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3,479,428

SUNSCREEN COMPOSITION AND METHOD OF USING THE SAME

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No Drawing. Filed July 8, 1964, Ser. No. 381,244
Claims priority, application Great Britain, July 12, 1963, 27,750/63

Int. Cl. A61L 23/00

U.S. Cl. 424—60

15 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a sunscreen composition comprising a suncreening agent in castor oil.

This invention relates to improvements in cosmetic preparations. In particular it relates to improved preparations for the protection of the skin from the harmful effect of solar radiation.

In addition to the well-known tanning effect of sunlight on the skin the ultra-violet radiation of wavelength 290 to 313 mμ may produce a severe erythema especially in fair skinned subjects whose skins contain only small amounts of the protective pigment melanin. Numerous protective agents have been discovered which absorb ultra-violet light of wavelength 290 to 314 mμ while the radiation of longer wavelength is transmitted. The most highly active selective protective agents of this type are so active that a very thin film on the surface of the skin will protect the skin against erythema but will transmit the longer wavelength radiation which imparts the much sought tan to the skin. Such compounds of this class which are pharmaceutically acceptable have been incorporated in creams, lotions, oils and foams for application to the skin to prevent sunburn and throughout this specification are referred to as sunscreen agents. The compositions are generally referred to as protecting the skin against sunlight but it is to be understood that the compositions may equally well be used for protection against ultra-violet radiation of 290 to 313 mμ whatever its source.

It is an object of the present invention to provide improved sunscreen compositions which afford a longer period of protection per application.

It is known that the base in which a substance is formulated for application to the skin may have a considerable effect on the amount of substrate remaining on the skin after any given time. A sunscreen agent can only exert its maximum effect if it remains in the surface of the skin for as long a time as possible.

We have now discovered that a high proportion of a sunscreen agent applied to the skin in association with castor oil or certain prepared lanolin fractions remains on the skin surface for a longer time than the same agent associated with conventional carriers. For the purposes of this invention we define the prepared lanolin fractions as those available commercially under the trademark "Fluilan," "Lantrol" and "Westbrook's liquid lanolin" (which are liquid lanolins or lanolin oils produced by low vacuum distillation or fractional solvent crystallization, see de Navarre, Chemistry and Manufacture of Cosmetics, vol. 2, Cosmetic Material (1962), p. 202).

According to the present invention there are provided compositions for the protection of skin against ultra-violet radiation comprising a sunscreen agent and a cosmetically acceptable diluent or carrier comprising not less than 5% of castor oil, and/or a prepared lanolin fraction as herein before defined.

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The compositions according to the present invention comprise oils, lotions, sprays, creams and foams containing a sunscreen agent within the range of 0.2 to 10% and preferably about 2% of the composition. Suitable sunscreen agents comprise derivatives of benzoic acid, salicylic acid and benzophenone. We prefer to use esters of N-alkyl p-aminobenzoic acids, particularly ethyl p-dimethylaminobenzoate which in addition to its excellent sunscreen properties, is economic in use, readily available and is readily soluble in the formulation bases.

In addition to the sunscreen agents other compatible, pharmaceutically acceptable, active ingredients may be included, for example insect repellants. Suitable insect repellents which may form part of the compositions according to the present invention include dimethyl phthalate, dibutyl phthalate and N,N-diethyltoluamide.

The essential components of the bases according to the invention are castor oil.

In addition to the essential components, the formulation base may also contain additional solvents, preservatives, antioxidants, emulsifiers, perfumes, colouring matter and water. Any pharmaceutically acceptable solvent may be employed which is compatible with the remaining ingredients. We have found that ethanol is especially useful in those oil compositions containing castor oil as it prevents undue stickiness of the preparation. It is generally desirable to include a preservative in aqueous preparations according to the invention and we have found that esters of p-hydroxybenzoic acid are particularly valuable. Those compositions based on castor oil tend to deteriorate on keeping due to the atmospheric oxidation of the oil. It is desirable to include an anti-oxidant in such compositions to prevent this deterioration and well-known compounds such as butylated hydroxyanisole and butylated hydroxytoluene give excellent results. Emulsifying agents which may also be added to the compositions according to the invention include those sold under the trademark "Polawax" which is prepared from cetostearyl alcohol and containing a polyoxyethylene derivative of a fatty acid ester of sorbitan (see Martindale, The Extra Pharmacopoeia, vol. 1, 24th ed., page 698), and the trademark "Lanette Wax SX" which is a mixture of partially sulphated octyl and stearyl alcohols. Cosmetically acceptable perfumes and colouring matter may be added as desired.

The sunscreen oils according to the invention comprise the sunscreen dissolved in the liquid base. It may be desirable to incorporate a thinning agent in castor oil and prepared lanolin fraction formulations and up to 20% of ethanol may be added for this purpose. In castor oil based preparations, which are the preferred compositions about 5 to 10% of ethanol is normally sufficient to give an acceptable composition.

The lotions according to the invention comprise a solution of the sunscreen agent in the oil to which is added aqueous ethanol consistent with complete miscibility. Castor oil is the preferred base for lotions as it is more soluble in alcohol than "Fluilan."

The creams according to the invention contain 0.2 to 10%, preferably about 2% of the sunscreen agent, may be liquid or solid with either water or oil as the continuous phase or they may be vanishing creams or foams. To all of these it is preferable to add a preservative. A liquid water-in-oil cream for example may contain 35 to 85% of total oily phase comprising prepared lanolin fraction or castor oil, together with other oily components such as insect repellants, sunscreen agents and other water insoluble materials, emulsified with water and emulsifying agents where necessary. Liquid oil-in-water creams may contain 5 to 60% of the oil phase together with a suitable emulsifier, for example that available commer-

cially under the trademark "Lanbritol Wax M21" which is a non-ionic self-emulsifying wax prepared from higher fatty alcohols melting at 97° C. (see Martindale, The Extra Pharmacopoeia, vol. 1, 24th edition, p. 1003).

Solid sunscreen creams according to the invention are prepared similarly to the liquid creams but they may contain a higher proportion of the oil phase. Solid water-in-oil creams may contain from 35 to 90% of the oil phase and oil-in-water creams may contain 10 to 80% oil. Suitable emulsifiers are included where necessary.

Vanishing cream or sunscreen foams may comprise 5 to 30% of the oil phase emulsified with a suitable emulsifier such as "Polawax," triethanolamine stearate or self-emulsifying glyceryl monostearate. In addition to the additives already mentioned for other cream formulations it may be desirable to incorporate a humectant such as glycerol to reduce drying out of the compositions.

The efficacy of the compositions of the present invention has been demonstrated in the following ways. Sunscreen agents were dissolved in various solvents to give a concentration of 2%, a concentration frequently employed in commercial preparations. The solutions were applied to human skin and, after 5 minutes, the skin was extracted with ethanol and the ethanol solution assayed spectrophotometrically for the content of sunscreen. A similar quantity of sunscreen solution applied to another patch of skin was allowed to remain for 2 hours before extracting with ethanol and assayed for sunscreen content as before. Assuming the figure obtained 5 minutes after application to correspond to the presence of 100% of the screen in the skin the percentage remaining after 2 hours showed the efficiency of the solvent or base in retaining the sunscreen within extractable of the skin surface. This figure is quoted in the following table for a number of solutions of sunscreen agents.

Solvent	Percent residual sunscreen agent after 2 hours			
	Methyl p-dimethyl-amino-benzoate	Ethyl p-di-methyl-amino-benzoate	Ethyl p-di-ethyl-amino-benzoate	2-hydroxy-methoxy-4-methyl-benzophenone
Dimethyl phthalate	42	51	40	42
Arachis oil	55	68	65	61
Liquid paraffin	Insoluble	64	76	Insoluble
	70	85	89	78
Oleyl alcohol		51		71
"Fluilan"		92		96
Castor oil	84	96	100	88
Castor oil +1% polyethylene glycol 400 dilaurate		87		
Castor oil +1% triethanolamine oleate		85		
Liquid paraffin/castor oil (2:1)		84	91	
Liquid paraffin/castor oil (1:2)		90	90	

A comparison between the effect of 2% solutions of ethyl p-diethylaminobenzoate in dimethyl phthalate and castor oil has been made as follows. The flanks of guinea pigs were shaved, depilated and were irradiated for certain times with ultra-violet radiation from a Kromayer lamp fitted with a Woods glass filter. The wavelength of the transmitted radiation, 290 to 360 mμ approximated to that of normal sunlight in each case the left flank was used as a control area and was irradiated for 3 minutes. Similar areas on the right flank of each animal were treated with standard amounts of sunscreen solution and 2 hours after application they were irradiated for 9 minutes. The degree of erythema was assessed visually after 20 hours and graded numerically as follows:

- 0 No effect
1 Erythema just visible

- 2 Moderate erythema
3 Severe erythema without oedema
4 Severe erythema with oedema

Animal	Sunscreen dissolved in—	Control 3 min. exposure	Treated 9 min. exposure
A-----	Dimethyl phthalate-----	4	3
B-----		4	3
C-----		4	2
D-----		3	1
E-----		4	1
F-----	Castor oil-----	4	2
G-----		3	1
H-----		3	1

Summing the numerical gradings for all the animals on each treatment, the control flanks scored 15 against 8 for those treated with the sunscreen agent dissolved in dimethyl phthalate. The control flanks scored 14 against only 5 for those treated with the same sunscreen agent dissolved in castor oil.

Rectangular areas of 4" x 5" were marked out on the back of each of 4 human volunteers, and test solutions were evenly applied to the areas on each back in random order. After allowing a period of 15 to 30 minutes in the shade to allow the individual preparations to penetrate the skin, each back was exposed to the sun for one hour. The volunteers then remained in the shade, and four hours later definite erythematous response was obtained from surrounding areas, while the treated areas showed little or no reddening. Adjacent areas were compared visually for comparative whiteness, the greater the whiteness the better the protection which had been afforded, and this was scored in favour of that solution giving the best protection from the sun's actinic rays. Where no difference could be seen this was recorded.

- 35 Five solutions were prepared, each containing as active

sunscreen agent 2% w./v. of ethyl p-dimethylaminobenzoate. The cosmetic bases of the sunscreen solutions were as follows:

- 55 Solution B—Fluilan (registered trade name)
Solution C—Castor oil
Solution D—Dimethyl phthalate
Solution E—Arachis oil

60 The solutions were compared individually with each other in 10 different ways, and the following table shows whether better protection was given by one or other of a particular pair or whether no difference could be noted.

65 For example, under the column for the combination C/D the figure 8.0 occurs in the second line. This indicates that for this particular pair of solutions, solution C gave the better protection in 8 tests, and in none of the tests did D give the better protection.

Combination of pairs	B/C	B/D	B/E	C/D	C/E	D/E
No. of times better protection given	3, 3	6, 0	4, 0	8, 0	6, 0	1, 0
No. of times no difference	5	0	1	3	3	1
Total No. of comparisons	11	6	5	11	9	2

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It would appear from these tests that castor oil (C) is equal to or slightly better than Fluilan (B) while arachis oil (E) and dimethyl phthalate (D) have the poorest figures for sunscreen agents.

The cream formulations described in Examples 12 and 13 have been tested experimentally on human volunteers as follows. A known amount, about 10 to 20 mg. of the cream was applied with a glass rod to an area of 3 sq. cm. of the inner forearm ensuring that the cream was broken down on application to the skin. At the end of the contact period (5 minutes or 2 hours) the treated skin was extracted with three successive 15 ml. quantities of cold ethanol applied to the skin from a wide-mouthed glass container, which was shaken for one minute against the arm. The bulked extractives were made up to 50 ml. with ethanol and the amount of sunscreen agent was determined spectrophotometrically. The compositions described in Examples 9 and 10 were compared with a commercially available sunscreen cream of the following composition.

COMPOSITION A

	Percent
Stearic acid	2
Wool alcohol	1
Cetyl alcohol	3.5
Polawax (registered trademark)	5
Arachis oil	15
Ethyl p-dimethylaminobenzoate	1.2
Ethyl p-diethylaminobenzoate	0.75
Butylated hydroxytoluene	0.02
Glycerol	3
Sodium citrate	0.05
Methyl p-hydroxybenzoate	0.1
Silicone fluid MS200 ¹	1
Perfume oil, v./w.	0.4
Water	to 100

¹A range of dimethylsiloxane polymers covering a viscosity range of 0.65 to 100,000 centistokes, the Extra Pharmacopoeia, *ibid.*, p. 1005.

With the exception of the perfume oil all percentages are w./w.

The results were as follows:

Composition	Percent w./w. of sunscreen in composition	Percent total sunscreen recovered		2 hour recovery as percent of 5 min. recovery
		After 5 mins.	After 2 hrs.	
Example 12	1.95	95.6	89.4	93.5
Example 13	1.83	87.5	91.7	104.0
Commercial composition A	2.02	94.0	71.7	76.3

The following non-limitative examples illustrate our invention. In the examples all percentages are w./w. with the exception of the perfume oil in Examples 8, 9 and 10, where the percentage is v./w.

EXAMPLE 1

A sunscreen oil was prepared from the following ingredients:

Ethyl p-diethylaminobenzoate	2
Eethyl p-diethylaminobenzoate	2
Castor oil	90
Butylated hydroxytoluene (B.H.T.)	0.02
Ethanol	to 100

The sunscreen ester was dissolved in the castor oil together with the antioxidant (B.H.T.) and ethanol was added to 100% with stirring.

EXAMPLE 2

A sunscreen oil was prepared as in Example 1 from the following ingredients:

Ethyl p-dimethylaminobenzoate	Percent 2
"Fluilan"	85
Ethanol	to 100

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EXAMPLE 3

A sunscreen lotion was prepared by dissolving ethyl p-diethylaminobenzoate and butylated hydroxyanisole in castor oil and adding 90% ethanol to give a lotion with the following composition:

	Percent
Ethyl p-diethylaminobenzoate	2
Castor oil	20
Butylated hydroxyanisole	0.02
90% aqueous ethanol	to 100

EXAMPLE 4

A pourable oil-in-water sunscreen cream was prepared from the following ingredients:

	Percent
Castor oil	10
"Fluilan (registered trademark)"	5
"Lanbritol Wax M21"	4
o/w stabiliser ¹	3
Methyl p-hydroxybenzoate	0.1
B.H.T.	0.02
Ethyl p-diethylaminobenzoate	2
Water	to 100

¹Known under the trademark "Myrj 49," polyoxyethylene monostearate (see International Encyclopedia of Cosmetic Material Tradenames, Moore Publishing Company, 1957, p. 178.

The screening agent and B.H.T. were dissolved in the previously melted castor oil, "Lanbritol Wax" and "Myrj." After adjusting the temperature to 75° C., the water, at the same temperature and containing the dissolved methyl p-hydroxybenzoate, was added with high speed stirring. Stirring was continued until the product was cold.

EXAMPLE 5

By a similar method to that described in Example 4, a more solid cream was prepared from the following ingredients:

	Percent
Castor oil	40
"Lanbritol Wax M21"	10
Ethyl p-dimethylaminobenzoate	21
Methyl p-hydroxybenzoate	0.1
B.H.T.	0.02
Water	to 100

EXAMPLE 6

A cream similar to that described in Example 5 was prepared from the following ingredients:

	Percent
Castor oil	40
Polyglycol 400 distearate	10
Methyl p-hydroxybenzoate	0.1
B.H.T.	0.02
Ethyl p-diethylaminobenzoate	2
Water	to 100

EXAMPLE 7

A sunscreen cream in a vanishing base was prepared with the following composition:

	Percent	
Castor oil -----	20	5
Stearic acid -----	8	
Triethanolamine -----	4	
Ethyl p-diethylaminobenzoate -----	2	
B.H.T. -----	0.02	
Methyl p-hydroxybenzoate -----	0.1	10
Water -----	to 100	

EXAMPLE 8

A soft sunscreen cream was prepared with the following composition:

	Percent	
Castor oil -----	20	
Glyceryl monostearate (self-emulsifying) -----	5	
Cetyl alcohol -----	3	20
Solan E (registered trademark) ¹ -----	5	
Ethyl p-dimethylaminobenzoate -----	2	
Methyl p-hydroxybenzoate -----	0.1	
Butylated hydroxytoluene -----	0.02	
Perfume oil, v./w. -----	0.4	25
Water -----	to 100	

¹ An ethoxylated lanolin (see International Encyclopedia of Cosmetic Material Tradenames, *ibid.*, p. 245).

EXAMPLE 9

A fluid sunscreen, insect repellent, cream was prepared containing the following ingredients:

	Percent	
Fluilan (registered trademark). A liquid lanolin preparation -----	10	35
N,N-diethyltoluamide -----	15	
Ethyl p-dimethylaminobenzoate -----	2	
Glyceryl monostearate (non self-emulsifying) -----	10	
Stearic acid -----	2	
Polychol 5 (registered trademark) ¹ -----	1	40
Butylated hydroxytoluene -----	0.02	
Cellosize QP 15000 (registered trademark). A hydroxyethyl cellulose -----	0.25	
Ethyl p-hydroxybenzoate -----	0.15	
Triethanolamine B.P.C. -----	1	45
Perfume oil, v./w. -----	0.5	
Water -----	to 100	

¹ An ethoxylated lanolin alcohol preparation (see International Encyclopedia of Cosmetic Material Tradenames, *ibid.*, p. 213).

EXAMPLE 10

A fluid sunscreen, insect repellent, cream was prepared containing the following ingredients:

	Percent	
Castor oil -----	10	
N,N-diethyltoluamide -----	15	
Ethyl p-dimethylaminobenzoate -----	2	
Glyceryl monostearate (non-self-emulsifying) -----	10	60
Stearic acid -----	2	
Polychol 5 (registered trademark), an ethoxylated lanolin alcohol preparation -----	2	
Butylated hydroxytoluene -----	0.02	
Cellosize QP 15000 (registered trademark), a hydroxyethyl cellulose -----	0.25	65
Methyl p-hydroxybenzoate -----	0.15	
Triethanolamine B.P.C. -----	1	
Perfume oil, v./w. -----	0.5	
Water -----	to 100	70

We claim:

1. A sunscreen composition comprising a sunscreen agent which absorbs ultra-violet radiation of wavelengths in the erythema producing range of about 290 to 313 m μ and a cosmetically acceptable diluent comprising not less than 5% of castor oil.

2. An oily composition as claimed in claim 1 comprising castor oil and comprising also a thinning liquid compatible with said castor oil.

3. An oily composition as claimed in claim 2 wherein the thinning liquid is ethanol.

4. A composition as claimed in claim 1 comprising also an insect repellent.

5. A composition as claimed in claim 4 wherein the insect repellent is N,N-diethyltoluamide.

6. A composition as claimed in claim 1 in which the sunscreen agent is present in a concentration of 0.2 to 10 w./w.

7. A composition as claimed in claim 6 wherein the sunscreen agent is ethyl p-dimethylaminobenzoate.

8. A composition as claimed in claim 6 wherein the sunscreen agent is ethyl p-diethylaminobenzoate.

9. A liquid, water-in-oil, sunscreen cream as claimed in claim 1 in which the total oily phase comprising the castor oil comprises 35 to 85% of the composition.

10. A solid, water-in-oil, sunscreen cream as claimed in claim 1 in which the total oil phase comprising the castor oil comprises 35 to 90% of the composition.

11. A liquid, water-in-oil, sunscreen cream as claimed in claim 1 in which the total oily phase comprising the castor oil comprises 5 to 60% of the composition.

12. A solid, water-in-oil, sunscreen cream as claimed in claim 1 in which the total oily phase comprising the castor oil comprises 10 to 80% of the composition.

13. A vanishing cream as claimed in claim 1 in which the total oily phase comprising the castor oil comprises 5 to 30% of the composition.

14. A sunscreen composition as claimed in claim 1 also comprising an effective amount of an antioxidant for said castor oil.

15. A method of protecting the skin from the harmful effect of solar radiation comprising applying to the skin a composition comprising a sunscreen agent which absorbs ultra-violet radiation of wavelengths in the erythema producing range of about 290 to 313 m μ and a cosmetically acceptable diluent therefor comprising not less than 5% of castor oil.

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U.S. Cl. X.R.

424—59, 308, 310, 320, 365