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# SUN SCREEN COMPOSITIONS

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The object of this invention relates to the synthesis of a new group of organic compounds with unique and valuable properties for the prevention of erythema upon excess exposure of skin to the sun.

These materials can be compounded and formulated into oils, tinctures, lotions and creams with ease. We have found them to be effective in low concentrations, physiologically innocuous and devoid of many of the undesirable side effects associated with the sunscreens commonly known.

It has been found that the erythemal producing rays of the sun are mainly found within the wavelength region 2800 angstrom units to 3150 angstrom units. The point of maximal erythemal production is centered at 2970 angstrom units approximately. The cosmetically desirable effect of tanning or bronzing of the skin is due to rays in the wavelength region 3150 angstrom units to 4100 angstrom units. Thus it will be found that products offered to the public as sunburn protectants usually contain an organic compound whose ultra violet absorption spectrum is such that it absorbs most of the rays below 3150 angstrom units and little of the rays above this value, at the concentration used.

These screening agents will usually be found in concentrations of from 1–10% in suitable vehicles.

In order to achieve maximal absorption of ultra violet light these sunscreens are always composed of conjugated unsaturated organic materials having their maximum ultra violet absorptions in the erythemal region 2800 A.–3150 A.

There are many other properties necessary for an ideal sunscreening agent besides having the proper ultra violet absorption characteristics. These can be listed as follows:

(1) They should not be easily absorbed through the skin or cause any pahtological side effects such as primary irritation, inducing sensitivity or allergic response, they should not impede melanogenesis, and they should not induce any trophic changes in the skin, and should not interfere with any normal growth or metabolic processes of the skin and mucous membranes and associated organs.

(2) The proper solubility is a very important property of an effective sunscreen. Aqueous solubility is undesirable due to the probability of the removal of the protective material by bathing. Sufficient oil and solvent solubility is desirable for versatility in formulating in a variety of vehicles and for stability in oil-water emulsions.

(3) The sunscreening material should be of such a character that it is capable of forming continuous films on skin when applied in a convenient vehicle for uniform protective effects.

(4) The sunscreen material should exhibit no odor or should be easily masked so as not to interfere with perfuming of a product.

(5) The material used as a sunscreen should exhibit little residual staining to skin and clothing, especially in



the presence of sunlight, heat, laundry detergents, perspiration and the like.

Sunscreens in common use all lack one or more of the advantageous properties enumerated above. These screens consist of individual members or mixtures of the families of salicylates, para-aminobenzoates, cinnamates, naphthoates and gallates.

(*a*) The salicylates have the disadvantage of screening out of a considerable portion of the rays in the tanning region. In addition, they exhibit a low absorptive capacity which therefore requires the use of high concentrations of the order of 10% in order to be effective. Furthermore, many members have a high undesirable odor level and a pronounced analgesic and numbing effect when applied to the skin. Their oil solubility is rather limited in most cases.

(*b*) The para-aminobenzoates which along with the salicylates are among the most popular sunscreens in use have the disadvantage of having an analgesic effect on application to the skin. Para-aminobenzoic acid, which has poor overall solubility, lends itself to alteration by esterification with the proper alcohol to produce solubilities of the desired nature to a limited extent. However, all of the para-aminobenzoates have the great disadvantage of imparting a high degree of yellow to brown permanent stain to fabrics, especially in the presence of or exposure to ultra violet light.

(*c*) The naphthoates have poor solubility characteristics, an overly broad absorptive spectrum, and low absorptivities.

(*d*) The cinnamates generally have good absorptivities, good solubilities and exhibit little or no staining. However, their absorption maxima do not extend for enough into the erythemal range. In addition, when the esters of cinnamic acid are derivatives of volatile alcohols, the resulting cinnamate tends to be an irritant and often has a high odor. Forming esters of high molecular weight or low volatility reduces these tendencies to a satisfactory level but also reduces the sunscreening efficiency by lowering the absorptivity.

We have found that by esterifying the phenolic group of a salicylate with cinamic acid a diaromatic ester is formed which has the following desirable characteristics:

(1) Good absorptivity in the erythemal region and good transmission in the tanning region.

(2) Low volatility and therefore low odor.

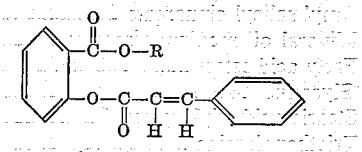
(3) No staining.

(4) An absorption maximum in the erythemal region.

(5) No irritation or senstization or other pathological phenomena can be observed.

(6) The solubility in aqueous solution is essentially nil while the solvent solubility can be tailored to the needs of the vehicle by the selection of the proper aliphatic portion of the salicylate ester.

The structures of the above mentioned diaromatic esters are as follows:



"R" represents phenyl group, benzyl group, aliphatic chain or derivatives thereof.

Among the derivatives which have been synthesized and found to be effective are methyl salicyl cinnamate, ethyl salicyl cinnamate, isopropyl salicyl cinnamate, n-propyl salicyl cinnamate, n-butyl salicyl cinnamate, isobutyl salicyl cinnamate, n-amyl salicyl cinnamate, benzyl salicyl cinnamate, phenyl salicyl cinnamate, phenylethyl salicyl cinnamate, n-hexyl salicyl cinnamate, octyl salicyl

cinnamate, cycohexyl salicyl cinnamate, fenchyl and allyl salicyl cinnamate.

These compounds are readily prepared by the treatment of the proper salicylate ester with cinnamoyl chloride. Unreacted cinnamoyl chloride and cinnamic acid are removed by sodium carbonate solution washes. The product is further purified by recrystallization and vacuum drying. Thus:

532 grams of methyl salicylate (3.5 moles) and 583 grams of cinnamoyl chloride (3.5 moles) are placed into a one liter, three-necked round-bottom flask equipped with reflux condenser, thermometer, mechanical stirrer and glas-col heating mantle. The mechanical stirrer is then turned on and the temperature of the reaction is gradually raised to a mean temperature in the range of 135°–145°±5° C. (this should take approximately one half hour), and maintained at this temperature range for 5½ hours. During the reaction, hydrogen chloride fumes are expelled through the condenser.

After the stated amount of reaction time, the reaction mixture is cooled down to room temperature, dissolved in three times its volume of ethyl ether and washed several times with 20% solution sodium carbonate, until washings are no longer acid to litmus paper, and then washed with water until the water washings are neutral to pH paper. At this point a slight emulsion may develop, which can be broken by the addition of a few milliliters of alcohol. The ether layer is then separated, dried over anhydrous sodium sulfate and passed through a fluted filter paper. This ether portion is then evaporated to approximately ⅙ its volume under reduced pressure or on a steam bath. The resulting material is then dissolved in 3 volumes of hot alcohol. Upon cooling, a crystal mass forms which is then removed by vacuum filtration and dried in an oven at 40° C. overnight. The product is white and has a melting point of 71.2+2° C.

| | |
|---|---|
| Theoretical yield ----------grams-- | 978 |
| Experimental yield ---------- | 60%±5% |

When the reaction time was extended from 5½ hours to 12 hours, the product was obtained in a 90% yield.

The synthesis of ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-amyl, benzyl, phenyl, phenylethyl, n-hexyl, octyl, cyclohexyl, fenchyl and allyl esters of salicyl cinnamate, were carried out in the same manner as the methylester.

Examples of suitable sunscreen compositions are as follows:

| | Parts by weight |
|---|---|
| (1) Alcoholic solution: | |
| Methyl salicyl cinnamate ---------- | 2–4 |
| methyl phenyl polysiloxane ------- | 1–2 |
| Propylene glycol ---------- | 5–10 |
| Alcohol ---------- | 70–80 |
| Perfume ---------- | 0.5 |
| Water, q.s. to a total of 100. | |
| (2) Oil in water emulsion: | |
| Amyl salicyl cinnamate ---------- | 3–4 |
| Mineral oil medium viscosity ------ | 2–8 |
| Fatty acid esters ---------- | 5–10 |
| Glycerine ---------- | 3–5 |
| Stearic acid triple pressed --------- | 1.9–2.3 |
| Triethanolamine ---------- | 0.9–1.2 |
| Perfume ---------- | 0.5 |
| Water, q.s. to a total of 100. | |
| (3) Suntan oil: | |
| Benzyl salicyl cinnamate --------- | 3–5 |
| Mineral oil ---------- | 70–80 |
| Acetylated wool wax alcohols ----- | 0.5–1.0 |
| Fatty acid esters ---------- | 1–2 |
| Perfume ---------- | 0.5 |
| Sesame oil ---------- | 9.5 |
| (4) Suntan jelly for sensitive skin: | |
| Ethyl salicyl cinnamate ---------- | 2.5–4.5 |
| Petrolatum ---------- | 20–25 |
| Paraffin ---------- | 5.0–10.0 |
| Perfume ---------- | 0.5 |
| Fatty acid esters ---------- | 2.0–4.0 |
| Mineral oil ---------- | 70.0–58.0 |

In the use of the phenyl, cyclohexyl and allyl cinnamates the carrier may be in accordance with any of the foregoing examples, the latter being illustrative only. It will also be understood that mixtures of the recited cinnamates may be employed.

Although the cinnamates have been set forth above as 2–4 parts by weight, as preferred, they are operative in a range beginning with 1 part by weight in suitable carriers such as shown in the examples.

These have been tested in the laboratory on white male and female human skin under ultra violet lamps in dosages of radiation which have caused erythema of unprotected skin.

These tests have shown that this new series of sunscreen agents affords maximum protection from erythema while it also allows very efficient tanning to occur.

The above specified group members have utility in conjunction with sunscreen compositions having lower sunburn protection power. Thus propylene glycol salicylate requires a ratio of 7–8% in its commercially used carriers, as compared with not more than 2% of our sunscreen active components. By adding 0.750% of one of our compounds or a mixture of two or more, the propylene glycol salicylate may be reduced from 7% to 3.5%, as an example. Should the material to which our compound is added be satisfactory except that in the proportion required, when used alone, it has deleterious factors, such as staining, the reduction in proportion may retain such satisfactory action and satisfactorily reduce the deleterious factors.

Having described our invention, what we claim and desire to secure by Letters Patent is as follows:

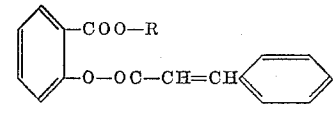
1. A sunscreen composition comprising methyl salicyl cinnamate 1 to about 4 parts by weight; methyl phenyl polysiloxane 1 to about 2 parts by weight; propylene glycol 5 to about 10 parts by weight; alcohol 70 to about 80 parts by weight; and water, with a minor proportion of perfume, to bring the volume to a total of 100 parts by weight.

2. A sunscreen composition comprising amyl salicyl cinnamate 3 to about 4 parts by weight; mineral oil medium viscosity 2 to about 8 parts by weight; fatty acid ester 5 to about 10 parts by weight; glycerine 3 to about 5 parts by weight; stearic acid 1.9 to about 2.3 parts by weight; triethanolamine 0.9 to about 1.2 parts by weight; and water to bring the volume to a total of 100 parts by weight, and with a minor proportion of perfume.

3. A sunscreen composition comprising benzyl salicyl cinnamate 3 to about 5 parts by weight; mineral oil 70 to about 80 parts by weight; acetylated wool wax alcohols 0.5 to about 1.0 part by weight; fatty acid ester 1 and 2 parts by weight; and sesame oil about 9.5 parts by weight.

4. A sunscreen composition comprising ethyl salicyl cinnamate 2.5 to about 4.5 parts by weight; petrolatum 20 to about 25 parts by weight; paraffin 5.0 to about 10.0 parts by weight; perfume 0.5 part by weight; fatty acid ester 2.0 to about 4.0 parts by weight; and mineral oil 70.0 to about 58.0 parts by weight.

5. The method of protecting the skin against sunburn while allowing tanning to take place, which comprises topically applying to the skin a compound having the formula



in which the hydrocarbon radical R is selected from the group consisting of methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-amyl, and benzyl radicals, and a fluid cosmetic carrier therefor, the compound having said structure constituting 1% to about 5% by weight, of the said fluid carrier.

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