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SUN-SCREENING COMPOSITIONS

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This application is a continuation-in-part of co-pending application Ser. No. 129,248, filed Aug. 4, 1961, now abandoned.

This invention relates to sun-screening compositions, and more particularly, it relates to improved clear, mobile single phase liquid compositions for use in protecting the skin from certain ultraviolet radiation.

There are numerous compositions known for application to human skin to protect it from erythema-producing actinic ultraviolet irradiation, and particularly to protect the skin from such components of sunlight. These known compositions contain a sun-screening agent, that is, a material which will absorb ultraviolet radiation in the erythema-producing region of the electromagnetic spectrum. It is generally known that radiation having a wavelength of 2900 to about 3200 Angstrom units (A.) is erythema-producing and it is such radiation that produces painful, and sometimes injurious, sunburns.

It is known that certain chemical substances absorb radiation in the 2900–3200 A. range, and these materials have been used for the preparation of sun-screening compositions. Sun-screening compositions are generally in the form of creams and cream lotions. These materials have been relatively easy to formulate and to prepare and give a degree of sun-screening. However, in addition to the sun-screening agent, these compositions contain large amounts of non-volatile components, particularly components of an oily character, such as fatty acids, fatty alcohols, fatty acid esters, and the like. Such creams and cream lotions leave an oily film on the skin. The oil frequently transfers to garments and to other surfaces with which the skin comes into contact. Thus, the surfaces or the garments become soiled, and in some cases irretrievably soiled. Further, the oily residue may be sticky or tacky and uncomfortable, especially in hot weather.

In order to avoid an oily residue, a number of liquid preparations have been made which contain a sun-screening substance, a surface active agent, and a vehicle. Such preparations do not leave an oily, sticky deposit which transfers to other surfaces, but unfortunately these prior art preparations have possessed a disadvantage of their own: Two applications on the skin do not produce twice the protection against ultraviolet radiation that one coating or application produces. In fact, in many cases the effect of two or more applications is scarcely more than the effect of a single application. The disadvantage of this lack of cumulative effect is that the protection afforded by clear, mobile preparations is of much shorter duration than the protection afforded by prior art cream lotions and ointments. Moreover, with certain sun-screening compounds, sensitive persons may not be able to apply to their skin a protective layer of sun-screening material adequate to prevent painful burns. Accordingly prior art clear mobile lotions have had a limited range of use.

One remedy for this problem would appear to be the use of a higher concentration of the sun-screening agent in the composition. This has not been a satisfactory answer, however, because the heavy concentration of sun-screening agent has not deposited evenly on the skin as a continuous film, but seems to form a layer of microscopic globules. The result of this is that solar ultraviolet

radiation can reach the skin unhindered and produce an erythema.

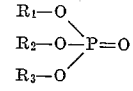
This invention provides a well-balanced sun-screening composition which will give cumulative protection (hereinafter referred to as a cumulative protection effect) through multiple applications of the preparation so that the individual user can obtain the desired amount of protection.

This invention also makes it possible to provide a single-strength formulation which will be adequate for use by substantially all individuals, notwithstanding their individual susceptibility to sunburn.

This invention further provides compositions containing a sun-screening agent which will absorb ultraviolet light to an extent directly proportional to the concentration of the sun-screening agent in the preparation.

Further and more specific objects, features, and advantages will clearly appear from the detailed description given below.

The protective sun-screening compositions of this invention are clear, mobile liquids containing at least one vehicle such as water and/or alkanol, a sun-screening agent, and a phosphoric acid ester having the formula:



wherein R_1 is an alkoxy fatty alcohol radical, and R_2 and R_3 are either hydrogen or alkoxy fatty alcohol radicals and can be the same or different.

It has been found that the use of such phosphoric acid esters in the preparation of clear, mobile liquid sun-screening compositions surprisingly permits their effect to be cumulative, as has been the case for prior art creams and cream lotions, but they do not suffer from the attendant oiliness or leave on the skin a residue of materials which are extraneous to the sun-screening effect. It is believed that the above-mentioned phosphoric acid esters, as used in the practice of this invention, solve the problem of producing a proper hydrophilic-lipophilic balance between the fatty skin secretions and the aqueous skin secretions, with the result that after evaporation of the vehicle the sun-screening agent deposits on the skin in the form of a continuous film of material, instead of depositing in the form of a discontinuous or uneven film of relatively large particles or droplets as has been the case with prior art clear, mobile liquid compositions. Thus, ultraviolet light cannot bypass the sun-screen deposited by the compositions of this invention and penetrate into the skin to produce erythema and burning.

The clear, mobile liquid sun-screening compositions of this invention give protection proportional both to the amount of lotion applied and also proportional to the concentration of sun-screening agent contained therein despite the fact that they are free of oily materials used in creams and cream lotions. This unexpected result is obtained by the formulation of the composition to contain a phosphoric ester of an alkoxylated fatty alcohol having at least about 12 carbon atoms in its carbon chain. This fatty alcohol is condensed with an alkoxylating agent and then the phosphoric acid ester is formed.

The fatty alcohols used in the esters have a chain length of at least about 12 carbon atoms, and desirably from about 12 to about 20 carbon atoms. Particularly good results have been obtained with preferred fatty alcohols having from about 12 to about 18 carbon atoms in the chain. The fatty alcohols can be fully saturated alcohols such as lauryl, tridecyl, myristyl, cetyl, or stearyl, or they can be unsaturated fatty alcohols such as myristoleyl or oleyl.

The esters can be regarded as formed from fatty alcohols alkoxylated with an alkoxylating agent such as

alkylene oxides to produce alkoxy fatty alcohol radicals. Preferred alkylene oxides used to react with the fatty alcohols are ethylene oxide and propylene oxide. The fatty alcohols are desirably alkoxylated with from about 4 to about 30 moles of the alkylene oxide per mole of fatty alcohol, and it is especially preferred to condense from about 4 to about 8 moles of alkylene oxide with each mole of the fatty alcohol. The preferred alkoxylated fatty alcohols are the lauryl tetraethyleneglycols and lauryl octaethyleneglycols.

The commercial phosphoric acid esters can be prepared by conventional methods of esterification of phosphoric acid derivative, for example, by reacting the phosphorus oxychloride or phosphorus pentoxide with an alkoxylated fatty alcohol. The mono-, di-, and tri-esters of phosphoric acid can be used in the practice of this invention. For purposes of this invention, the esters will be considered as orthophosphoric acids in which one or more hydrogen atoms are replaced by alkoxy fatty alcohol radicals prepared as described above.

The amount of such esters used in the compositions of this invention can be varied over a wide range. Generally it is desirable that the compositions contain from about 0.1% to about 20% of the esters, and it is preferred that they contain from about 1% to about 5% of such esters. Such phosphoric acid esters are sold, under the trademark "Hostaphat." All parts, proportions, and percentages herein are by weight, unless otherwise indicated.

The sun-screening agents can be any substances which are not injurious to the skin and which will absorb ultraviolet radiation in the desired wavelength, preferably in the range of from about 2900–3200 A. Preferred sun-screening substances include:

(1) Derivatives of p-aminobenzoic acid in a concentration of from 0.5% to 10%, and preferably 1% to 4%, including esters, for example, the ethyl ester, propyl esters including the isopropyl ester sold under the trade name "Cycloform," the butyl ester, the glyceryl ester (sold under the trademark "Escalol 106" and disclosed in United States Patent 2,327,899), as well as higher alcohol esters; ethyl, propyl, isopropyl, butyl esters of paradimethylaminobenzoic acid; ethyl, propyl, isopropyl, butyl esters of paradiethylaminobenzoic acid; alkoxylated p-aminobenzoic acid including condensation products of p-aminobenzoic acid with polyethylene glycol or polypropylene glycol, such as N-mono- and N,N-disubstituted aminohydroxyalkyl benzoates disclosed in United States Patent 2,561,468.

(2) Derivatives of o-aminobenzoic acid including the methyl, ethyl, menthyl, phenyl and butyl esters used in amounts of from 0.5% to 10%, and preferably 1% to 5%.

(3) Derivatives of salicylic acid including esters such as the ethyl, propyl, isopropyl, isobutyl, benzyl, phenyl, menthyl, homomenthyl, 2-ethylhexyl and dipropylene glycol esters of salicylic acid and N-salicoyl-p-aminophenol disclosed in United States Patent 2,874,090. These derivatives of salicylic acid are used in amounts of from 0.5% to 20%, and preferably 2% to 8%.

(4) Derivatives of β-resorcylic acid in amounts of from 0.5% to 5%, and preferably 1% to 4%. Such derivatives are disclosed, for example, in United States Patent 2,880,140. Such derivatives include the sodium and trialkanolamine and other inorganic and organic salts of β-resorcylic acid and glyceryl and cetyl esters of β-resorcylic acid.

(5) Derivatives of cinnamic acid in amounts of from 0.5% to 10%, preferably from 1% to 5%, such as the benzyl and methyl esters of cinnamic acid and 2-ethoxyethyl-p-methoxycinnamate ("Giv-Tan F," British Patent 856,411).

(6) Derivatives of benzophenone in amounts of from 0.5% to 10%, and preferably 1% to 5%, including the methoxy-, ethoxy- and dihydroxy-benzophenones.

(7) Digalloyl trioleate used in amounts of from 1% to 10%, and preferably 2% to 4%.

Thus, the compositions of this invention contain from about 0.5% to about 20% of a sun-screening agent. These compositions preferably contain from about 1% to about 8% of sun-screening agent so that a single application of the protective compositions will be adequate for those who have considerable resistance to erythema, and they can be used in multiple applications to protect those who are more sensitive to ultraviolet radiation.

The preparations of this invention accordingly contain the phosphoric acid ester, a sun-screening agent or agents, and the vehicle. The compositions can also contain other constituents of this invention essentially contain the ester, sun-screening agents, and vehicles, they can also include a perfuming agent, lubricants, thickeners, and the like. They can further be admixed with propellants for aerosol spray compositions, as described herein.

The vehicle is water, an alkanol, or a mixture of these. Where alkanols are used, the volatile lower alkanols are desirably used, preferably those containing from 1 to about 6 carbon atoms in the molecule. For cosmetic acceptability, volatile alcohols such as propanol and isopropanol are preferred, and ethanol is especially preferred because of its overall performance in the compositions.

As used herein, it will be understood that "clear" refers to the transparency of the composition. It can be colored, either by the sun-screening agents, the esters, or with added dyes, or it can be water-white. The clarity of the compositions is due to freedom from undissolved or emulsified materials. Thus, the compositions of this invention are essentially single-phase liquids. The term "mobile" as used herein refers to the relatively high fluidity, spreadability, and pourability of the compositions. While thickeners can, if desired, be used to increase the viscosity, these compositions should still be readily pourable.

The phosphoric acid esters not only act as effective surface-active agents to disperse the sun-screening materials on the skin without adverse effects, in addition to apparently establishing a hydrophilic-lipophilic balance to effect good dispersion of the sun-screening agent on the surface of the skin as disclosed above. The compositions of this invention possess the ability to give a cumulative protection effect. Further, they absorb ultraviolet light in an amount directly proportional to the concentration of the sun-screening agent in the composition. Thus, compositions of this invention are unique in providing for the first time a clear liquid preparation giving a cumulative protection effect, so that multiple applications provide multiple protection.

The compositions are simply prepared by mixing the constituents in the desired proportions. For example, the sun-screening agent in either alkanolic or aqueous solution is mixed at a convenient temperature, preferably room temperature, with an alkanolic or aqueous solution of the phosphoric acid ester. Other constituents, if used, are added to either the solution of the ester or to the solution of the sun-screening agent. They can also be added to the mixture.

Where a product is to be prepared for dispensing in the form of a spray from an aerosol container, the composition as above disclosed is introduced into the spray container and a propellant of any known type, such as hydrocarbons and preferably halogenated hydrocarbons such as the Freons and Genetrons, are also introduced into the container. Conventional aerosol packaging techniques can be used, such as refrigerating the container containing the sun-screening composition and introducing the propellant in the liquid form.

The following examples are given to illustrate preferred embodiments of this invention and should not be considered as limiting the scope of the invention, the scope being determined by the claims appended hereto.

Example I

A composition is prepared by mixing 4% monolauryl tetraethyleneglycolether phosphate and 5% dipropyleneglycol salicylate with 91% of ethanol at room temperature to obtain a clear liquid. When applied to skin, this composition gives protection proportional to the concentration of the salicylate sun screening agent present therein. Thus, this composition demonstrates the proper hydrophilic-lipophilic balance which assures complete dispersion of the sun-screening agent in the fatty as well as in the aqueous secretions of the skin.

Example II

A clear liquid composition (Composition A) is prepared by admixing 45.00 parts of ethanol, 51.50 parts of water, 1.00 part of "Hostaphat KO–280" alkoxylated fatty alcohol ester of phosphoric acid, and 2.50 parts of propoxylated p-aminobenzoic acid. For comparison purposes a mixture of 45.00 parts of ethanol, 51.25 parts of water, 0.7 part of sodium dioctylsulfosuccinate surface active agent and 3.00 parts of propoxylated p-benzoic acid is prepared (Composition B).

The minimum perceptible erythema (MPE) is then determined according substantially to the procedure used by W. W. Coblentz et al. of the National Bureau of Standards in Research Paper 370 (Journal of Research of National Bureau of Standards, volume VII, October 1931) entitled, "Balanced Thermocouple and Filter Method of Ultraviolet Radiometry With Practical Applications." In these tests the ultraviolet light source used is a quartz mercury lamp provided with a Corex D filter to eliminate essentially all radiation below 2900 A. The input to the lamp is held constant at 500 watts, and all tests are carried out on untanned skin. The distance between the surface of the skin and the ultraviolet light source is adjusted to 10 inches.

The test procedure consists of two steps. In the first step, small unprotected areas of human skin about ½-inch on a side are irradiated in progressive time intervals of 1, 1.5, 2, 2.5, and 3 minutes to determine the exposure time required to develop the MPE on unprotected skin. The amount of erythema is judged 12–24 hours after exposure to the ultraviolet lamp.

In the second step, exactly 0.1 gram of the sun-screening composition under test is applied in the form of a uniform film to a second skin area of 1 x 3.5 inches. (The film thickness is thus 0.0044 centimeter, disregarding evaporation of volatile constituents which reduces the film thickness.) The area treated with the sun-screening preparation to be tested is then divided into four or five small squares which are exposed to the ultraviolet light source, as above, in progressive time intervals to determine the exposure time that is required to develop the MPE on skin covered with the compositions.

In tests involving two applications of the test composition, a second 0.1 gram of the protective sun-screening composition is applied in a uniform film to the same skin area as used for the first application after the first application has been allowed to dry for about five minutes. The test procedure to determine MPE is otherwise the same as for MPE determination in the single-application test.

These data are then used to determine the "protective ratio," that is the ratio of the exposure time needed to develop MPE under standardized conditions on untanned skin protected with the test composition to the exposure time needed for development of the same MPE under the same conditions on skin which has not been protected with any composition. At least four individuals are used for each test.

The protective ratios obtained for Composition A, the sun-screening composition of this invention and for Composition B, a liquid composition typical of the prior art, are shown in Table I.

TABLE I

Composition	Protective Ratio	
	Single Application	Double Application
A	8:1	15:1
B	10:1	10:1

It can readily be appreciated from Table I that the composition of this invention containing a phosphoric acid ester gives almost twice as much protection for a second application, while Composition B does not give any measurable increase in protection upon a second application. These results for Composition B are typical of those obtained with prior art clear liquid sun-screening preparations prepared with other sun-screening agents and surface active agents.

Example III

A mixture of 60.0 parts of ethanol, 34.5 parts of water, 3.0 parts of "Hostaphat KO–280" alkoxylated fatty alcohol ester of phosphoric acid, and 2.5 parts of 2 - ethoxyethyl - p - methoxycinnamate is prepared. When this material is tested according to the procedure set forth in Example II the protective ratio for a single application is found to be 6:1 and for a double application 12:1. Thus, a proportionate increase in protection is obtained for a second application.

Example IV

A mixture of 60.0 parts of ethanol, 36.5 parts of water, 1.0 part of "Hostaphat KO–280" alkoxylated fatty alcohol ester of phosphoric acid, and 2.5 parts of ethoxylated p-aminobenzoic acid is prepared. When tested according to the procedure of Example II, the protective ratio for a single application is found to be 6:1 and for a double application 11:1.

Example V

A mixture of 50 parts of ethanol, 46 parts of water, 2 parts of dilauryl tetraethyleneglycolether phosphate, and 2 - ethoxymethyl - p - methoxycinnamate ("Giv-Tan F") is prepared. This mixture is found to have the cumulative protective effect.

Example VI

A mixture of 96 parts of water, 2 parts of trilauryl tetraethyleneglycolether phosphate, and 2 parts of ethoxylated p-aminobenzoic acid is prepared. This composition is found to have the cumulative protective effect.

Example VII

An aerosol composition is prepared by admixing 36 parts of anhydrous ethanol with 1.5 parts of monooleyl-octaethyleneglycolether phosphate and 2.5 parts of glyceryl p-aminobenzoic acid. This mixture is prepared at room temperature, introduced into a spray container, and refrigerated. After the mixture has cooled, a 50–50 mixture of Freon 11 and Freon 12 is added in the liquid phase and the container is sealed. This aerosol spray product exhibits the cumulative protective effect.

Example VIII

A mixture of 65.0 parts of ethanol, 30.5 parts of water, 2.5 parts of 2-ethoxymethyl-p-methoxycinnamate, 1.0 part of tridecyloctaethyleneglycolether phosphate, and 1.0 part of sodium lauryl sulfate is prepared. This composition is found to exhibit the cumulative protective effect.

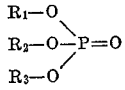
Example IX

A mixture of 65.0 parts of ethanol, 2.5 parts of 2-ethoxymethyl-p-methoxycinnamate, 1.0 part of di-(tridecylhexaethyleneglycolether) phosphate, and 1.0 part of eth-

oxylated nonylphenol is prepared. This composition is found to exhibit the cumulative protective effect.

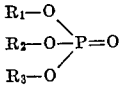
What is claimed is:

1. A protective composition for effectively protecting the human skin from erythema-producing ultraviolet radiation containing from about 0.5% to about 20% of a sunscreening agent, from about 0.1% to about 20% of a phosphoric acid ester having the formula:



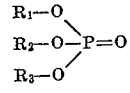
wherein R_1 is an alkoxy fatty alcohol radical formed by the reaction of a fatty alcohol having from about 12 to about 20 carbon atoms with from about 4 to about 30 moles of alkylene oxide per mole of fatty alcohol and R_2 and R_3 are selected from the group consisting of hydrogen and said alkoxy fatty alcohol radicals, and at least one vehicle selected from the group consisting of water and lower alkanol, the composition being a clear, mobile, single phase liquid.

2. A protective composition for effectively protecting the human skin from erythema-producing ultraviolet radiation containing from about 0.5% to about 20% of a sunscreening agent, from about 0.1% to about 20% of a phosphoric acid ester having the formula:



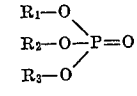
wherein R_1 is an alkoxy fatty alcohol radical formed by the reaction of a fatty alcohol having from about 12 to about 20 carbon atoms with from about 4 to about 8 moles of an alkylene oxide per mole of fatty alcohol and R_2 and R_3 are selected from the group consisting of hydrogen and said alkoxy fatty alcohol radicals, and from about 87% to about 98% of at least one vehicle selected from the group consisting of water, ethanol, and propanol, said composition being a clear, mobile, single phase liquid.

3. A protective composition for effectively protecting the human skin from erythema-producing ultraviolet radiation containing from about 0.5% to about 10% of a sunscreening agent which is a derivative of p-aminobenzoic acid; from about 1% to about 5% of an orthophosphoric acid ester having the formula:



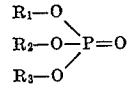
wherein R_1 is an alkoxy fatty alcohol radical formed by the reaction of a fatty alcohol having from about 12 to about 20 carbon atoms with about 4 to about 8 moles of an alkylene oxide selected from the group consisting of ethylene oxide and propylene oxide per mole of fatty alcohol, and R_2 and R_3 are selected from the group consisting of hydrogen and said alkoxy fatty alcohol radicals; and from about 60% to about 99.4% of a vehicle selected from the group consisting of water and ethanol, said composition being a clear, mobile, single phase liquid.

4. A protective composition for effectively protecting the human skin from erythema-producing ultraviolet radiation containing from about 0.5% to about 20% of a sunscreening agent which is a derivative of salicylic acid; from about 1% to about 5% of a phosphoric acid ester having the formula:



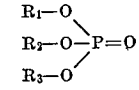
wherein R_1 is an alkoxy fatty alcohol radical formed by the reaction of a fatty alcohol having from about 12 to about 20 carbon atoms with from about 4 to about 8 moles of an alkylene oxide selected from the group consisting of ethylene oxide and propylene oxide per mole of fatty alcohol; and R_2 and R_3 are selected from the group consisting of hydrogen and said alkoxy fatty alcohol radicals; and from about 60% to about 99.4% of at least one vehicle selected from the group consisting of water and ethanol, said composition being a clear, mobile, single phase liquid.

5. A protective composition for effectively protecting the human skin from erythema-producing ultraviolet radiation containing from about 0.5% to about 10% of a sunscreening agent which is a derivative of cinnamic acid; from about 1% to about 5% of the phosphoric acid ester having the formula:



wherein R_1 is an alkoxy fatty alcohol radical formed by the reaction of a fatty alcohol having from about 12 to about 20 carbon atoms with from about 4 to about 18 moles of an alkylene oxide selected from the group consisting of ethylene oxide and propylene oxide per mole of fatty alcohol, and R_2 and R_3 are selected from the group consisting of hydrogen and said alkoxy fatty alcohol radicals; and from about 60% to about 99.4% of at least one vehicle selected from the group consisting of ethanol and water, said composition being a clear, mobile, single phase liquid.

6. A protective comopsition for effectively protecting the human skin from erythema-producing ultraviolet radiation containing from about 0.5% to about 10% of a sunscreening agent which is a derivative of benzophenone; from about 1% to about 5% of a phosphoric acid ester having the formula:



wherein R_1 is an alkoxy fatty alcohol radical formed by the reaction of a fatty alcohol having from about 12 to about 20 carbon atoms with from 4 to about 8 moles of alkylene oxide selected from the group consisting of ethylene oxide and propylene oxide per mole of fatty alcohol, and R_2 and R_3 are selected from the group consisting of hydrogen and said alkoxy fatty alcohol radicals; and from about 60% to about 99.4% of at least one vehicle selected from the group consisting of water and ethanol, said composition being a clear, mobile, single phase liquid.

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