments, that is to say, magnesium ascorbyl phosphate and ascorbyl glucoside. More recently, a study has shown that magnesium ascorbyl phosphate can reduce the dendricity of melanocytes (Pigment. Cell. Res., 13, 2000, p. 89-98 and p. 190-192).

OBJECTS OF THE INVENTION

[0013] One object of the present invention is to provide a composition comprising an oxidation-sensitive active principle selected from the group consisting of ascorbic acid and its derivatives, which exhibits good cosmetic properties, both with regard to touch and with regard to tolerance, the preservation of which over time does not require specific precautions, and which retains the depigmenting and/or lightening ability of the active principle.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The Inventors have discovered that the use of non-crosslinked N-vinylimidazole polymers or copolymers in compositions in which the aqueous phase includes an oxidation-sensitive active principle, such as ascorbic acid, makes it possible to achieve the abovementioned object.

[0015] In the prior art, some compounds having an imidazole structure have been disclosed for their stabilizing properties. Thus, in Patent Application EP 0 586 106, several imidazole-based molecules are used to stabilize certain retinoids against chemical decomposition. Furthermore,

polymeric emulsifiers composed of N-vinylimidazole, of alkyl acrylates and of vinyl acetates are disclosed in U.S. Pat. No. 4,057,622. They are used for the purpose of replacing known emulsifiers in order to overcome their disadvantages, in particular with regard to smell, and to stabilize water-in-oil emulsions. Finally, N-vinylimidazole/N-vinylcaprolactam/N-vinylpyrrolidone copolymers are disclosed in U.S. Pat. No. 6,191,188. They are used in the manufacture of hair-strengthening compositions.

[0016] To the knowledge of the inventors, polymers or copolymers comprising N-vinylimidazole units have never been used in combination with hydrophilic active principles sensitive to decomposition by oxidation for the purpose of improving their stability in an aqueous medium. This is true in particular in the case of ascorbic acid.

[0017] One embodiment of the present invention is therefore the preferably cosmetic and/or dermatological use of a composition for depigmenting and/or lightening the skin and/or hair, including body hair, the composition comprising, preferably in a physiologically acceptable medium comprising an aqueous phase, at least one oxidation-sensitive hydrophilic active principle selected from the group consisting of ascorbic acid and its derivatives and at least one non-crosslinked N-vinylimidazole polymer or copolymer, the active principle and the polymer or copolymer both being present in the aqueous phase. The copolymer is preferably present in an amount sufficient to stabilize the said oxidation-sensitive hydrophilic active principle.

[0018] The use of such a composition furthermore exhibits the advantage of acting both by inhibiting tyrosinase, thus reducing melanogenesis, and also by inhibiting the dendricity of melanocytes. The depigmenting effect thus obtained is much greater than that obtained, for example, with ascorbic acid alone, which acts solely on melanogenesis.

[0019] Another embodiment of the present invention is the use of a combination composed of at least one oxidation-sensitive hydrophilic active principle selected from the group consisting of ascorbic acid and its derivatives and of at least one non-crosslinked N-vinylimidazole polymer or copolymer, the active principle and the polymer or copolymer both being in the aqueous phase, in a cosmetic composition, as depigmenting agent.

[0020] According to the invention, the term "hydrophilic active principle" is understood to mean a compound having a solubility in water of at least 0.25% at ambient temperature (25° C.).

[0021] According to the invention, the term "oxidation-sensitive hydrophilic active principle" is understood to mean any active principle of natural or synthetic origin capable of undergoing decomposition by an oxidation mechanism. This oxidation phenomenon can have several causes, in particular the presence of oxygen, of light or of metal ions, a high temperature or certain pH conditions.

[0022] Mention may be made, by way of example and without implied limitation, of: ascorbic acid and its derivatives, such as salts and esters thereof, particularly the 5,6-di-O-dimethylsilylascorbate (sold by Exsymol under the reference PRO-AA), the potassium salt of dl- α -tocopheryl dl-ascorbyl phosphate (sold by Senju Pharmaceutical under the reference SEPIVITAL EPC), magnesium ascorbyl phosphate or sodium ascorbyl phosphate (sold by Roche under the reference Stay-C 50).

[0023] In a particularly advantageous aspect, the oxidation-sensitive hydrophilic active principle is ascorbic acid. Other preferred principles meet the above requirements and possess the ability to lighten the skin and/or the hair.

[0024] The oxidation sensitive hydrophilic active principle is preferably present in an amount sufficient to lighten the hair and/or skin, which amount is determinable by one of ordinary skill without undue effort. Example amounts include 1-10% based on total weight.

[0025] According to the invention, the term "non-crosslinked N-vinylimidazole polymer or copolymer" is understood to mean any polymer comprising N-vinylimidazole units and not comprising a crosslinking agent. Copolymers suitable for the implementation of the invention are copolymers combining N-vinylimidazole with N-vinylpyrrolidone and/or N-vinylcaprolactam subunits.

[0026] In an advantageous aspect of the invention, the copolymer has a molar fraction of N-vinylimidazole units of between 0.1 and 1, more preferably between 0.4 and 0.9.

[0027] According to an advantageous aspect of the invention, the molar ratio of the N-vinylimidazole unit equivalent to the oxidation-sensitive hydrophilic active principle varies between 0.004 and 16 and preferably between 0.01 and 1.

[0028] Use is preferably made of an N-vinylimidazole/N-vinylpyrrolidone copolymer.

[0029] The weight-average molar mass of the N-vinylimidazole polymers is preferably between 1 000 and 1×10^7 and more preferably between 5 000 and 5×10^6 .

[0030] Use may be made, to this end, of the vinylpyrrolidone/vinylimidazole (50/50) copolymer having a weight-average molar mass of 1 200 000 sold under the reference LUVITEC VPI 55K72W by BASF or the vinylpyrrolidone/vinylimidazole (50/50) copolymer having a weight-average molar mass of 10 000 sold under the reference LUVITEC VPI 55K18P by BASF. The polymers or copolymers according to the invention can, for example, be prepared according to the method disclosed in Patent Application WO-97/45517.

[0031] The at least one polymer or copolymer is preferably present in the composition according to the invention in an amount sufficient to produce the desired effect, that is to say in an amount sufficient to stabilize the oxidation-sensitive hydrophilic active principle. Preferably, the polymer or copolymer is present at a concentration of between 0.1 and 5% by weight with respect to the total weight of the aqueous phase and more particularly at a concentration of between 0.1 and 2% by weight with respect to the total weight of the aqueous phase.

[0032] The compositions used according to the invention are preferably intended for topical application to the skin and/or its superficial body growths and therefore comprise a physiologically acceptable medium, that is to say a medium compatible with cutaneous tissues, such as the skin, scalp, eyelashes, eyebrows, hair, nails and mucous membranes. This physiologically acceptable medium comprises at least one aqueous phase and optionally a physiologically acceptable organic solvent chosen, for example, from lower alcohols comprising from 1 to 8 carbon atoms and in particular from 1 to 6 carbon atoms, such as ethanol, isopropanol, propanol or butanol; polyethylene glycols having from 6 to

80 ethylene oxide units; or polyols, such as propylene glycol, isoprene glycol, butylene glycol, glycerol or sorbitol.

[0033] When the physiologically acceptable medium is an aqueous medium, it generally has a pH which is compatible with the skin, preferably ranging from 3 to 9 and better still from 3.5 to 7.5.

[0034] The compositions according to the invention can be provided in any form, including any pharmaceutical dosage form used for topical application and in particular in the form of aqueous or aqueous/alcoholic solutions, of oil-inwater (O/W) or water-in-oil (W/O) or multiple (triple: W/O/W or O/W/O) emulsions, of aqueous gels or of dispersions of a fatty phase in an aqueous phase using spherules, it being possible for these spherules to be polymeric nanoparticles, such as nanospheres and nanocapsules, or lipid vesicles of ionic and/or nonionic type (liposomes, niosomes or oleosomes). These compositions are prepared according to the usual methods.

[0035] In addition, the compositions used according to the invention can be more or less fluid and can have the appearance of a white or coloured cream, of an ointment, of a milk, of a lotion, of a serum, of a paste or of a foam. They can optionally be applied to the skin in the form of an aerosol. They can also be provided in a solid form, for example in the form of a stick.

[0036] When the composition used according to the invention comprises an oily phase, the latter preferably comprises at least one oil. It can additionally comprise other fatty substances.

[0037] Mention may be made, as oils which can be used in the composition of the invention, of, for example:

[0038] hydrocarbonaceous oils of animal origin, such as perhydrosqualene;

[0039] hydrocarbonaceous oils of vegetable origin, such as liquid triglycerides of fatty acids comprising from 4 to 10 carbon atoms, such as triglycerides of heptanoic acid or octanoic acid, or alternatively, for example, sunflower, maize, soybean, gourd, grape seed, sesame, hazelnut, apricot, macadamia, arara, castor or avocado oils, triglycerides of caprylic/capric acids, such as those sold by Stéarineries Dubois or those sold under the names Miglyol 810, 812 and 818 by Dynamit Nobel, jojoba oil, or karite butter oil;

[0040] synthetic esters and ethers, in particular of fatty acids, such as the oils of formulae R¹COOR² and R¹OR² in which R¹ represents the residue of a fatty acid comprising from 8 to 29 carbon atoms and R² represents a branched or unbranched hydrocarbonaceous chain comprising from 3 to 30 carbon atoms, such as, for example, purcellin oil, isononyl isononanoate, isopropyl myristate, 2-ethylhexyl palmitate, 2-octyldodecyl stearate, 2-octyldodecyl erucate or isostearyl isostearate; hydroxylated esters, such as isostearyl lactate, octyl hydroxystearate, octyldodecyl hydroxystearate, diisostearyl malate, triisocetyl citrate or heptanoates, octanoates or decanoates of fatty alcohols; polyol esters, such as propylene glycol dioctanoate, neopentyl glycol

diheptanoate and diethylene glycol diisononanoate; and pentaerythritol esters, such as pentaerythrityl tetraisostearate;

[0041] linear or branched hydrocarbons of mineral or synthetic origin, such as volatile or nonvolatile liquid paraffins and their derivatives, liquid petrolatum, polydecenes or hydrogenated polyisobutene, such as parleam oil;

[0042] fatty alcohols having from 8 to 26 carbon atoms, such as cetyl alcohol, stearyl alcohol and their mixture (cetearyl alcohol), octyldodecanol, 2-butyloctanol, 2-hexyldecanol, 2-undecylpentadecanol, oleyl alcohol or linoleyl alcohol;

[0043] partially hydrocarbon-comprising and/or silicone-comprising fluorinated oils, such as those disclosed in the document JP-A-2-295912;

[0044] silicone oils, such as volatile or nonvolatile polymethylsiloxanes (PDMS) comprising a linear or cyclic silicone chain which are liquid or pasty at ambient temperature, in particular cyclopolydimethylsiloxanes (cyclomethicones), such as cyclohexasiloxane; polydimethylsiloxanes comprising pendent alkyl, alkoxy or phenyl groups or alkyl, alkoxy or phenyl groups at the end of the silicone chain, which groups have from 2 to 24 carbon atoms; or phenyl atted silicones, such as phenyl trimethicones, phenyl dimethicones, phenyl dimethicones, in phenyltrimethylsiloxydiphenylsiloxanes, diphenyl dimethicones, diphenyltrimethylsiloxydiphenyltrisiloxanes, (2-phenylethyl)trimethylsiloxysilicates and polymethylphenylsiloxanes;

[0045] their mixtures.

[0046] The term "hydrocarbonaceous oil" is understood to mean, in the list of the oils mentioned above, any oil predominantly comprising carbon and hydrogen atoms and optionally ester, ether, fluorinated, carboxylic acid and/or alcohol groups.

[0047] The other fatty substances which can be present in the oily phase are, for example, fatty acids comprising from 8 to 30 carbon atoms, such as stearic acid, lauric acid, palmitic acid and oleic acid; waxes, such as lanolin, beeswax, carnauba or candelilla wax, paraffin or lignite waxes or microcrystalline waxes, ceresin or ozokerite, or synthetic waxes, such as polyethylene waxes or Fischer-Tropsch waxes; silicone resins, such as trifluoromethyl C_{1-4} alkyl dimethicone and trifluoropropyl dimethicone; and silicone elastomers, such as the products sold under the names "KSG" by Shin-Etsu, under the names "Trefil", "BY29" or "EPSX" by Dow Corning or under the names "Gransil" by Grant Industries.

[0048] These fatty substances can be chosen in a way varied by a person skilled in the art in order to prepare a composition having the desired properties, for example of consistency or of texture, in view of this disclosure.

[0049] According to a specific embodiment of the invention, the composition according to the invention is a waterin-oil (W/O) or oil-in-water (O/W) emulsion. The proportion of the oily phase in the emulsion can range from 5 to 80% by weight and preferably from 5 to 50% by weight with respect to the total weight of the composition.

[0050] The emulsions generally preferably comprise at least one emulsifier selected from the group consisting of amphoteric, anionic, cationic or nonionic emulsifiers, used alone or as a mixture, and optionally a coemulsifier. The emulsifiers are appropriately chosen according to the emulsion to be obtained (W/O or O/W). The emulsifier and the coemulsifier are generally preferably present in the composition in a proportion ranging from 0.3 to 30% by weight and preferably from 0.5 to 20% by weight with respect to the total weight of the composition.

[0051] Mention may be made, for the W/O emulsions, for example, as emulsifiers, of dimethicone copolyols, such as the mixture of cyclomethicone and of dimethicone copolyol sold under the name "DC 5225 C" by Dow Corning, and alkyl dimethicone copolyols, such as the laurylmethicone copolyol sold under the name "Dow Corning 5200 Formulation Aid" by Dow Coming and the cetyl dimethicone copolyol sold under the name Abil EM 90^R by Goldschmidt. Use may also be made, as surfactant of W/O emulsions, of a crosslinked solid organopolysiloxane elastomer comprising at least one oxyalkylenated group, such as those obtained according to the procedure of Examples 3, 4 and 8 of the document U.S. Pat. No. 5,412,004 and the examples of the document U.S. Pat. No. 5,811,487, in particular the product of Example 3 (synthetic example) of U.S. Pat. No. 5,412, 004, and such as that sold under the reference KSG 21 by Shin Etsu. Use may also be made, as emulsifier, of a polyolefin-derived oligomer or polymer comprising a succinic ending; the latter is preferably a polyolefin comprising an esterified or amidated succinic ending or a salt of such a polyolefin and in particular polyisobutylene comprising an esterified or amidated succinic ending such as the products sold under the names L5603 and L2721 and OS131769 by

[0052] Mention may be made, for the O/W emulsions, for example, as emulsifiers, of nonionic emulsifiers, such as esters of fatty acids and of glycerol which are oxyalkylenated (more particularly polyoxyethylenated); esters of fatty acids and of sorbitan which are oxyalkylenated; esters of fatty acids which are oxyalkylenated (oxyethylenated and/or oxypropylenated); ethers of fatty alcohols which are oxyethylenated (oxyethylenated and/or oxypropylenated); sugar esters, such as sucrose stearate; and their mixtures, such as the mixture of glyceryl stearate and of PEG-40 stearate.

[0053] The cosmetic or dermatological composition of the invention can also comprise adjuvants known in the cosmetics or dermatological field, such as hydrophilic or lipophilic gelling agents, preservatives, solvents, fragrances, fillers, UV screening agents, bactericides, odour absorbers, colouring materials, plant extracts or salts. The amounts of these various adjuvants are those generally used in the field under consideration, for example from 0.01 to 20% of the total weight of the composition. These adjuvants, depending on their nature, can be introduced into the fatty phase, into the aqueous phase and/or into the lipid spherules.

[0054] Mention may be made, as fillers which can be used in the composition of the invention, for example, of pigments, silica powder; talc; particles of polyamide and in particular those sold under the name Orgasol by Atochem; polyethylene powders; microspheres based on acrylic copolymers, such as those made of ethylene glycol dimethacrylate/lauryl methacrylate copolymer which are

sold by Dow Corning under the name Polytrap; expanded powders, such as hollow microspheres and in particular the microspheres sold under the name Expancel by Kemanord Plast or under the name Micropearl F 80 ED by Matsumoto; silicone resin microbeads, such as those sold under the name Tospearl by Toshiba Silicone; and their mixtures. These fillers can be present in amounts ranging from 0 to 20% by weight and preferably from 1 to 10% by weight with respect to the total weight of the composition.

[0055] According to a preferred embodiment, the compositions in accordance with the invention can additionally comprise at least one organic photoprotective agent and/or at least one inorganic photoprotective agent which is active in the UV-A and/or UV-B regions (absorbers), and which are soluble in water or in fats or else are insoluble in the cosmetic solvents commonly used.

[0056] The organic photoprotective agents are chosen in particular from anthranilates; cinnamic derivatives; dibenzoylmethane derivatives; salicylic derivatives; camphor derivatives; triazine derivatives, such as those disclosed in Patent Applications U.S. Patent No. 4,367,390, EP 863 145, EP 517 104, EP 570 838, EP 796 851, EP 775 698, EP 878 469, EP 933 376, EP 507 691, EP 507 692, EP 790 243 and EP 944 624; benzophenone derivatives; β,β-diphenylacrylate derivatives; benzotriazole derivatives; benzalmalonate derivatives; benzimidazole derivatives; imidazolines; bisbenzoazolyl derivatives as disclosed in Patents EP 669 323 and U.S. Pat. No. 2,463,264; p-aminobenzoic acid (PABA) derivatives; methylenebis(hydroxyphenylbenzotriazole) derivatives as disclosed in Applications U.S. Pat. No. 5,237, 071, U.S. Pat. No. 5,166,355, GB 2 303 549, DE 197 26 184 and EP 893 119; screening polymers and screening silicones, such as those disclosed in particular in Application WO 93/04665; dimers derived from α -alkylstyrene, such as those disclosed in Patent Application DE 198 55 649; 4,4-diarylbutadienes as disclosed in Applications EP 0 967 200, DE 197 46 654, DE 197 55 649, EP-A-1 008 586, EP 1 133 980 and EP 133 981; and their mixtures.

[0057] By way of illustration, mention may be made, as photoprotective agents which are active in the UV-A and/or UV-B regions, denoted below under their INCI names, of:

[0058] p-aminobenzoic acid (PABA) derivatives, in particular PABA, ethyl PABA, ethyl dihydroxypropyl PABA, ethylhexyl dimethyl PABA (sold in particular under the name "Escalol 507" by ISP), glyceryl PABA or PEG-25 PABA (sold under the name "Uvinul P25" by BASF),

[0059] salicylic derivatives, in particular homosalate (sold under the name "Eusolex HMS" by Rona/EM Industries), ethylhexyl salicylate (sold under the name "Neo Heliopan OS" by Haarmann and Reimer), dipropylene glycol salicylate (sold under the name "Dipsal" by Scher), or TEA salicylate (sold under the name "Neo Heliopan TS" by Haarmann and Reimer),

[0060] dibenzoylmethane derivatives, in particular butyl methoxydibenzoylmethane (sold in particular under the trade name "Parsol 1789" by Hoffmann-LaRoche), or isopropyl dibenzoylmethane,

[0061] cinnamic derivatives, in particular ethylhexyl methoxycinnamate (sold in particular under the trade

name "Parsol MCX" by Hoffmann-LaRoche), isopropyl methoxycinnamate, isoamyl methoxycinnamate (sold under the trade name "Neo Heliopan E 1000" by Haarmann and Reimer), cinoxate, DEA methoxycinnamate, diisopropyl methyl cinnamate, or glyceryl ethylhexanoate dimethoxycinnamate,

[0062] β , β -diphenylacrylate derivatives, in particular octocrylene (sold in particular under the trade name "Uvinul N539" by BASF) or etocrylene (sold in particular under the trade name "Uvinul N35" by BASF),

[0063] benzophenone, in particular benzophenone-1 (sold under the trade name "Uvinul 400" by BASF), benzophenone-2 (sold under the trade name "Uvinul D50" by BASF), benzophenone-3 or oxybenzone (sold under the trade name "Uvinul M40" by BASF), benzophenone-4 (sold under the trade name "Uvinul MS40" by BASF), benzophenone-5, benzophenone-6 (sold under the trade name "Helisorb 11" by Norquay), benzophenone-8 (sold under the trade name "Spectra-Sorb UV-24" by American Cyanamid), benzophenone-9 (sold under the trade name "Uvinul DS-49" by BASF), benzophenone-12, or n-hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate,

[0064] benzylidene camphor derivatives, in particular 3-benzylidene camphor (manufactured under the name "Mexoryl SD" by Chimex), 4-methylbenzylidene camphor (sold under the name "Eusolex 6300" by Merck), benzylidene camphor sulphonic acid (manufactured under the name "Mexoryl SL" by Chimex), camphor benzalkonium methosulphate (manufactured under the name "Mexoryl SO" by Chimex), terephthalylidene dicamphor sulphonic acid (manufactured under the name "Mexoryl SX" by Chimex), or polyacrylamidomethyl benzylidene camphor (manufactured under the name "Mesoryl SW" by Chimex),

[0065] benzimidazole derivatives, in particular phenylbenzimidazole sulphonic acid (sold in particular under the trade name "Eusolex 232" by Merck), or disodium phenyl dibenzimidazole tetrasulphonate (sold under the trade name "Neo Heliopan AP" by Haarmann and Reimer),

[0066] triazine derivatives, in particular anisotriazine (sold under the trade name "Tinosorb S" by Ciba Specialty Chemicals), ethylhexyl triazone (sold in particular under the trade name "Uvinul T150" by BASF), diethylhexyl butamido triazone (sold under the trade name "Uvasorb HEB" by Sigma 3V) or 2,4,6-tris(diisobutyl 4'-amino-benzalmalonate)-s-triazine,

[0067] benzotriazole derivatives, in particular drometrizole trisiloxane (sold under the name "Silatrizole" by Rhodia Chimie) or methylene bisbenzotriazolyl tetramethylbutylphenol (sold in the solid form under the trade name "Mixxim BB/100" by Fairmount Chemical or in the micronized form in aqueous dispersion under the trade name "Tinosorb M" by Ciba Specialty Chemicals),

[0068] anthranilic derivatives, in particular menthyl anthranilate (sold under the trade name "Neo Heliopan MA" by Haarmann and Reimer), [0069] imidazoline derivatives, in particular ethylhexyl dimethoxybenzylidene dioxoimidazoline propionate,

[0070] benzalmalonate derivatives, in particular polyorganosiloxane comprising benzalmalonate functional groups (sold under the trade name "Parsol SLX" by Hoffmann-LaRoche),

[0071] 4,4-diarylbutadiene derivatives, in particular 1,1'-dicarboxy (2,2'-dimethyl-propyl)-4,4-diphenylbutadiene,

[0072] and their mixtures.

[0073] The organic photoprotective agents which are more particularly preferred are selected from the group consisting of ethylhexyl salicylate, ethylhexyl methoxycinnamate, octocrylene, phenylbenzimidazole sulphonic acid, benzophenone-3, benzophenone-4, benzophenone-5, 4-methylbenzylidene camphor, terephthalylidene dicamphor sulphonic acid, disodium phenyl dibenzimidazole tetrasulphonate, 2,4,6-tris(diisobutyl 4'-aminobenzalmalonate)-s-triazine, anisotriazine, ethylhexyl triazone, diethylhexyl butamido triazone, methylene bisbenzotriazolyl tetramethylbutylphenol, drometrizole trisiloxane, dicarboxy (2,2'-dimethylpropyl)-4,4-diphenylbutadiene, and their mixtures.

[0074] The inorganic photoprotective agents may be selected from the group consisting of pigments or alternatively nanopigments (mean size of the primary particles: generally between 5 nm and 100 nm, preferably between 10 nm and 50 nm) formed from coated or uncoated metal oxides, such as, for example, titanium oxide (amorphous or crystalline in the rutile and/or anatase form), iron oxide, zinc oxide, zirconium oxide or cerium oxide nanopigments, which are all UV photoprotective agents well known per se. Conventional coating agents are, furthermore, alumina and/or aluminium stearate. Such nanopigments formed from coated or uncoated metal oxides are disclosed in particular in Patent Applications EP 518 772 and EP 518 773.

[0075] The photoprotective agents are generally present in the compositions according to the invention in proportions ranging from 0.1 to 20% by weight with respect to the total weight of the composition and preferably ranging from 0.2 to 15% by weight with respect to the total weight of the composition.

[0076] In another advantageous aspect of the invention, the composition used can additionally comprise at least one other depigmenting or anti-pigmentation active principle in addition to the hydrophilic active principle mentioned above.

[0077] The depigmenting or anti-pigmentation agents capable of being incorporated in the composition according to the present invention include, for example, the following compounds: kojic acid; ellagic acid; arbutin and its derivatives, such as those disclosed in Applications EP-895 779 and EP-524 109; hydroquinone; aminophenol derivatives, such as those disclosed in Applications WO 99/10318 and WO 99/32077, in particular N-cholesteryloxycarbonyl-paraaminophenol and N-ethyloxycarbonyl-para-aminophenol; iminophenol derivatives, in particular those disclosed in Application WO 99/22707; L-2-oxothiazolidine-4-carboxylic acid or procysteine, and its salts and esters; ascorbic acid

and its derivatives, in particular ascorbyl glucoside and magnesium ascorbyl phosphate; 4-butylresorcinol or lucinol; thiourea and its derivatives; calcium D-pantetheine-sulphonate; and plant extracts, in particular extracts of manzanita, of liquorice, of mulberry and of skullcap, without this list being limiting.

[0078] The composition according to the invention can be applied to, for example, the skin, hair, including body hair, eyelashes, nails or lips. It can thus be used in a cosmetic treatment process for depigmenting and/or lightening the skin and/or hair, including body hair, comprising the application of the composition according to the invention to the skin and/or hair, including body hair

[0079] In an alternative form, the composition according to the invention can be used for the manufacture of a dermatological preparation comprising an aqueous phase which is intended to depigment the skin and/or hair, including body hair.

[0080] The examples which follow serve to illustrate the invention without, however, exhibiting a limiting nature. The compounds are, depending on the situation, cited according to chemical names or according to CTFA (International Cosmetic Ingredient Dictionary and Handbook) names.

EXAMPLES

Example 1

[0081] Accelerated Storage Test.

[0082] The aim of this test is to study the decomposition of an oxidation-sensitive hydrophilic active principle after storing for two months at 45° C. Various solutions were prepared and their compositions are collated in the following table:

TABLE I

Compositions (in water)	Solution A (Control)	Solution B	Solution C	Solution D
Ascorbic acid	15%	15%	15%	15%
Polymer 1	_	1%	_	_
Polymer 2	_	_	1%	_
Polymer 3	_	_	_	1%

[0083] All the solutions are brought to pH 6 with 8.9 mol/l KOH.

[0084] The percentages of the polymers are given as active material.

[0085] Polymer 1: Vinylpyrrolidone/vinylimidazole (50/50) copolymer sold under the reference Luvitec VPI 55K72W of BASF (Weight-average molecular mass 1.2×10⁶).

[0086] Polymer 2: Vinylpyrrolidone/vinylimidazole (50/50) copolymer sold under the reference Luvitec VPI 55K18P of BASF (Weight-average molecular mass 10 000).

[0087] Polymer 3: Polyvinylpyrrolidone sold under the reference Kollidon 12PF of BASF (Weight-average molecular mass 3 000).

[0088] The degree of decomposition measured is given by the ratio:

$$(C_0$$
- $C_{2 \text{ months}})/C_0$

[0089] with C_0 concentration of ascorbic acid at t=0 and $C_{2 \text{ months}}$ the concentration of ascorbic acid at t=2 months, under the conditions indicated in the above table.

[0090] The concentration of ascorbic acid is determined by the HPLC technique (LaChrom Merck system). The analytical conditions are as follows:

[0091] Column: Lichrosphere100 RP18 (250 mm)

[0092] Eluent: 0.1 M phosphate buffer, pH 2.1

[0093] Flow rate: 1 ml/min

[0094] Detection at 257 nm

[0095] Dilution of the sample such that the concentration of ascorbic acid is between 0.05 and 1 mg/ml.

[0096] The results obtained are collated in the following Table II:

TABLE II

	Degree of decompos	of decomposition after 2 months at 45° C. (in %)	
	under air, amber glass bottle	under nitrogen, aluminium flask	
Solution A	43	19.4	
Solution B	10.8	1	
Solution C	23.4	4.5	
Solution D	35.8	15.7	

[0097] It is found, from Table II, that the stability of ascorbic acid is improved in the presence of Polymer 1 and Polymer 2 of the invention, even in the presence of atmospheric oxygen, in comparison with the control. It is also found that the N-vinylpyrrolidone homopolymer alone is not sufficient to effectively stabilize the ascorbic acid solution. As the polymers mentioned are hydrophilic, it will be sufficient to add them to an aqueous ascorbic acid solution to stabilize the ascorbic acid.

Example 2

[0098] Demonstration of the Activity With Regard to the Dendricity of Melanocytes:

[0099] The aim of this test is to show the effect of the combination of ascorbic acid with a polymer or copolymer according to the invention on adjusting the melanogenesis of human keratinocyte-melanocyte cocultures.

[0100] Method: The cells are treated from inoculation with the ascorbic acid/vinylpyrrolidone-vinylimidazole copolymer combinations for 7 days.

[0101] Observations:

[0102] The melanocytes are labelled using the NK1beteb antibody (green colouring), which recognizes the melanosomes at every stage of maturation. The nuclei of all the cells, melanocytes and keratinocytes, are stained using propidium iodide (red colouring).

[0103] Results:

[0104] In the absence of the ascorbic acid/vinylpyrrolidone-vinylimidazole copolymer combinations, the melanocytes in cocultures are highly dendritic. The pigment is visibly transferred to the neighbouring keratinocytes.

[0105] In the presence of the ascorbic acid/vinylpyrrolidone-vinylimidazole copolymer combinations, the majority of the melanocytes show a reduced dendricity and some melanocytes become bipolar.

[0106] For a higher concentration, the majority of the melanocytes are bipolar and the amount of pigment transferred to the keratinocytes is reduced.

Example 3

[0107] O/W Anti-Blemish Cream

[0108] The following composition is prepared in a way conventional to a person skilled in the art.

A_1	Sorbitan tristearate	0.7	g	
	Polyethylene glycol (40 EO) stearate	1.6	g	
	Cetyl alcohol	3.2	g	
	Glyceryl mono-, di-, tripalmitate/stearate	2.4	g	
	Myristyl myristate	2	g	
	Liquid fraction of karite butter	2	g	
	Preservative	0.2	g	
A_2	Cyclopentadimethylsiloxane	15	g	
В	Demineralized water	60.53	g	
	Glycerol	3	g	
	Ascorbic acid	5	g	
	50% Potassium hydroxide	3.07	g	
	Vinylpyrrolidone/vinylimidazole copolymer	1	g	
	Preservative	0.2	g	
С	Fragrance	0.1	g	

[0109] This cream which is soft on application makes it possible to reduce pigmentary blemishes and confers good stability on ascorbic acid.

Example 4

[0110] Depigmenting Gel

[0111] The following composition is prepared in a way conventional to a person skilled in the art.

Demineralized water	78.58 g
Polyacrylamide/C ₁₃ -C ₁₄ isoparaffin/Laureth-7	2 g
(Sepigel 305)	
Silicone oil	10 g
Ascorbic acid	5 g
50% Potassium hydroxide	3.07 g
Vinylpyrrolidone/vinylimidazole copolymer	1 g
Preservative	0.25 g
Sequestering agent	0.1 g

[0112] A fresh gel is obtained, which gel makes it possible to combat cutaneous blemishes and in which gel ascorbic acid has good stability.

[0113] The above description of the invention, as illustrated by Examples, allows one of ordinary skill in the art to lighten the skin and/or hair, including body hair, using a composition comprising, in a physiologically acceptable

medium comprising an aqueous phase, at least one oxidation-sensitive hydrophilic active principle selected from the group consisting of, e.g., ascorbic acid and its derivatives, and at least one non-crosslinked N-vinylimidazole polymer or copolymer, the said active principle and the said polymer or copolymer both being in the aqueous phase. Also made available is the use of a combination composed of at least one oxidation-sensitive hydrophilic active principle selected from the group consisting of ascorbic acid and its derivatives and of at least one non-crosslinked N-vinylimidazole polymer or copolymer in the aqueous phase of a cosmetic composition as agent for lightening the skin and/or hair, including body hair. In addition, this invention makes available the use of at least one oxidation-sensitive hydrophilic active principle selected from the group consisting of ascorbic acid and its derivatives and of at least one noncrosslinked N-vinylimidazole polymer or copolymer for the preparation of a dermatological composition comprising an aqueous phase which is intended to depigment the skin and/or hair, including body hair. Similarly made available is the use of a combination composed of at least one oxidationsensitive hydrophilic active principle selected from the group consisting of ascorbic acid and its derivatives and of at least one non-crosslinked N-vinylimidazole polymer or copolymer in the aqueous phase of a cosmetic composition as agent for lightening the skin and/or hair, including body hair, and the use of at least one oxidation-sensitive hydrophilic active principle selected from the group consisting of ascorbic acid and its derivatives and of at least one noncrosslinked N-vinylimidazole polymer or copolymer for the preparation of a dermatological composition comprising an aqueous phase which is intended to depigment the skin and/or hair, including body hair. A preferred embodiment of the invention fully described and made available herein is a method for lightening the skin and/or hair, comprising applying thereto a composition comprising a physiologically acceptable medium comprising an aqueous phase; at least one oxidation-sensitive hydrophilic active principle selected from the group consisting of ascorbic acid and its derivatives, and at least one non-crosslinked N-vinylimidazole polymer or copolymer, the active principle and the polymer or copolymer both being present in the aqueous phase.

[0114] French patent application 0115375 is hereby incorporated by reference, as are all references, texts, documents, standards, applications, patents, etc., mentioned above.

[0115] Also incorporated herein by reference are the following U.S. applications, all filed Nov. 27, 2002, where the present application is listed for information only:

U.S. Ser. No. . . . (Atty. Docket 230634US0)
U.S. Ser. No. . . . (Atty. Docket 230608US0)
U.S. Ser. No. . . . (Atty. Docket 230616US0)
U.S. Ser. No. . . . (Atty. Docket 230614US0)
U.S. Ser. No. . . . (Atty. Docket 230615

- 1. A method for lightening the skin and/or hair, comprising applying to hair and/or skin to be lightened a composition comprising:
 - a physiologically acceptable medium comprising an aqueous phase;
 - at least one lightening oxidation-sensitive hydrophilic active principle selected from the group consisting of ascorbic acid and its derivatives present in an amount sufficient to lighten the skin and/or hair, and:
 - at least one non-crosslinked N-vinylimidazole polymer or copolymer, the at least one active principle and the at least one polymer or copolymer both being present in the aqueous phase.
- 2. The method according to claim 1, wherein the hydrophilic active principle is selected from the group consisting of ascorbic acid esters and salts.
- 3. The method according to claim 1, wherein the hydrophilic active principle is selected from the group consisting of 5,6-di-O-dimethylsilylascorbate, dl- α -tocopheryl dl-ascorbyl phosphate potassium salt, magnesium ascorbyl phosphate and sodium ascorbyl phosphate.
- 4. The method according to claim 1, wherein the oxidation-sensitive hydrophilic active principle is ascorbic acid.
- 5. The method according to claim 1, wherein said composition comprises a non-crosslinked copolymer that is a combination of the N-vinylimidazole with N-vinylpyrrolidone and/or N-vinylcaprolactam subunits.
- **6**. The method according to claim 1, wjerein said composition comprises a non-crosslinked N-vinylimidazole/N-vinylpyrrolidone copolymer.
- 7. The method according to claim 1, wherein the composition comprises a non-crosslinked copolymer selected from the group consisting of a vinylpyrrolidone/vinylimidazole (50/50) copolymer having a weight-average molar mass of 1 200 000 and a vinylpyrrolidone/vinylimidazole (50/50) copolymer having a weight-average molar mass of 10 000.

- **8**. The method according to claim 1, wherein the molar ratio of N-vinylimidazole unit equivalent in said polymer or copolymer to the oxidation-sensitive hydrophilic active principle varies between 0.004 and 16.
- **9**. The method according to claim 8, wherein the molar ratio of the N-vinylimidazole unit equivalent to the oxidation-sensitive hydrophilic active principle varies between 0.01 and 1.
- 10. The method according to claim 1, wherein the polymer or copolymer is present in said composition in a concentration of from 0.1 to 5% by weight of the aqueous phase.
- 11. The method according to claim 10, wherein the polymer or copolymer is present at a concentration of between 0.1 and 2% by weight of the aqueous phase.
- 12. The method according to claim 1, wherein the polymer or copolymer has a molar fraction of N-vinylimidazole units of between 0.1 and 1.
- 13. The method according to claim 12, wherein the polymer or copolymer has a molar fraction of N-vinylimidazole units of between 0.4 and 0.9.
- 14. The method according to claim 1, wherein the composition further comprises a depigmenting or anti-pigmentation agent which is different from the oxidation-sensitive hydrophilic active principle.
- 15. The method according to claim 14, wherein the depigmenting or anti-pigmentation agent is selected from the group consisting of kojic acid; ellagic acid; arbutin and its derivatives; hydroquinone; aminophenols; iminophenols; L-2-oxothiazolidine-4-carboxylic acid or procysteine, and its salts and esters; 4-butylresorcinol or lucinol; thioureas; calcium D-pantetheinesulphonate; ascorbyl glucoside, magnesium ascorbyl phosphate; and plant extracts.

* * * * *