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ULTRAVIOLET ABSORBING COMPOSITIONS AND METHODS
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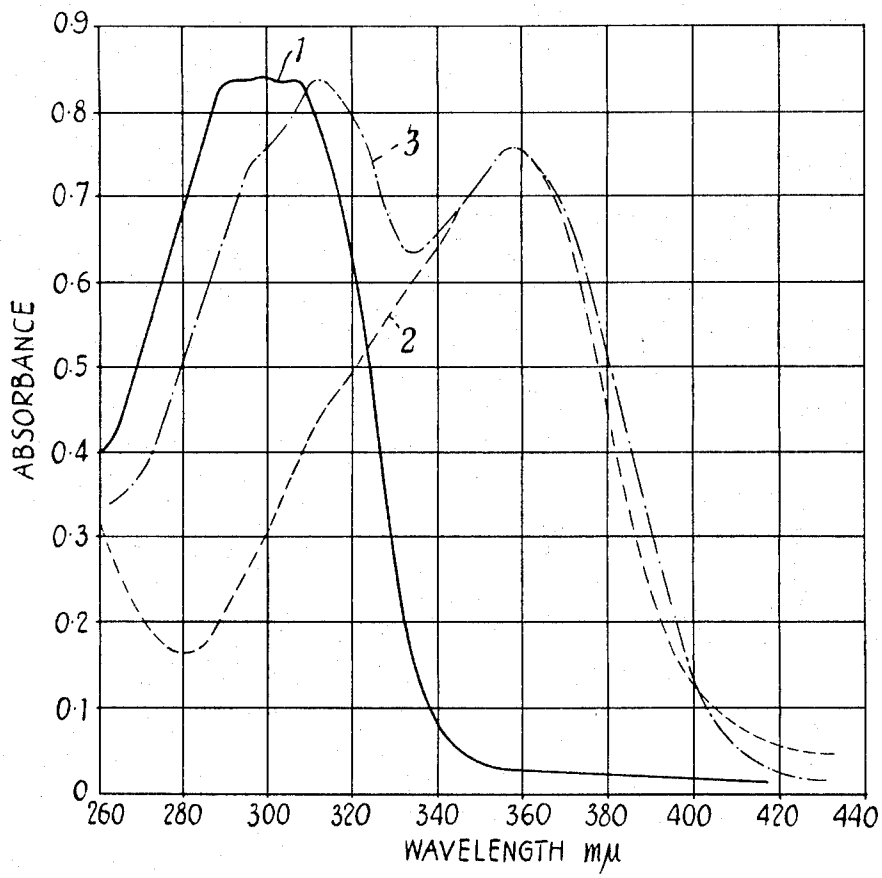

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DIALKYLAMINOCINNAMATES AND DIALKYLBENZALMALONATES IN ULTRAVIOLET ABSORBING COMPOSITIONS AND METHODS

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This invention relates to ultraviolet absorbing compositions and is particularly, but not exclusively, concerned with cosmetic sun-screening compositions for topical application to the skin.

It is known that in the case of normal light-skinned persons, it is not the whole of the ultraviolet portion of the radiation of the sun that causes erythema or burning; it is that portion of the ultraviolet radiation of a wavelength between about 280 or 290 mμ and about 320 mμ which is responsible for the distressing burning suffered by normal white persons exposing their skin to strong and/or prolonged sunlight, whilst ultraviolet radiation of longer wavelengths up to about 400 or 420 mμ causes tanning, namely a brownish or golden coloration of the skin which is usually aesthetically acceptable, as opposed to the unsightly reddish coloration denoting burning, which is usually accompanied by discomfort or pain.

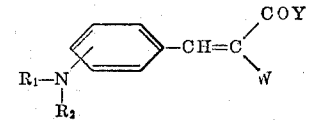
It is widely desired to secure tanning of the skin as by sunbathing for purposes of health and/or appearance and to enable or aid persons to subject themselves to the tanning process while avoiding or diminishing the discomfort and even dangers of erythema, there have been made available so-called sunscreening compositions, usually in the form of creams or lotions, for topical application, which sunscreening compositions are adapted to or intended to form, deposit or leave on the surface of the skin after application a film comprising a sunscreening agent which will absorb at least the bulk of that portion of the radiation of the sun of a wavelength between about 290 and 320 mμ, while permitting the passage of at least the bulk of that portion of the ultraviolet range of a wavelength exceeding about 320 mμ, whereby tanning (as opposed to burning) of the subject will not be substantially hindered.

It is, however, the case that a proportion of persons differ from the norm, particularly persons suffering from certain illnesses such as photophobia or types of dermatitis, in having skins which are subject to burning not only by ultraviolet radiation of wavelengths between 290 and 320 mμ but also by other ranges of ultraviolet radiation from 320 mμ up to 400 or even 420 mμ. The use of conventional sunscreening compositions intended to permit or facilitate tanning will not enable such persons to sunbathe or otherwise expose themselves to the sun with comfort and safety since such compositions will not provide a film which will filter out the ultraviolet radiation of longer wavelengths.

It is an object of the present invention to provide a cosmetic sunscreening composition appropriate for topical use by persons liable to suffer erythema on exposure to ultraviolet radiaton of a wavelength exceeding 320 mμ.

According to one aspect of the present invention, an ultraviolet absorbing composition for topical application comprises a dermatologically acceptable liquid or semi-

liquid carrier having dissolved or dispersed therein a proportion of at least one dermatologically acceptable compound represented by the general formula:



I

wherein W represents hydrogen or a COZ group; Y and Z, which may be the same or different, each represent an alkyl group, on OR_3 group, where R_3 represents hydrogen or an alkyl or alkoxyalkyl group, or an OB group, where B represents a dermatologically acceptable cationic group; and R_1 and R_2, which may be the same or different, each represent hydrogen or an alkyl or aralkyl group, for example benzyl, or R_1 and R_2 together represent a straight or branched chain alkylene group, optionally interrupted by a hetero atom, for example a pyrrolidino, piperidino, morpholino or piperazino group. It is preferred to employ a compound of Formula I in which W represents hydrogen and in which Y is represented by OR_3, where R_3 is an alkyl group containing from one to four carbon atoms, such as methyl, ethyl, n-propyl or isobutyl.

When W in Formula I represents a COZ group, it is preferred that at least one, and advantageously both, of Y and Z is represented by OR_3, where R_3 is an alkyl group containing from one to four carbon atoms, such as methyl, ethyl, n-propyl or n-butyl, or a lower alkoxyalkyl group, such as one having the general formula $—C_xH_{2x}OC_yH_{2y+1}$, wherein x and y represent integers totalling at least 3, and preferably from 4 to 6, for example methoxypropyl, ethoxyethyl, n-butoxyethyl or methoxybutyl.

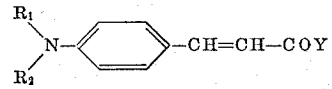
When Y and/or Z in Formula I represents OB, B may be, for example, an alkali metal, such as sodium or potassium, or an ammonium group, or an acceptable substituted ammonium group, such as trishydroxyethylammonium.

In the preferred compounds, advantageously R_1 and R_2 both represent alkyl groups having from 1 to 4 carbon atoms, such as methyl, ethyl, n-propyl or n-butyl, and most advantageously one or two carbon atoms.

The group

is preferably attached to the benzene ring in the para position.

The especially preferred class of compounds for use in accordance with the present invention is that having the general structural formula:

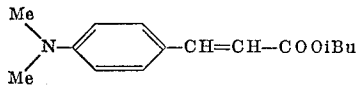


II

wherein R_1 and R_2, which may be the same or different, each represent an alkyl group having from one to four and most advantageously one or two carbon atoms, and Y represents an OR_3 group, where R_3 is an alkyl group having from one to four and most advantageously two or four carbon atoms.

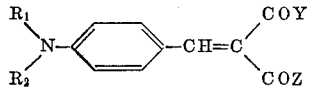
A specific example of a compound falling within the difinition of Formula II and hence illustrative of the compounds which may be used in the compositions of the

present invention is isobutyl p-dimethylamino-cinnamate, which has the structural formula:



wherein Me represents a methyl group and iBu represents an isobutyl group.

When W in Formula I represents a COZ group, the especially preferred class of compounds is that having the general structural formula:



wherein R_1 and R_2, which may be the same or different, each represent an alkyl group having from one to four and most advantageously one or two carbon atoms, and Y and Z, which may be the same or different, each represent an OR_3 group, where R_3 is an alkyl group having from one to four and most advantageously one or two carbon atoms. A specific example of a compound of the foregoing class is diethyl p-dimethylamino-benzalmalonate.

The substituted malonates for use in accordance with the present invention may be made by condensing an appropriate aminobenzaldehyde with an appropriate ester of malonic acid, for example by heating the reactants (conveniently under reflux with provision for the separation of formed water) in solution in a mutual solvent in the presence of at least one condensation catalyst, for example piperidine. If the desired end product is an acid or a salt, the ester may be carefully hydrolysed under alkaline conditions, the acid liberated, and, for a salt, neutralized with the appropriate base. If the desired end product contains a primary amino group, that is if $R_1=R_2=H$, the group must be protected during the course of the condensation by an appropriate protecting group such as acetyl, which is removed by appropriate means at the end of the reaction.

The substituted cinnamates for use in accordance with the present invention may be made by condensing an appropriate aminobenzaldehyde with an appropriate ester of acetic acid in a mutual solvent (conveniently an excess of the ester), in the presence of a condensation catalyst, for example sodium metal or sodium hydride. If the desired end product is an acid it may be obtained by hydrolysis of the ester, but is better obtained by condensation of the appropriate aminobenzaldehyde with malonic acid in a mutual solvent in the presence of a condensation catalyst such as piperidine. If the desired end product is a salt it may be obtained by neutralisation of the acid with an appropriate base. If the desired end product contains a primary amino group, the group must be protected during the course of the condensation by an appropriate protecting group, such as acetyl, which is removed by appropriate means at the end of the reaction.

Insofar as is presently known, all but three of the compounds falling within the definition of Formula I are novel compounds. Thus according to another aspect of the present invention, there are provided novel compounds represented by Formula I above, the values of W, Y, R_1 and R_2 being chosen so that when R_1 and R_2 are both methyl and the group.

is in the para position, W is not hydrogen when Y is a hydroxy or ethoxy group and W is not a carbethoxy group when Y is an ethoxy group.

It has been found that compounds falling within the definition of Formulae I and II absorb ultraviolet radiation strongly at wavelengths exceeding the range of about 290 to 320 mμ conventionally regarded as the burning range and give a useful measure of absorption up to about 400 mμ, and that these compounds may be formulated with a dermatologically acceptable liquid or semi-liquid carrier, for example in the form of a cream or lotion, to provide a composition which on topical application will constitute or leave on the skin a film or coating which will absorb at least a substantial proportion of ultraviolet light falling upon it and so prevent or diminish burning even in the case of persons liable to suffer burning from irradiation within wavelengths exceeding about 320 mμ and extending up to about 400 or even 420 mμ.

Novel sunscreening compositions such as cosmetic oils, alcoholic solutions, lotions, lipsticks, ornaments, creams and other emulsified products may be prepared with the compounds proposed according to this invention. These compositions may be formulated as cosmetic preparations in otherwise conventional fashion. It is preferred that the should be not only dermatologically but also cosmetically or aesthetically acceptable.

Depending on the degree of protection desired and on the vehicle employed, satisfactory results may be obtained with compositions containing from 0.5 to 10% by weight of the compounds of this invention. Preferably from 0.9 to 3% by weight and most advantageously from 1 to 3% by weight is employed although larger amounts may be used if desired. The optimum proportion to employ will depend particularly on the nature of the coating or film formed or left on the skin, since some types of formulation will permit of the formation of a screen of a greater concentration of screening agent per unit of area than others, depending for example on viscosity, spreading power, and the permanence or otherwise of the vehicle or constituents thereof.

The novel sunscreening compositions of this invention are not confined to any particular classes of cosmetics or to any particular formulations. Nevertheless, it is preferred to employ the novel compounds of this invention along with a substantially greater amount of a dermatologically acceptable vehicle compatible with the skin, such as corn oil, aqueous ethanol, isopropanol, sesame oil, propylene glycol, benzyl alcohol, oleyl alcohol, isopropyl esters of fatty acids, such as myristic and palmitic acids, or a mineral oil or wax. The vehicle should be of such a viscosity and/or wetting power that the composition may be satisfactorily applied to the skin as a continuous film or coating, despite the natural oilness thereof.

The novel sunscreening compositions are applied to the skin in known and conventional manner, normally just prior to the user exposing himself or herself, as the case may be, to the rays of the sun.

at least one compound falling within the definition of the present invention, an ultraviolet absorbing composition comprises a dermatologically acceptable liquid or semi-liquid carrier having dissolved or dispersed therein at least one compound falling within the definition of Formula I above and also at least one other dermatologically acceptable ultraviolet absorbing compound, whereby the combined effect of the plurality of ultraviolet absorbing compounds enhances the total ultraviolet absorbing properties of films or coatings resulting from or formed by the application of the composition to the skin.

The second compound is advantageously one whose ultraviolet absorption is complementary to that of the first ultraviolet absorbing compound whereby the extent of the range and/or the extent of the amount of ultraviolet radiation absorbed by the film or coating is increased.

Advantageously, the first compound shall exert its maximum absorption of ultraviolet light at a wavelength between 320 and 400 mμ and the second compound shall exert its maximum absorption thereof at a wavelength between 290 and 320 mμ.

The composition according to this feature of the invention may contain the two compounds in a combined amount of from 0.5 to 10% by weight, and most advantageously from 0.9 to 5% by weight, of the total weight of the composition. The molar ratio of the two compounds one to the other may be from 1:10 to 10:1, preferably from 5:1 to 1:5 and most advantageously from 2:1 to 1:2.

It is preferred that the two compounds and the ratio in which they are employed are such that a 0.5% solution of the compounds (taken in that ratio) in a solvent transparent to ultraviolet radiation (for example ethanol) in a layer 1 cm. thick shall reduce the intensity of all radiation between the wavelengths 290 and 400 mμ which passes into it by at least 90%.

Examples of sunscreening compounds which may be used as the second ultraviolet absorbing component of a composition according to the invention are isobutyl dimethylaminobenzoate, menthyl salicylate and ethoxyethyl and other lower alkoxyalkyl p-methoxycinnamates, particularly such as have at least four, and preferably from four to six carbon atoms, in the alkoxyalkyl group, such as 2-ethoxyethyl p-methoxy-cinnamate. Other suitable sunscreening compounds may, however, be employed, the second such component advantageously being one adapted to absorb in the erythematogenic range as it is normally understood, so complementing the absorption in the tanning range (as it is normally understood) provided by the first component.

A difficulty frequently experienced in formulating topical sunscreening compositions is that of securing the presence in an acceptable base or vehicle of a sufficiently high concentration of the screening agent to provide after application a film or coating the screening contact or power of which will be sufficient to achieve the desired purpose. This is because of the quite limited solubility of many otherwise acceptable screening agents in carrier bases which are acceptable on dermatological and cosmetic grounds. The present invention in providing in accordance with one embodiment thereof compositions containing at least two distinct screening agents tends to obviate this difficulty to the extent that each agent has its own solubility in the base employed, thus permitting a total concentration of the two agents greater than that which might be obtainable with a single agent, whereby the overall ultraviolet absorption effect resulting from the use of the compositions is enhanced not only in the sense that the absorption spectra of the two compounds is complementary, but also to the extent that the ultraviolet absorption spectra of the two compounds so far as they overlap supplements one another.

The foregoing advantage of compositions containing at least two distinct screening agents in accordance with one embodiment of the invention is illustrated more clearly in the accompanying drawing which shows in graphic form the ultraviolet absorption of three blackout lotions, the spectra of which were obtained from smears of lotion formulations of the sunscreening agents in a lotion base on silica plates, without drying. Curve 1 was obtained from a lotion containing 1.5% by weight of the known screening agent 2-ethoxyethyl p-methoxy-cinnamate; curve 2 was obtained from a lotion containing 1.5% by weight of a novel screening agent in accordance with the invention, namely isobutyl p-dimethylamino-cinnamate; and curve 3 was obtained from a lotion containing 1.5% by weight of each of the screening agents used in the lotions relating to curves 1 and 2. The curves have been adjusted to compensate for variations in thickness between the three smears.

The lotion base used in formulating the lotions incorporating the screening agents was as follows:

Ingredients:	Amount (in grams)
Cetyl alcohol	0.5
Stearic acid	3.0
Lanolin	0.5
Mineral oil	5.0
Preservative	0.2
Triethanolamine	3.0
Glycerine	3.0
Distilled water	83.3

The present invention also provides as a further aspect thereof a method of protecting the skin against erythema-producing or other undesired ultraviolet radiation, which comprises applying to the skin a film or coating of a composition comprising a cosmetic carrier having disseminated therethrough an effective proportion of one or more ultraviolet absorbing compounds represented by Formula I. The invention is not limited to the protection of the person or parts thereof against erythematogenic radiation since, for example, the invention also finds application in the protection against tanning of normal white persons, such as those who may wish to remain wholly or in part untanned despite exposure to tanning radiation, such as on the grounds of appearance. In this connection it is contemplated that the invention will find application in those cases where the extent of clothing of the person will vary from time to time and it is desired to avoid the appearance of visible marking as to the extent of dress or undress on a previous occasion under tanning conditions.

The invention still further provides a concentrate composition containing at least two ultraviolet absorbing compounds as described above which may be employed in the manufacture of topically applicable compositions according to the invention by incorporation in a suitable proportion in a dermatologically acceptable liquid or semi-liquid carrier. A concentrate composition according to the invention may consist only of the two or more compounds to the extent that they are compatible and/or the concentrate composition may additionally comprise an extender or diluent material which may ultimately form a component of the ultraviolet absorbing composition or which is more or less readily separable from the mixture of compounds prior to or on incorporation in the eventual composition, as by evaporation.

The expression "dermatologically acceptable" is used herein to indicate not only that the material or compound referred to is acceptable on strictly dermatological grounds, but also that it is acceptable on other physiological grounds, that is to say that if, for example, the material or compound is absorbed through the skin into the blood-stream, it shall not be toxic in the amounts and by the route it is absorbed.

The following examples are illustrative of the invention. Examples 1 to 6 illustrate the preparation of ultraviolet absorbing compounds which may be used in formulating ultraviolet absorbing compositions in accordance with the invention and Examples 7 to 10 illustrate compositions in accordance with the invention.

EXAMPLE 1

Diethyl p-dimethylamino-benzalmalonate

A solution of p-dimethylamino-benzaldehyde (10.5 g.), piperidine (1 ml.), benzoic acid (0.3 g.) and ethyl malonate (9.4 ml.) in dry benzene (20 ml.) was heated under reflux at 130–140° C. until no more water could be separated out from the refluxing distillate by means of a Dean & Starke phase separator associated with the reflux column. On cooling the desired compound crystallized. Yield (on recrystallization from aqueous ethanol) 14 g. of pale yellow crystals, M.P. 111–112° C., solubility in water (20° C.) <0.1%, λmax. 370 mμ, molecular extinction coefficient=33,000.

EXAMPLE 2

p-Dimethylamino-cinnamic acid

p-Dimethylamino-benzaldehyde (50 g.) and malonic acid (35 g.) were heated in pyridine (250 ml.) and piperidine (20 ml.) on the steam bath for twelve hours. The reaction mixture was then poured into a mixture of crushed ice (1 kg.) and glacial acetic acid (500 ml.) with stirring. The resulting product was collected, washed with dilute acetic acid and water. After drying it was crystallized from ethanol to give the desired compound. Yield 39 g. of a yellow solid, M.P. 227–232° C. (with decompositon).

EXAMPLE 3

Ethyl p-dimethylamino-cinnamate

Sodium hydride (7 g. of a 50% dispersion in oil) was added in portions to a cooled, stirred mixture of dimethylaminobenzaldehyde (16.7 g.) and ethyl acetate (200 ml.). After standing overnight, glacial acetic acid was added and excess of ethyl acetate was distilled off in vacuo. The residue was triturated with water, filtered off, dried and crystallized from light petroleum to give the desired compound as a yellow crystalline solid, M.P. 70–72° C. Yield 12 g.

EXAMPLE 4

Isobutyl p-dimethylamino-cinnamate

Sodium hydride (33 g. of a 50% dispersion in oil) was added in portions to a cooled, stirred mixture of dimethylamino-benzaldehyde (18 g.) and isobutyl acetate (400 ml.). After standing overnight, glacial acetic acid (42 g.) was added and excess of isobutyl acetate was distilled off in vacuo. The residue was triturated with water, filtered off, dried and crystallized from light petroleum to give the desired compound as pale yellow crystals, M.P. 60–63° C. Yield 63 g.

Found: C, 72.8%; H, 8.6%; N, 5.6%. $C_{15}H_{21}O_2N$ requires: C, 72.8%; H, 8.4%; N, 5.7%.

EXAMPLE 5

Triethanolamine p-dimethylamino-cinnamate

P-Dimethylamino-cinnamic acid (3.8 g.) and triethanolamine (3 g.) were heated together on the steam bath until a homogeneous melt was obtained and was then allowed to cool. The solidified melt was crystallized from ethyl acetate to give the desired product as a yellow waxy solid, M.P. 129–134° C.

EXAMPLE 6

Di-isobutyl p-dimethylamino-benzalmalonate

A solution of p-dimethylamino-benzaldehyde (10.5 g.), piperidine (1 ml.), benzoic acid (0.3 g.) and di-isobutyl malonate (9.4 g.) in dry benzene (50 ml.) was heated under reflux at 130–140° C. until no more water could be separated out from the refluxing distillate by means of a Dean & Starke phase separator associated with the reflux column. On cooling the desired compound crystallized. Yield (on recrystallization from ethanol) 14.8 g. of crystals, M.P. 99–100° C.

Found: C, 69.2%; H, 8.4% N, 4.3%. $C_{20}H_{29}O_4N$ requires: C, 69.1%; H, 8.4%; N, 4.0%.

EXAMPLE 7

Blackout lotion

Isopropyl myristate (98 g.) and diethyl p-dimethylamino-benzalmalonate (0.5 g.) were warmed at 50° C. to effect solution of the latter. 2-ethoxyethyl p-methoxycinnamate (0.5 g.) was added and the resulting mixture was cooled to room temperature.

EXAMPLE 8

Blackout lotion

Ingredient:	Amount, grams
(1) Cetyl alcohol	0.5
(2) Stearic acid	3.0
(3) Lanolin	0.5
(4) Mineral oil	5.0
(5) Preservative	0.2
(6) 2-ethoxyethyl p-methoxy-cinnamate	2.0
(7) Diethyl p-dimethylamino-benzalmalonate	2.0
(8) Triethanolamine	3.0
(9) Glycerine	3.0
(10) Distilled water	83.3

Ingredients 1 to 7 were mixed together and heated to 95° C., this temperature being maintained until the mixture was homogeneous. The mixture was then cooled to 70° C.

Ingredients 8 to 10 were heated to 70° C. and were then added with stirring to the mixture of ingredients 1 to 7 while the mixture cooled to 35° C. The resulting mixture was then allowed to stand overnight to form the desired blackout loation.

EXAMPLE 9

Blackout cream

Ingredient:	Amount, grams
(1) Mineral oil	5.0
(2) Lanolin	0.5
(3) Polyoxyethylene lanolin derivative (Solulan 98)	3.0
(4) Glyceryl monostearate S.E. (self-emulsifying)	5.0
(5) Stearic acid	15.0
(6) Preservative	0.2
(7) 2-ethoxyethyl p-methoxycinnamate	2.0
(8) Diethyl p-dimethylaminobenzalmalonate	2.0
(9) Propylene glycol	5.0
(10) Distilled water	62.3

Ingredients 1 to 8 were homogenised at 80° C. Ingredients 9 and 10 were heated to 80° C. and added to the mixture of ingredients 1 to 8 at this temperature with mechanical stirring while cooling to 35° C. The resulting product was immediately packed in jars.

EXAMPLE 10

Blackout lotion

Ingredient:	Amount
(1) Cetyl alcohol	0.5
(2) Stearic acid	3.0
(3) Lanolin	0.5
(4) Mineral oil	5.0
(5) Preservative	0.2
(6) 2-ethoxyethyl p-methoxycinnamate	1.5
(7) Isobutyl p-dimethylaminocinnamate	1.5
(8) Triethanolamine	3.0
(9) Glycerine	3.0
(10) Distilled water	81.8
	100.0

Ingredients 1 to 8 were homogenised at 80° C. Ingredients 9 and 10 were heated to 80° C. and added to the mixture of ingredients 1 to 8 at this temperature with mechanical stirring while cooling to 35° C. The resulting cream was immediately packed in jars.

In the foregoing Examples 7 to 10, the primary sunscreening compound may be replaced by another compound according to the invention having a comparable ultraviolet absorption spectrum and the 2-ethoxyethyl p-methoxycinnamate may likewise be replaced by a comparable known sunscreening agent.

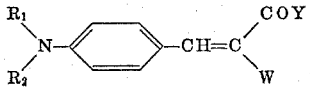
The terms "blackout loation" and "blockout cream" employed in Examples 7 and 10 are used as referring to the absorption not only of the burning range of the ultraviolet portion of the spectrum, but also of that portion

which in the case of normal white persons is regarded as the tanning range. The lotions and creams exemplified are illustrative of the many forms which the compositions of the invention may take; the lotions and cream can be employed in the same fashion as conventional lotions and creams.

We claim:

1. Triethanolamine p-dimethylamino-cinnamate.

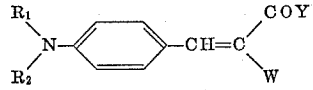
2. A dermatologically acceptable liquid or semi-liquid carrier having therein from 0.5 to 10% by weight of at least one dermatologically acceptable ultraviolet absorbing compound of the formula:



wherein W represents hydrogen or COZ; Y and Z, which may be the same or different, each represent OR_3 where R_3 is hydrogen, alkyl of from 1 to 4 carbons or represent OB where B is a dermatologically acceptable group selected from alkali metal, ammonium and substituted ammonium; and R_1 and R_2, which may be the same or different, each represent alkyl of from 1 to 4 carbons, said composition being such as to form on topical application a continuous film or coating on the skin, and wherein there is also present in the composition an effective amount of at least one other dermatologically acceptable ultraviolet absorbing compound which is effective at a wavelength between 290 and 320 mμ.

3. A composition as claimed in claim 2 wherein the dermatologically acceptable compounds are present in a molar ratio of one compound to the other of from 1:10 to 10:1.

4. Method of protecting the skin against erythema-producing or other undesired ultraviolet radiation, which comprises applying to the skin a film or coating of a composition comprising a cosmetic carrier having disseminated therethrough an effective proportion of at least one dermatologically acceptable ultraviolet absorbing compound of the formula:



wherein W represents hydrogen or COZ; Y and Z, which may be the same or different, each represent OR_3 where R_3 is hydrogen, alkyl of from 1 to 4 carbons or represent OB where B is a dermatologically acceptable group selected from alkali metal, ammonium and substituted ammonium; and R_1 and R_2, which may be the same or different, each represent alkyl of from 1 to 4 carbons.

5. A dermatologically acceptable liquid or semi-liquid carrier having therein an effective amount of the dermatologically acceptable ultraviolet absorbing compound triethanolamine p-dimethylaminocinnamate which forms on topical application a continuous film or coating on the skin.

6. Method of protecting the skin against erythema-producing or other undesired ultraviolet radiation, which comprises applying to the skin a film or coating of a composition comprising a cosmetic carrier having disseminated therethrough an effective proportion of diethyl p-dimethylaminobenzalmalonate.

7. Method of protecting the skin against erythema-producing or other undesired ultraviolet radiation, which comprises applying to the skin a film or coating of a composition comprising a cosmetic carrier having disseminated therethrough an effective proportion of triethanolamine p-dimethylaminocinnamate.

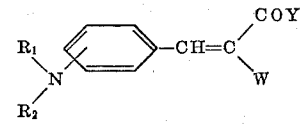
8. Method of protecting the skin against erythema-producing or other undesired ultraviolet radiation, which comprises applying to the skin a film or coating of a composition comprising a cosmetic carrier having disseminated therethrough an effective proportion of p-dimethylamino-cinnamic acid.

9. Method of protecting the skin against erythema-producing or other undesired ultraviolet radiation, which comprises applying to the skin a film or coating of a composition comprising a cosmetic carrier having disseminated therethrough an effective proportion of di-isobutyl p-dimethylamino-benzalmalonate.

10. Method of protecting the skin against erythema-producing or other undesired ultraviolet radiation, which comprises applying to the skin a film or coating of a composition comprising a cosmetic carrier having dissemintaed therethrough an effective proportion of isobutyl p-dimethylamino-cinnamate.

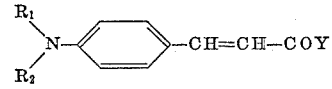
11. Method of protecting the skin against erythema-producing or other undesired ultraviolet radiation, which comprises applying to the skin a film or coating of a composition comprising a cosmetic carrier having disseminated therethrough an effective proportion of ethyl p-dimethylamino-cinnamate.

12. Method of protecting the skin against erythema-producing or other undesired ultraviolet radiation, which comprises applying to the skin a film or coating of a composition comprising a cosmetic carrier having disseminated therethrough an effective proportion of at least one dermatologically acceptable ultraviolet absorbing compound of the formula:



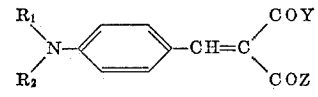
wherein W represents hydrogen or COZ, Y and Z, which may be the same or different, each represent OR_3 where R_3 is hydrogen, alkyl of from 1 to 4 carbons or represent OB where B is a dermatologically acceptable group selected from alkali metal, ammonium and substituted ammonium and R_1 and R_2, which may be the same or different, each represent alkyl of from 1 to 4 carbons and wherein there is also present in the composition at least one other dermatologically acceptable ultraviolet absorbing compound which exerts effective absorption of ultraviolet light at a wavelength between 290 and 320 mμ.

13. Method of protecting the skin against erythema-producing or other undesired ultraviolet radiation, which comprises applying to the skin a film or coating of a composition comprising a cosmetic carrier having disseminated therethrough an effective proportion of at least one dermatologically acceptable ultraviolet absorbing compound of the formula:



wherein Y is OR_3, where R_3 is alkyl of from 1 to 4 carbons and R_1 and R_2, which may be the same or different, each represent alkyl of from 1 to 4 carbons and the salts thereof selected from the group consisting of alkali metal, ammonium and substituted ammonium.

14. Method of protecting the skin against erythema-producing or other undesired ultraviolet radiation, which comprises applying to the skin a film or coating of a composition comprising a cosmetic carrier having disseminated therethrough an effective proportion of at least one dermatologically acceptable ultraviolet absorbing of the formula:



wherein Y and Z are OR_3, where R_3 is alkyl of from 1 to 4 carbons and R_1 and R_2, which may be the same or different, each represent alkyl of from 1 to 4 carbons and the salts thereof selected from the group consisting of alkali metal, ammonium and substituted ammonium.

(References on following page)

References Cited

UNITED STATES PATENTS

2,798,881 7/1957 Baer et al. ---------- 260—471

OTHER REFERENCES

Journal of the Amer. Chem. Soc., vol. 82, pp. 1907–11 (1960).

Zabicky, Journal Chem. Soc. (London), 1961, pp. 683–687, Chem. Abst., vol. 55, col. 5410g (1961).

Chem. Abst., vol. 55, col. 16468h (1961).

Chem. Abst., vol. 57, col. 4586d (August 1962).

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