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SUN SCREENING COMPOSITIONS

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This application is a continuation-in-part of my copending application, Serial No. 307,927, filed September 4, 1952, now abandoned.

The present invention relates to sun screening compositions. More particularly, it relates to cosmetic preparations containing beta-resorcylic acid, its salts, esters, amides, and similar organic derivatives in sufficient concentration to screen out the solar ultraviolet rays within the range of from about 2970 A. to about 3150 A. while allowing those sun rays which cause tanning without burning to be effective.

Various sun screening preparations have been employed in the past, but none of them have been entirely satisfactory; and it is desirable that cheaper, more effective, and versatile sun screening preparations be made available. Some of the sun screening agents employed in the past have been unstable. In some, the amount of active ingredient required was too high. Some were poorly soluble in the vehicle. Some did not give a continuous film on skin. Other sun screening agents employed in the past have produced sensitivity in certain individuals which has prevented their general acceptance. One other disadvantage of the prior art sun screening agents has been their lack of versatility as they could not be used interchangeably in fatty and water-miscible vehicles.

In accordance with the present invention, it has been discovered that the class of compounds comprising beta-resorcylic acid, its salts with organic and inorganic bases, its esters and amides, are excellent agents for screening out the ultraviolet rays within the range of from 2970 A. to 3150 A. when incorporated in cosmetic preparations in concentration of from about 0.5% to 5% by weight. My preferred concentration range is about 1% to 4% by weight. My preferred specific concentration is about 3% by weight since the sun screening effects are good, and it represents an economical quantity. The exact percentage, of course, varies with the type of product made.

The ingredients or excipients which, with the beta-resorcylic acid derivative, make up the cosmetic compositions, generally include water and alcohol in a total concentration of not more than about 90% by weight, and at least 5% and generally not more than about 20% by weight of a bland, high-boiling, non-volatile excipient which is liquid at body temperature and which serves to distribute the beta-resorcylic acid derivative uniformly over the skin and to maintain it in solution and prevent crystallization. Among such bland non-volatile excipients are lanolin, lanolin alcohols, mineral and vegetable oils and fats, alkyl ethers of ethylene glycol, alkyl esters of phthalic acid, alkyl esters of fatty acids containing twelve or more carbon atoms, glycerol, propylene glycol, fatty acid esters of polyhydric alcohols and like materials having boiling points of at least about 180° C. Colors, preservatives and perfumes in a total concentration of generally less than 1% by weight are usually desirable. Also desirable are certain cosmetic ingredients which contribute to the physical properties of the cosmetic formulations without affecting the sun screening characteristics thereof.

Such materials include cetyl alcohol, stearic acid, vegetable gums and certain water-soluble polymers of natural origin. The concentration of these ingredients is usually not more than 5% by weight and often is less than 1% by weight. When the sun screening agent is suspended in an aqueous emulsion, emulsifiers such as alkali metal salts of fatty acids, amine salts of fatty acids, amine salts of aromatic sulfonic acids and the like are added in concentration not greater than 10% by weight.

It is surprising that beta-resorcylic acid is extremely effective for absorbing the injurious ultraviolet rays, and it is also surprising that the inorganic salts, organic salts, esters, and amides of beta-resorcylic acid in equivalent concentrations produce essentially the same sun screening effect as beta-resorcylic acid. In this connection, I have conducted experiments which show that a 1% by weight concentration of beta-resorcylic acid will give less than 10% transmission of ultraviolet rays in the range of 2970 A. to 3150 A. Concentrations of 0.5% by weight are also effective, and concentrations up to 5% by weight may be used with good effects. The salts and organic derivatives of beta-resorcylic acid in equivalent concentrations give essentially the same transmission effect. It appears, therefore, that the beta-resorcylic acid molecule is the principal ray-absorbing portion in my sun screening agent.

My discovery that beta-resorcylic acid and its various organic derivatives possess similar sun screening effects permits the preparation of different types of cosmetic preparations adapted for topical application to human skin in the form of thin films. This is extremely important because some individuals may prefer the fatty-type cosmetic preparation; while others prefer the emulsified or washable-type bases. Others may prefer oil, aqueous, or hydro-alcoholic solutions. In some cases it may be desired to have both a water-soluble and fat-soluble sun screen in the same preparation, as in the case of some emulsions, and my invention includes such combinations.

Beta-resorcylic acid, sometimes referred to as 2,4-dihydroxy-benzoic acid, is readily available. The sodium, potassium, ammonium, mono-, di-, and trialkanolamine, and similar salts may be prepared by reacting the acid with the desired base as is or in a mutual solvent; or if desired, the salts can be prepared during the preparation of the cosmetic. Among the salts that I have found suitable as sun screening agents in my compositions are the sodium, ammonium, triethanolamine and tri-isopropanolamine salts.

The esters of beta-resorcylic acid with either mono- or polyhydric alcohols are well suited for use in my sun screening compositions. In general, I prefer the higher alcoholic esters such as those of lauryl, myristyl, and cetyl alcohols. Among the esters of beta-resorcylic acid which I have found suitable for use in my sun screening compositions are included the cetyl ester as an example of a higher alcohol, and the glyceryl ester as an example of a polyhydric alcohol.

The esters listed above may be, in general, prepared by reacting beta-resorcylic acid with the desired alcohol under esterifying conditions. The cetyl ester of beta-resorcylic acid is one of my preferred agents, and it may be prepared in accordance with the following specific directions:

A mixture of cetyl alcohol, methyl beta-resorcylate, methanol, and sodium hydroxide was refluxed. Methanol began to be evolved at 135° C. After continued heating for three hours, the temperature reached 170° C. with the methanol being completely evolved. After eight more hours of heating, the remaining traces of methanol were removed by vacuum steam distillation at 20 mm. and 170–175° C. The crude ester was purified by washing in water and recrystallizing; M.P. 84–86° C.

The glyceryl ester of beta-resorcylic acid was prepared

by first making the isopropylidene glycerol, i.e., methyl beta-resorcylate was reacted with isopropylidene glycerol followed by acid hydrolysis of the ketal. The glyceryl ester obtained has a melting point of 141–145° C.

In addition to the inorganic and organic salts and esters mentioned above, I have found that other organic derivatives prepared by reaction with the carboxylic group of beta-resorcylic acid are suitable for use in my sun screening compositions. For example, the amides prepared by reacting beta-resorcylic acid with ammonia or primary and secondary amines are useful in my compositions. As an example of a suitable amide of beta-resorcylic acid for use in my sun screening compositions may be included the amide prepared as follows:

Beta-resorcylamide was prepared by refluxing the acid with $SOCl_2$, adding a few drops of pyridine, followed by the addition of concentrated ammonia water. The amide was filtered off, washed with dilute sodium carbonate solution, then distilled water and dried; M.P. 218–220° C.

In tests carried out to determine the spectral transmittance of my sun screening agents, it was found that a 1% by weight solution of beta-resorcylic acid in an alcoholic solution gave less than 10% transmission in the ultraviolet range of 2970 A. to 3150 A. The monoglyceryl ester in alcoholic solution gave similar results. Likewise, the cetyl ester of beta-resorcylic acid in a concentration of 1% by weight in an alcoholic solution and 1% by weight in an oil solution gave a transmission of less than 10% in the range of 2970 A. to 3150 A. Following the above tests, it was shown that beta-resorcylic acid and the derivatives listed herein can be used in the various accepted types of cosmetic formulations in concentrations ranging from 0.5% to 5% by weight; and when spread on the skin, they produce the desired sun screening effect.

The following specific examples will serve to illustrate my invention using some of the various types of cosmetic formulations; it being understood, of course, that the examples are given by way of illustration, and they can be varied considerably. Quantities of materials are given in parts by weight.

EXAMPLE 1

Emulsion-type formulation

	Parts
Stearic acid	5
Lanolin anhydrous	7
Mineral oil	12
Triethanolamine	5
Beta-resorcylic acid	3
Monethyl ether of diethylene glycol	15
Water to make 150 parts.	

A mixture of the fats is heated to 70° C., the beta-resorcylic acid added and dissolved. A mixture of the water, alkali, and ether is heated to 72° C. The water mixture is added to the fats mixture and stirred until cool.

EXAMPLE 2

Aqueous-type formulation

	Parts
Sodium beta-resorcylate	3
Propylene glycol	10
Gum mucilage, preservative, color and perfume	1
Water	86

Mix the ingredients, dissolve and strain.

EXAMPLE 3

Oil-type formulation

	Parts
Cetyl beta-resorcylate	3
Vegetable oil	25
Mineral oil, certified color, and perfume q.s.	0.5
Alcohol	71.5

Dissolve the ingredients and strain.

EXAMPLE 4

Fast-drying, greaseless, hydroalcoholic lotion-type formulation

	Parts
Monoglyceryl resorcylate	3
Propylene glycol	25
Perfume and color	0.8
Alcohol and water	71.2

Dissolve the ingredients and filter.

EXAMPLE 5

Sun screen-repellent

	Parts
Cetyl beta-resorcylate or beta-resorcylic acid	3
Dimethyl phthalate	96
Color and perfume	1

Mix the ingredients and dissolve.

In the foregoing examples, I have employed the sun screening agents which are preferred because of their effectiveness, availability, and cheapness. Instead of the particular beta-resorcylic acid derivative employed, I may use any one of those which I have previously mentioned. Likewise, instead of the particular ester employed, I may use an equivalent concentration of the acid itself, its esters or amides which I have previously listed.

In general, the concentrations of beta-resorcylic acid or derivatives may be varied from about 0.5% to 5% by weight, usually about 3% to 4% by weight. However, my invention includes compositions containing the beta-resorcylic acid compounds in quantity sufficient to screen out at least 90% of the sun rays within the range of from about 2970 A. to about 3150 A. when applied in a thin film to the human skin.

My choice of compound is somewhat dependent on cost, type of product in which it is to be used, and availability of materials. In my composition, solution of the sunscreen is believed necessary to produce a stable product as well as one that both looks right and does what it is supposed to do. In some cases, my active ingredient is readily soluble. In other cases, heat may be necessary to dissolve the sunscreen in the vehicle.

I claim:

1. A sun screening composition comprising a cosmetic preparation containing sodium beta-resorcylate incorporated in a cosmetic formulation and in a concentration of from about 0.5% to 5% and effective for screening out the sun rays within the range of from about 2970 A. to 3150 A. when applied in a thin film to the human skin, said formulation containing at least 5% of a bland, high-boiling nonvolatile, organic excipient which is liquid at body temperature with a boiling point of at least about 180° C. and serves to distribute the resorcylate over the body surface and maintain it in solution and containing a total of not more than 90% of water and alcohol.

2. A sun screening composition comprising a cosmetic preparation containing triethanolamine beta-resorcylate incorporated in a cosmetic formulation and in a concentration of from about 0.5% to 5% and effective for screening out the sun rays within the range of from about 2970 A. to 3150 A. when applied in a thin film to the human skin, said formulation containing at least 5% of a bland, high-boiling nonvolatile, organic excipient which is liquid at body temperature with a boiling point of at least about 180° C. and serves to distribute the resorcylate over the body surface and maintain it in solution and containing a total of not more than 90% of water and alcohol.

3. A sun screening composition comprising a cosmetic preparation containing monoglyceryl beta-resorcylate incorporated in a cosmetic formulation and in a concentration of from about 0.5% to 5% and effective for screening out the sun rays within the range of from about 2970

A. to 3150 A. when applied to a thin film to the human skin, said formulation containing at least 5% of a bland, high-boiling nonvolatile, organic excipient which is liquid at body temperature with a boiling point of at least about 180° C. and serves to distribute the resorcylate over the body surface and maintain it in solution and containing a total of not more than 90% of water and alcohol.

4. A sun screening composition comprising a cosmetic preparation containing cetyl beta-resorcylate incorporated in a cosmetic formulation and in a concentration of from about 0.5% to 5% and effective for screening out the sun rays within the range of from about 2970 A. to 3150 A. when applied in a thin film to the human skin, said formulation containing at least 5% of a bland, high-boiling nonvolatile, organic excipient which is liquid at body temperature with a boiling point of at least about 180° C. and serves to distribute the resorcylate over the body surface and maintain it in solution and containing a total of not more than 90% of water and alcohol.

5. A sun screening composition comprising an emulsion-type cosmetic formula containing triethanolamine beta-resorcylate in a concentration of about 3%, a bland high-boiling nonvolatile, organic excipient which is liquid at body temperature with a boiling point of at least about 180° C. in a concentration of at least 5% and water and alcohol in a total concentration not greater than 90%.

6. A sun screening composition comprising an aqueous mucilage-type cosmetic formula containing sodium beta-resorcylate in a concentration of about 3%, a bland high-boiling nonvolatile, organic excipient which is liquid at body temperature with a boiling point of at least about 180° C. in a concentration of at least 5% and water and alcohol in a total conecntration not greater than 90%.

7. A sun screening composition comprising an oil-type cosmetic formula containing cetyl beta-resorcylate in a concentration of about 3%, a bland high-boiling nonvolatile, organic excipient which is liquid at body temperature with a boiling point of at least about 180° C. in a concentration of at least 5% and water and alcohol in a total concentration not greater than 90%.

8. A sun screening composition comprising a hydroalcoholic lotion-type cosmetic formula containing glyceryl mono-beta-resorcylate in a concentration of about 3%, a bland high-boiling nonvolatile, organic excipient which is liquid at body temperature with a boiling point of at least about 180° C. in a concentration of at least 5% and water and alcohol in a total concentration not greater than 90%.

9. A sun screening composition adapted for topical administration comprising a substance selected from the group consisting of beta-resorcylic acid, salts of beta-resorcylic acid, esters of beta-resorcylic acid, and amides of beta-resorcylic acid in quantity sufficient to screen out at least 90% of the sun rays within the range from about 2970 A. to 3150 A. when applied in a thin film to the human skin, in a cosmetic vehicle having incorporated therein at least 5% of a bland nonvolatile high-boiling, organic excipient which is liquid at body temperature with a boiling point of at least about 180° C. and serves to distribute the substance over the body surface and to maintain it in solution, wherein the sum of the concentrations of water and alcohol in said vehicle is not greater than 90%.

10. A sun screening composition adapted for topical administration comprising beta-resorcylic acid in quantity sufficient to screen out at least 90% of the sun rays within the range from about 2970 A. to 3150 A. when applied to a thin film to the human skin, in a cosmetic vehicle having incorporated therein a bland nonvolatile high-boiling, organic excipient which is liquid at body temperature with a boiling point of at least about 180° C. and serves to distribute the substance over the body surface and to maintain it in solution, wherein the sum

of the concentrations of water and alcohol in said vehicle is not greater than 90% and wherein the concentration of bland nonvolatile excipient in said vehicle is at least 10%.

11. A sun screening composition adapted for topical administration comprising a salt of beta-resorcylic acid in quantity sufficient to screen out at least 90% of the sun rays within the range from about 2970 A. to 3150 A. when applied in a thin film to the human skin, in a cosmetic vehicle having incorporated therein a bland nonvolatile high-boiling, organic excipient which is liquid at body temperature with a boiling point of at least about 180° C. and serves to distribute the substance over the body surface and to maintain it in solution, wherein the sum of the concentrations of water and alcohol in said vehicle is not greater than 90% and wherein the concentration of bland nonvolatile excipient in said vehicle is at least 5%.

12. A sun screening composition adapted for topical administration comprising an ester of beta-resorcylic acid in quantity sufficient to screen out at least 90% of the sun rays within the range from about 2970 A. to 3150 A. when applied in a thin film to the human skin, in a cosmetic vehicle having incorporated therein a bland nonvolatile high boiling, organic excipient which is liquid at body temperature with a boiling point of at least about 180° C. and serves to distribute the substance over the body surface and to maintain it in solution, wherein the sum of the concentrations of water and alcohol in said vehicle is not greater than 90% and wherein the concentration of bland nonvolatile excipient in said vehicle is at least 5%.

13. A method of screening burning sun rays from human skin which comprises coating said skin with a sun screening composition containing a substance selected from the group consisting of beta-resorcylic acid, salts of beta-resorcylic acid, esters of beta-resorcylic acid and amides of beta-resorcylic acid in quantity sufficient to screen out at least 90% of the sun rays within the range of about 2970 A. to 3150 A. when applied in a thin film to human skin in a cosmetic vehicle having incorporated therein at least 5% of a bland high-boiling nonvolatile organic excipient which is liquid at body temperature with a boiling point of at least about 180° C. which serves to distribute the substance over the body surface and to maintain it in solution, wherein the sum of the concentrations of water and alcohol in said vehicle is not greater than 90%.

14. A sun screening composition adapted for topical administration comprising a cosmetic preparation containing beta-resorcylic acid incorporated in a cosmetic formulation in a concentration of from about 0.5% to 5% by weight and effective for screening out the sun rays within the range of from about 2970 A. to 3150 A. when applied in a thin film to the human skin, said formulation containing at least 5% of a bland nonvolatile high-boiling, organic excipient which is liquid at body temperature with a boiling point of at least about 180° C. which serves to distribute the acid over the body surface and maintain it in solution, wherein the total quantity of alcohol and water is not more than about 90% by weight of the total composition.

15. A sun screening composition adapted for topical administration comprising beta-resorcylic acid in a vehicle containing lanolin, mineral oil and a lower alkyl ether of ethylene glycol, said beta-resorcylic acid being present in a concentration of at least about 2% of the weight of the vehicle and said nonvolatile vehicle constituents being present in a total concentration of at least about 20% by weight.

16. A sun screening composition adapted for topical administration comprising beta-resorcylic acid in a vehicle consisting essentially of a nonvolatile alkyl ester of a fatty acid containing at least 12 carbon atoms, said beta-re-

sorcylic acid being present in a concentration of at least about 3% of the weight of the composition.

17. A sun screening composition in emulsion form adapted for topical administration comprising about 2% by weight of beta-resorcylic acid, about 23% of non-volatile oily materials selected from the group consisting of lanolin, mineral oil and the monoethyl ether of diethylene glycol, about 7% of triethanolamine stearate and the remainder water.

18. A sun screening composition adapted for topical administration comprising beta-resorcylic acid in a vehicle consisting essentially of a di-(lower alkyl) phthalate, said beta-resorcylic acid being present in a concentration of about 3% of the weight of the composition.

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