LIGHT PROTECTION AGENT FOR COSMETIC PURPOSES

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Claims priority, application West Germany, Oct. 22, 1970, P 20 51 824.5

Int. Cl. A61J 23/00

13 Claims

ABSTRACT OF THE DISCLOSURE

Topical cosmetic compositions containing as an ultraviolet absorbent comprising a compound of the formula

\[ O \quad CH-R \]

wherein R is p-tolyl or styryl.

This application is a continuation-in-part of our application Ser. No. 190,630, filed Oct. 19, 1971, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to cosmetic compositions containing a UV absorbent.

As is known, light rays of a wavelength range of 285-315 nm. cause sunburn and erythemas in normally fair-skinned humans, whereas radiation of the wavelength range of 310-400 nm. is responsible for the desired tanning of the skin. A normal cosmetic light-protection agent should thus absorb radiation from the sunlight spectrum in the range of 285-315 nm. as completely as possible, but should provide as complete a transmittance as possible of radiation of a longer wavelength.

On the other hand, there are persons who for health reasons must be protected also from radiation of a longer wavelength than 315 nm., to ensure that the sunlight is absorbed in the wavelength range of 285-360 nm. This is achieved by so-called broad-band filters.

The requirements of a good light protection agent, which are not always simultaneously fulfilled by the classes of compounds known as cosmetic light protection agents which are commercially available, are as follows:

(a) A high absorption capacity between 285 nm. and 315 nm., in order to provide adequate protection against sunburn at low concentrations;
(b) A low absorption capacity in the light range which promotes direct pigmentation, in order to achieve the desired tanning effect;
(c) Solubility in the solvents customary in cosmetics;
(d) Adequate stability of the final product under the conditions of use, e.g., sunlight, elevated temperature and perspiration; and
(e) Good compatibility with the skin.

It has now been found that all of these conditions are met in an excellent manner by 3-(4-methylbenzylidene)-DL-camphor (I; R = p-tolyl). Thus, for example, the solubility of this compound in paraffin oil is almost three times as high as that of 3-benzylidene camphor, the use of which as a stabilizer and protective agent of cosmetic preparations against light radiation is known from German published unexamined application DOS 1,913,489.

Whereas 3-(4-methylbenzylidene) -DL-camphor exhibits at 297 nm., i.e., in the center of the zone of erythema-producing radiation, only half the transmittance of the products A and B, the active compound of the composition of this invention exhibits at 330 nm., i.e., the center of the tanning radiation, a transmittance which is 1.5-2.5 times larger than the reference compounds.

The solubility of 3 - (4-methylbenzylidene) -DL-camphor in paraffin oil is 20% by weight at room temperature, which far exceeds the 10% by weight, which is generally considered the minimum limit of solubility. 3-benzylidene-DL-camphor, for example, is soluble in the same solvent at room temperature only to the extent of 7.5%.

The compositions of this invention containing 3-cinnamylidene-camphor can be employed especially advantageously as broad-band filters. This can be seen from the light absorption characteristic of 3-cinnamylidene camphor as shown in the following table, which gives the

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>A</th>
<th>B</th>
<th>4-methylbenzylidene camphor</th>
</tr>
</thead>
<tbody>
<tr>
<td>285</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>297</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>330</td>
<td>3</td>
<td>3.0</td>
<td>5.0</td>
</tr>
<tr>
<td>350</td>
<td>5</td>
<td>6.0</td>
<td>10.0</td>
</tr>
<tr>
<td>380</td>
<td>23</td>
<td>22.0</td>
<td>24.0</td>
</tr>
</tbody>
</table>

SUMMARY OF THE INVENTION

In a composition aspect, this invention relates to UV-absorbent-containing compositions adapted for cosmetic purposes containing at least one compound of Formula I

\[ O \quad CH-R \]

wherein R is p-tolyl or styryl, in mixture with a cosmetically acceptable carrier adapted for topical application to the human skin.

This invention also relates to such compositions which additionally contain one or more other U.V. absorbents.

In a method of use aspect, this invention relates to the use of one of the above-described agents for protection against an overdose of U.V. radiation of the range between 285 and 315 nm. and for the prevention of the associated burn manifestations of human skin known generally as "sunburn" and also to the use of such compositions for protection against light radiation in the range of from 285 to 380 nm.

The absorption maximum of the 3-(4-methylbenzylidene)-DL-camphor on which the agents of this invention are based is approximately 297 nm., lying exactly centrally in the erythema producing zone, so that this range of radiation is covered symmetrically and completely by the absorption band. Furthermore, the solubility of this compound in the solvents customary in cosmetics satisfies even the strictest requirements.

From the table set forth below, the superior light absorption behavior of the 3-(4-methylbenzylidene)-DL-camphor of the compositions of this invention can be seen when compared to two commercial products of proven capabilities, viz., p-methoxybenzylidene 2-ethoxyethyl ester (A), and the isopropyl ester of the p-methoxybenzylidene (B). The transmittance values of the U.V.-absorbers were all measured at 0.002% strength in isopropanol solutions.
3,781,417

transmittance of a 0.002% solution in isopropanol at various wavelengths.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Transmittance (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td>8</td>
</tr>
<tr>
<td>297</td>
<td>8</td>
</tr>
<tr>
<td>300</td>
<td>6</td>
</tr>
<tr>
<td>310</td>
<td>1</td>
</tr>
<tr>
<td>320</td>
<td>1</td>
</tr>
<tr>
<td>330</td>
<td>1</td>
</tr>
<tr>
<td>340</td>
<td>0</td>
</tr>
<tr>
<td>350</td>
<td>2</td>
</tr>
<tr>
<td>360</td>
<td>18</td>
</tr>
</tbody>
</table>

The U.V. absorbing compounds of the compositions of this invention are very stable thermally and with respect to the effects of light radiation. Thus, in a xenon test, after a 24-hour exposure no change in transmittance was observed. They are not decomposed in either acidic or alkaline reaction mediums. Their skin compatibility is good and there are no serious side-effects have been observed. These U.V. absorbers can be produced in a conventional manner by condensing the sodium salt of camphor with the corresponding aromatic aldehydes, preferably in an inert solvent, such as benzene, toluene or xylene. The sodium salt of camphor is formed by reaction of camphor with a strong non-aqueous base, e.g., sodium, sodium hydride, sodium amide or sodium alkoxy-

The cosmetic compositions of this invention are produced by blending one or both of the compounds of Formula I with ointment or cream bases, o!y or non-oily light-protective ointments or, by mixing with solvents, optionally with the addition of emulsifiers, liquid light-protective lotions, etc. Suitable additives and solvents are, for example: hydrocarbons, e.g., solid or liquid paraffin, white spirit, cereos, oxidized and montan wax; vegetable or animal oils, fats and waxes, e.g., olive oil, peanut oil, sesame oil or almond oil, cacao butter, beeswax, fossil wax, or carnauba wax, lanolin and spermaceti; fatty acids and fatty acid esters, e.g., stearic acid, palmitic acid, oleic acid, glycerin mono-, di- or tri-ester, glyc erin monola, isopropyl myristate, isopropyl stearate and butyl stearate; alcohols, e.g., ethyl, isopropyl, cetyl, stearyl, palmitl and hexadecyl alcohol; polyhydric alcohols, e.g., glycol, glycerin and sorbitol, which serve as moisturizing agents, emulsifiers for oil in water and water in oil emulsions, e.g., the commercially available iononic or nonionic, catonic or anonic or amphoteric emulsifiers; and thickeners, e.g., methyl, ethyl or carboxymethyl cellulose, polyacrylic acid, tragacanth, agar and gelatin. It is, of course, possible to also add, if required or desired, further additives such as perfumes, preservatives or physiologically acceptable coloring agents.

The cosmetic composition of this invention can additionally contain one or more other U.V. absorbents, e.g., the sodium salt of 2-phenyl-benzimidazole-5-sulfonic acid, the sodium salt of 3,4-dimethylphenyl-glyoxylic acid, 4-phenylbenzenophenone, the isooctyl ester of 4-phenylbenzenophenone - 2'- carboxylic acid, p-methoxyaminic acid esters, 2-phenyl - 5- methylbenzoxazolone and p-dimethylaminobenzene acid esters.

The compounds of Formula I are contained in the agents of this invention in concentrations effective to achieve the desired reduction in transmission of the burning rays. The exact concentration is not critical and depends primarily on the particular use. In general, the compositions of this invention contain 0.3 - 15.0% by weight, preferably 2.0 - 12.0% by weight, of one or both compounds of Formula I. When the compositions of this invention additionally contain other U.V. absorbents, the total content of all U.V.-absorbing compounds is usually about 0.3 to 16.5% by weight, preferably 2.0 to 12.0% by weight. The concentrations actually used depend on the aimed purpose: high concentrations are desired for compositions with especially high light-protecting factors whereas lower concentrations are sufficient for normal cases.

The numerical values in the formulation examples set forth below are parts by weight.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting of the remainder of the disclosure in any way whatsoever.

The compounds of Formula I can be prepared as described in the literature.

3-(4-methylbenzilidene)-D-L-camphor (I; R= p-tolyl) was prepared e.g. following the method of A. Haller and E. Bauer, Compt. rend. 148, 1493 (1909).

3 - cinnamylidene - camphor was prepared e.g. as described by H. Rupe and G. Frisell, Ber. dtsch. chem. Ges. 38, 110 (1905).

Example A

Suntan oil:

| 3-(4-methylbenzylidene)-D-L-camphor | 2          |
| Liquid paraffin                     | 48         |
| 2-ethyl dodecane                    | 50         |

Example B

Sunlight protection oil:

| 3-(4-methylbenzylidene)-D-L-camphor | 2          |
| Liquid paraffin                     | 48         |
| Isopropyl myristate                 | 50         |

Example C

Suntan lotion:

| 3-(4-methylbenzylidene)-D-L-camphor | 1.5        |
| Liquid paraffin                     | 10.0       |
| Polyol monostearate ethoxylate      | 10.0       |
| Isopropyl myristate                 | 10.0       |
| Sorbitol solution 70%               | 5.0        |
| Sodium lauryl ether sulfate         | 0.5        |
| Water                               | 63.0       |

Example D

Sunlight protection cream:

| 3-(4-methylbenzylidene)-D-L-camphor | 2.5        |
| Lanolin                             | 67.0       |
| Olive oil                           | 10.0       |
| Water                               | 20.5       |

Example E

Aerosol:

| Mixture according to Example A or B | 40         |
| Mixture of trichlorofluoromethane and dichlorodifluoromethane (T: 30) (propellant gas) | 60         |

Example F

Sunlight protection cream:

| 3-cinnamylidene-D-L-camphor          | 2          |
| Triethanolamine salt of 2-phenyl-benzimidazol 3-sulfonic acid, 50% | 3          |
| Cream base (system oil/water or water/oil) | 95         |

Example G

Lipstick: 100 g. of a commercial lipstick composition is melted and 2 g. of 3-cinnamylidene-D-L-camphor is dissolved therein. The composition is poured into cooled lipstick molds, and the molded products are removed after cooling. Such lipsticks provide effective protection against U.V. radiation in the range of 290-360 nm. The use of such a preparation is indicated particularly in the high mountain region.

Example H

Sunlight protection oil:

| 3-(4-methylbenzylidene)-D-L-camphor | 10         |
| Isopropyl myristate                 | 15         |
| Liquid paraffin                     | 75         |
Example I

Sunlight protection cream:

3-(4-methylbenzylidene)-D,L-camphor 5
2-phenylbenzimidazole-5-sulfonic acid 5
Isopropyl myristate 6
Petrolatum, white DAB 7 10
Glycerin 3
Cetyl-stearyl alcohol 13.5
Sodium cetyl-stearyl sulfate 1.5
4-hydroxybenzoic acid methylster 0.12
Water 55.88

The commercial mixture Lanette NS was used, containing 90% cetyl-stearyl alcohol and 10% medium cetyl-stearyl sulfate.

Example J

Sunlight protection cream:

3-(4-methylbenzylidene)-D,L-camphor 5
Glycerinmonostearate 2
Spermaceri 3
Eucerin® anhydricum 40
4-hydroxybenzoic acid methylster 0.12
Water 44.88

Example K

Sunlight protection oil:

3-(4-methylbenzylidene)-D,L-camphor 7.5
Isopropyl myristate 15
Liquid paraffin 77.5

Example L

Sunlight protection cream:

3-cinnamylidene-D,L-camphor 6
Glycerinmonostearate 2
Spermaceri 3
Eucerin® anhydricum 40
4-hydroxybenzoic acid methylster 0.12
Water 48.88

The preceding examples can be repeated with similar success by substituting the generically and specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

What is claimed is:

1. A U.V. radiation absorbing cosmetic composition containing a U.V. absorbing effective amount of at least one U.V. absorbing compound of the formula

2. A composition according to claim 1 containing 3-(4-methylbenzylidene)-D,L-camphor.
3. A composition according to claim 1 containing 3-cinnamylidene-D,L-camphor.
4. A composition according to claim 1 containing 0.3-3.5% by weight of the U.V. absorbing agent.
5. A composition according to claim 4 containing 0.3-5.5% by weight of 3-(4-methylbenzylidene)-D,L-camphor.
6. A composition according to claim 5 containing 1.0-3.0% by weight of 3-(4-methylbenzylidene)-D,L-camphor.
7. A composition according to claim 4 containing 0.3-5.5% by weight of 3-cinnamylidene-D,L-camphor.
8. A composition according to claim 7 containing 1.0-3.0% by weight of 3-cinnamylidene-D,L-camphor.
9. A composition according to claim 4 containing a total of 1.0-3.0% by weight of U.V. absorbing agent.
10. A method for the protection of human skin against an overdose of U.V. radiation in the region between 285 and 315 nm, which comprises coating the skin exposed to sunlight with a composition according to claim 1.
11. A method for the protection of human skin against an overdose of U.V. radiation in the region between 285 and 315 nm, which comprises coating the skin exposed to sunlight with a composition according to claim 5.
12. A method for the protection of human skin against an overdose of U.V. radiation in the region between 285 and 315 nm, which comprises coating the skin exposed to sunlight with a composition according to claim 7.
13. A method for the protection of human skin against an overdose of U.V. radiation in the region between 285 and 315 nm, which comprises coating the skin exposed to sunlight with a composition according to claim 9.

References Cited


SAM ROSEN, Primary Examiner

U.S. Cl. X.R.

424—332
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION


Inventor(s) Reiner Welters et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

IN THE CLAIMS:

CLAIM 4, COLUMN 6: "3.5%" should read -- 5.5% --.

CLAIM 10, COLUMN 6: "235" should read -- 285 --.

Signed and sealed this 9th day of April 1974.

(SEAL)
Attest:
EDWARD M. FLETCHER, JR. C. MARSHALL DANN
Attesting Officer Commissioner of Patents