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3,705,234

SKIN-PROTECTIVE SUN-SCREENING COMPOSITION AND METHOD

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517,443, Dec. 29, 1965. This application Apr. 1, 1969,
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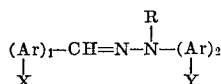
Int. Cl. A61L 23/00

U.S. Cl. 424—60

8 Claims

ABSTRACT OF THE DISCLOSURE

Novel sun-screening agents of the formula:



wherein (Ar)₁ and (Ar)₂ represent benzene rings; X and Y represent a member selected from hydrogen, and a carboxylic or sulfonic acid salt-forming cation, at least one of X and Y being other than hydrogen; and R represents an aliphatic radical, preferably a lower alkyl radical. Such compounds are useful as sun-screening agents as they absorb ultraviolet light in the region of from about 2900 Å. to about 3500 Å. Pharmaceutical compositions including a pharmaceutically acceptable carrier and the above sun-screening agents are effective compositions to screen out both the burning and tanning rays of the sun so as to provide excellent sun-screening protection.

This application is a continuation in part of U.S. application Ser. No. 517,443, filed Dec. 29, 1965 and now U.S. Pat. No. 3,462,479.

This invention relates to new and useful sun-screen compounds, to compositions containing such compounds, and to methods for protecting the human skin against the burning, tanning and degradation effects of sunlight, and in particular to cosmetic compositions incorporating the novel compounds of this invention which are outstandingly useful for protecting the skin against sunlight.

Sun-screening compounds in general have been developed which afford quite satisfactory protection against the burning rays of the sun but which would permit the tanning rays to be transmitted. In the approximate range of from about 2900 to 3100 Å. we find the most detrimental burning wavelengths in the sun's rays. The effect of these wavelengths on the human skin is to produce a severe burning, reddening, blistering and edema which is characteristic of many burns. Obviously, this is not only not desirable from an esthetic point of view, but is a severe detriment to human health. In order, therefore, to overcome this effect of the burning rays of the sun, quite satisfactory compounds have been heretofore employed to screen out these burning rays. On the assumption and general acceptance by the public that tanning is a desirable phenomenon and is somewhat related to "good health," the public has been educated to accept the numerous products currently available to screen out the burning rays of the sun but to permit tanning to occur. Within recent years it has become generally accepted that while tanning may have some beneficial effects especially in

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that it protects the skin from further burning where there is continued exposure to the sun, nevertheless tanning in and of itself is associated with a general deterioration of the skin due to the effect of the actinic radiation thereon.

While the great majority of people are not severely affected by tanning, there are a great number who are so sensitive to even the tanning rays of the sun that exposure to these wavelengths creates serious health hazards. Others have not quite accepted the notion that tanning is beautifying and would prefer to remain untanned. Consequently, for those who must have protection against both burning and tanning rays of the sun, and for those who do not desire to be tanned, there has been a need for a broad spectrum sun-screening composition, which would give adequate protection to the skin, which would be sufficiently stable under conditions of use to remain effective for several hours, which could be readily applied to the skin, and which would not be readily removable such as by simple water-wash. The need for the latter characteristic is evident since it would leave one with a false sense of security if the material were so readily removable as, for example, in bathing.

In order, therefore, to achieve the ends of the present invention it is necessary to provide a composition which has an outstanding filtering action on those rays of the sun from about 2900 Å., the range of from about 3200 Å. to 3500 Å. encompassing the tanning wavelengths present in sunlight.

It is also preferable to employ a composition which has distinct substantivity to the skin. In this case, the skin is "dyed" by the ultraviolet absorbing agent and the efficiency of the agent is maintained after subsequent wetting as by swimming.

One of the objects, therefore, of the present invention is to provide outstanding and useful compounds which have excellent filtering action on the ultraviolet rays of solar light and particularly those wavelengths of from about 2900 Å. to about 3500 Å.

It is still another object of the present invention to provide compositions, and particularly cosmetic compositions, which may be applied to the human skin to protect it against the burning and tanning rays of the sun.

It is a still further object of the present invention to provide compositions which, when applied to the human skin, have a distinct substantivity to the skin.

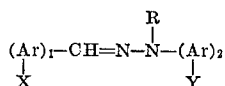
Other objects will appear hereinafter as the description proceeds.

In accordance with the objects of the present invention, it has now been discovered that a class of compounds hereinafter to be described as outstanding screening characteristics for the burning and tanning rays of the sun, and particularly those wavelengths in the ultraviolet region of from about 2900 Å. to about 3500 Å., and that such compounds have outstanding K values as well as unexpectedly superior light fastness and stability upon exposure to ultraviolet radiation. The K value is a measure of the efficiency of the compound to filter out specified wavelengths of light. A compound with a K value of 1 is one which, at a concentration of 0.1% in a thickness of 1 cm. reduces the light transmitted to 10% of the incident radiation. Thus, a compound with a K=10 at a given wave-length in a concentration of 0.1% will reduce the transmitted radiation to 10% of the incident radiation with a thickness of only 1 mm.

In copending application Ser. No. 517,443, it was found that related compounds having two sulfonic acid groups had substantivity toward skin and were, thus, useful as sun-tan agents.

We have now found that those related compounds having only one sulfonic acid group have a much higher degree of substantivity toward skin, and are therefore more valuable as sun-tan agents, especially in solutions of 5% strength or less.

The compounds of the present invention and those which are employed in the compositions and processes of this invention have the following general formula:



wherein (Ar)₁ and (Ar)₂ represent benzene rings; X and Y represent a member selected from hydrogen, and a carboxylic or sulfonic acid salt forming group in the form of a free acid or a salt-forming cation which preferably is an alkali metal anion, e.g., sodium, potassium, lithium, etc., or ammonium or amine at least one of X and Y being other than hydrogen; R is an aliphatic radical and preferably lower alkyl of 1 to 6 carbon atoms, preferably methyl. Suitable R groups and as representative of aliphatic groupings there are:

alkyl of 1 to 18 carbon atoms
alkenyl of 3 to 18 carbon atoms
cycloalkyl of 3 to 18 carbon atoms
cycloalkenyl of 5 to 18 carbon atoms
haloalkyl of 1 to 18 carbon atoms (e.g., chloroethyl, bromopropyl, fluoramyl, iodopentyl, etc.)
haloalkenyl of 3 to 18 carbon atoms
cyanoalkyl of 1 to 18 carbon atoms
hydroxyalkyl of 1 to 18 carbon atoms
carbalkoxyalkyl of 3 to 18 carbon atoms
alkoxyalkyl of 2 to 18 carbon atoms
hydroxyalkoxyalkyl of 2 to 50 carbon atoms

as well as the cyano-, hydroxy-, carbalkoxy-, hydroxy-, alkoxy-derivatives of alkenyls.

In accordance with the present invention the sun-screening compounds comprising those wherein one of X and Y is hydrogen are somewhat more substantive to the skin than those wherein each of X and Y is sulfonic acid or carboxylic acid.

The benzene nuclei may contain, in addition to the salt or salt forming group, other substituents which are non-chromophoric (i.e., avoid chromophores such as nitro, azo, azoxy and the like). Such groups as the following are suitable:

hydroxy
halogen
alkyl (as R above)
substituted alkyl (as R above)
alkenyl (as R above)
substituted alkenyl (as R above)
cyano
alkylsulfonyl (e.g. —SO₂CH₃)
carboxamido
sulfonamido
sulfonic acid
carboxylic acid, etc.

Since an oxy group (i.e., hydroxy, alkoxy or alkenoxy) is an auxochrome and is bathochromic in its effect, no more than one of such groups should be present since the absorption maxima of compounds with two or more oxy groups would in most instances be too close, if not in a visible region of the spectrum, tending thereby to lessen the effectiveness of these compounds for the use as sun-screen agents as herein contemplated. It is also preferred that the compounds of, and used in, this invention do not contain amine groups, particularly bonded directly to the benzene nuclei since such compounds, in

general, have inferior light fastness, albeit they may have satisfactory absorption characteristics for the purpose of the present invention.

The general procedure for preparing the compounds of this invention involves the condensation of a benzene aldehyde with a phenyl-(R-substituted) hydrazine at least one of which contains a sulfo or carboxy substituent. The condensation may be carried out in an aqueous medium or in any selected solvent medium and isolated in the usual way by distillation, extraction, crystallization or precipitation. Usually, refluxing of the reactants in the form of the sodium salts results in high yields after about 1 to 2 hours of refluxing. Among suitable aldehydes which may be employed as reactants in preparing the compounds of this invention are:

benzaldehyde
2,3 and 4-chlorobenzaldehyde
2,3 and 4-fluorobenzaldehyde
2,5-dichlorobenzaldehyde
4-iodobenzaldehyde
4-hydroxybenzaldehyde
2,3 and 4-methylbenzaldehyde
2-ethylbenzaldehyde
2-n-butylbenzaldehyde
2-methylsulfonylbenzaldehyde
2-carboxamidobenzaldehyde
2,3 and 4-methoxybenzaldehyde
2-ethoxybenzaldehyde
2-n-hexoxybenzaldehyde
2-hydroxyethylbenzaldehyde
2-ethoxyethylbenzaldehyde
2-carboethoxyethylbenzaldehyde
2 and 4-cyanobenzaldehyde
2-sulfobenzaldehyde (o-formyl benzene sulfonic acid)
4-chloro-2-sulfobenzaldehyde
5-chloro-2-sulfobenzaldehyde
6-chloro-2-sulfobenzaldehyde
4-hydroxy-2-sulfobenzaldehyde
3-sulfobenzaldehyde
4-bromo-3-sulfobenzaldehyde
4-chloro-3-sulfobenzaldehyde
4-fluoro-3-sulfobenzaldehyde
4-iodo-3-sulfobenzaldehyde
4-hydroxy-3-sulfobenzaldehyde
2,6-dichloro-3-sulfobenzaldehyde
4-sulfobenzaldehyde
2-chloro-4-sulfobenzaldehyde
2-methyl-4-sulfobenzaldehyde
2-ethyl-4-sulfobenzaldehyde
2-n-butyl-4-sulfobenzaldehyde
2-methylsulfonyl-4-sulfobenzaldehyde
2-carboxamido-4-sulfobenzaldehyde
2-methoxy-4-sulfobenzaldehyde
2-ethoxy-4-sulfobenzaldehyde
2-n-hexoxy-4-sulfobenzaldehyde
2-hydroxyethyl-4-sulfobenzaldehyde
2-ethoxyethyl-4-sulfobenzaldehyde
2-carboethoxyethyl-4-sulfobenzaldehyde
2-cyano-4-sulfobenzaldehyde
2-cyanoethyl-4-sulfobenzaldehyde
3-hydroxy-4-sulfobenzaldehyde
3-methoxy-4-sulfobenzaldehyde
3-hydroxy-6-sulfobenzaldehyde
2-hydroxy-5-sulfobenzaldehyde
3-methyl-2-sulfobenzaldehyde
3-methyl-6-sulfobenzaldehyde
4-chloro-3-methyl-6-sulfobenzaldehyde
4-methoxy-3-sulfobenzaldehyde
4-isopropoxy-3-sulfobenzaldehyde
4-carbethoxy-3-sulfobenzaldehyde
4-bromo-3-ethyl-6-sulfobenzaldehyde
4-ethoxy-3-isobutyl-6-sulfobenzaldehyde
4-cyano-3-methyl-6-sulfobenzaldehyde
2-formyl benzoic acid

3-formyl benzoic acid
 4-formyl benzoic acid
 2-chloro-3-formyl benzoic acid
 2,6-dichloro-3-formyl benzoic acid
 2,4,6-trichloro-3-formyl benzoic acid
 2-chloro-4-formyl benzoic acid
 2,5-dichloro-4-formyl benzoic acid
 2,3,6-trichloro-4-formyl benzoic acid
 4-formyl-o-toluic acid
 4-isopropoxy-3-formyl benzoic acid
 4-cyano-3-formyl benzoic acid
 4-chloro-3-formyl benzoic acid
 4-carbomethoxy-3-formyl benzoic acid
 4-fluoro-3-formyl benzoic acid
 4-propenyl-3-formyl benzoic acid
 4-methylsulfonyl-3-formyl benzoic acid

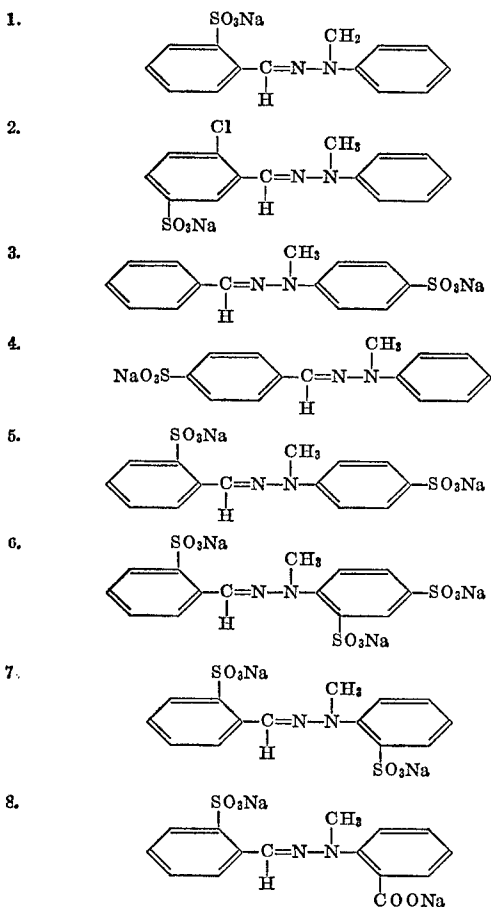
Examples of suitable phenyl hydrazines are as follows:

1-methyl-1-phenylhydrazine
 1-ethyl-1-phenylhydrazine
 1-isopropyl-1-phenylhydrazine
 1-n-hexyl-1-phenylhydrazine
 1-methyl-1-(p-tolyl)hydrazine
 1-ethyl-1-(o-tolyl)hydrazine
 1-propyl-1-(o-tolyl)hydrazine
 1-methyl-1-(4-chlorophenyl)hydrazine
 1-isobutyl-1-(4-cyanophenyl)hydrazine
 1-methyl-1-(4-methylsulfonyl)hydrazine
 1-methyl-1-(4-carboxamidophenyl)hydrazine
 1-methyl-1-(4-N,N-dimethylcarboxamidophenyl)hydrazine
 1-methyl-1-(4-carboethoxyphenyl)hydrazine
 1-methyl-1-(2-chlorophenyl)hydrazine
 1-isoamyl-1-(3-ethylphenyl)hydrazine
 1-n-hexyl-1-(3-carbomethoxyphenyl)hydrazine
 1-isohexyl-1-(2-fluorophenyl)hydrazine
 1-dodecyl-1-phenyl hydrazine
 1-tridecyl-1-(p-tolyl) hydrazine
 1-pentadecyl-1-(4-cyanophenyl)hydrazine
 1-hexadecyl-1-phenylhydrazine
 1-stearyl-1-phenylhydrazine
 1-stearyl-1-(o-tolyl)hydrazine
 1-stearyl-1-(2-chlorophenyl)hydrazine
 1-allyl-1-(2-chlorophenyl)hydrazine
 1-octene-1-phenyl hydrazine
 1-olyl-1-phenyl hydrazine
 1-olyl-1-(2-chlorophenyl)hydrazine
 1-chloroethyl-1-phenylhydrazine
 1-cyanopropyl-1-phenylhydrazine
 1-hydroxyethyl-1-phenylhydrazine
 1-(1-hydroxypropyl)-1-phenylhydrazine
 1-(2-hydroxybutyl)-1-phenylhydrazine
 1-(3-hydroxypentyl)-1-phenylhydrazine
 1-(5-hydroxy-n-hexyl)-1-(2-chlorophenyl)hydrazine
 1-chloroethyl-1-(2-chlorophenyl)hydrazine
 1-carboethoxyethyl-1-(2-bromophenyl)hydrazine
 1-cyclohexyl-1-phenylhydrazine
 1-methoxyethyl-1-(2-chlorophenyl)hydrazine
 1-cyanoethyl-1-(2-cyanophenyl)hydrazine
 1-cyanoethyl-1-(2-methylsulfonylphenyl)-hydrazine
 1-methyl-1-(4-carboxyphenyl)hydrazine
 1-methyl-1-(3-carboxyphenyl)hydrazine
 1-methyl-1-(2-carboxyphenyl)hydrazine
 1-isopropyl-1-(4-carboxyphenyl)hydrazine
 1-methyl-1-(6-chloro-2-carboxyphenyl) hydrazine
 1-methyl-1-(5-bromo-2-carboxyphenyl) hydrazine
 1-methyl-1-(6-methyl-2-carboxyphenyl) hydrazine
 1-methyl-1-(6-fluoro-2-carboxyphenyl) hydrazine
 1-methyl-1-(p-sulfophenyl)hydrazine
 1-ethyl-1-(p-sulfophenyl)hydrazine
 1-isopropyl-1-(p-sulfophenyl)hydrazine
 1-n-hexyl-1-(p-sulfophenyl)hydrazine
 1-decyl-1-(p-sulfophenyl)hydrazine
 1-dodecyl-1-(p-sulfophenyl)hydrazine

1-stearyl-1-(3-sulfo-4-methyl)hydrazine
 1-stearyl-1-(2-methyl-5-sulfophenyl)hydrazine
 1-methyl-1-(3-sulfo-4-methyl phenyl)hydrazine
 1-ethyl-1-(3-sulfo-4-methyl phenyl)hydrazine
 5 1-methyl-1-(2-methyl-3-sulfo phenyl)hydrazine
 1-ethyl-1-(2-methyl-3-sulfo phenyl)hydrazine
 1-methyl-1-(2-methyl-5-sulfo phenyl)hydrazine
 1-n-propyl-1-(2-methyl-5-sulfo phenyl)hydrazine
 1-ethyl-1-(sulfo-4-ethyl phenyl)hydrazine
 10 1-methyl-1-(2-sulfo-4-chlorophenyl)hydrazine
 1-methyl-1-(2-sulfo-4-methylphenyl)hydrazine
 1-n-propyl-1-(2-sulfo-4-methylphenyl)hydrazine
 1-isobutyl-1-(2-sulfo-4-cyanophenyl)hydrazine
 1-methyl-1-(2-sulfo-4-methylsulfonyl phenyl)hydrazine
 15 1-methyl-1-(2-sulfo-4-carboxamido phenyl)hydrazine
 1-methyl-1-(2-sulfo-4-N,N-dimethyl carboxamido phenyl)hydrazine
 1-methyl-1-(2-sulfo-4-carboethoxy phenyl)hydrazine
 1-ethyl-(2-sulfo-4-methylsulfonyl phenyl)hydrazine
 20 1-methyl-(3-chloro-4-sulfophenyl)hydrazine
 1-methyl-(2-cyano-4-sulfophenyl)hydrazine
 1-ethyl-(3-cyano-4-sulfophenyl)hydrazine
 1-isoamyl-(3-ethyl-4-sulfophenyl)hydrazine
 1-n-hexyl-(3-carbomethoxy-4-sulfophenyl)hydrazine
 25 1-isohexyl-(2-fluoro-4-sulfophenyl)hydrazine
 1-allyl-(2-chloro-4-sulfophenyl)hydrazine
 1-chloroethyl-1-(2-sulfophenyl)hydrazine
 1-chloroethyl-1-(4-sulfophenyl)hydrazine
 1-cyanopropyl-1-(4-sulfophenyl)hydrazine
 30 1-hydroxyethyl-1-(4-sulfophenyl)hydrazine
 1-chloroethyl-1-(2-chloro-4-sulfophenyl)hydrazine
 1-carboethoxyethyl-1-(2-bromo-4-sulfophenyl)hydrazine
 1-cyclohexyl-1-(2-sulfophenyl)hydrazine
 1-cyclohexyl-1-(4-sulfophenyl)hydrazine
 35 1-cyclohexyl-1-(2-chloro-4-sulfophenyl)hydrazine
 1-cyclopentyl-1-(2-methyl-4-sulfophenyl)hydrazine
 1-methoxyethyl-1-(2-chloro-4-sulfophenyl)hydrazine
 1-cyanoethyl-1-(2-cyano-4-sulfophenyl)hydrazine
 1-cyanoethyl-1-(2-fluoro-4-sulfophenyl)hydrazine
 40 1-cyanoethyl-1-(2-methylsulfonyl-4-sulfophenyl)hydrazine
 1-allyl-1-(2-ethyl-4-sulfophenyl)hydrazine
 1-methyl-1-(4-carboxyphenyl)hydrazine
 1-methyl-1-(3-carboxyphenyl)hydrazine
 45 1-methyl-1-(2-carboxyphenyl)hydrazine
 1-ethyl-1-(4-carboxyphenyl)hydrazine
 1-isopropyl-1-(4-carboxyphenyl)hydrazine
 1-isohexyl-1-(4-carboxyphenyl)hydrazine
 1-decyl-1-(2-carboxyphenyl)hydrazine
 50 1-dodecyl-1-(3-carboxyphenyl)hydrazine
 1-hexadecyl-1-(5-carboxyphenyl)hydrazine
 1-stearyl-1-(2-carboxyphenyl)hydrazine
 1-ethyl-1-(3-carboxyphenyl)hydrazine
 1-ethyl-1-(2-carboxyphenyl)hydrazine
 55 1-methyl-1-(2-chloro-6-carboxyphenyl)hydrazine
 1-methyl-1-(2-bromo-6-carboxyphenyl)hydrazine
 1-methyl-1-(3-bromo-6-carboxyphenyl)hydrazine
 1-methyl-1-(3-chloro-6-carboxyphenyl)hydrazine
 1-ethyl-1-(3-chloro-6-carboxyphenyl)hydrazine
 60 1-ethyl-1-(3-bromo-6-carboxyphenyl)hydrazine
 1-methyl-1-(4-chloro-6-carboxyphenyl)hydrazine
 1-methyl-1-(5-chloro-6-carboxyphenyl)hydrazine
 1-methyl-1-(5-bromo-6-carboxyphenyl)hydrazine
 1-ethyl-1-(4-bromo-6-carboxyphenyl)hydrazine
 65 1-ethyl-1-(5-bromo-6-carboxyphenyl)hydrazine
 1-n-propyl-1-(5-bromo-6-carboxyphenyl)hydrazine
 1-ethyl-1-(5-chloro-6-carboxyphenyl)hydrazine
 1-methyl-1-(2-methyl-6-carboxyphenyl)hydrazine
 1-methyl-1-(3-methyl-6-carboxyphenyl)hydrazine
 70 1-methyl-1-(4-methyl-6-carboxyphenyl)hydrazine
 1-ethyl-1-(4-methyl-6-carboxyphenyl)hydrazine
 1-methyl-1-(5-methyl-6-carboxyphenyl)hydrazine
 1-ethyl-1-(5-methyl-6-carboxyphenyl)hydrazine
 1-methyl-1-(2-chloro-3-carboxyphenyl)hydrazine
 75 1-methyl-1-(4-chloro-3-carboxyphenyl)hydrazine

1-methyl-1-(5-chloro-3-carboxyphenyl)hydrazine
 1-methyl-1-(6-chloro-3-carboxyphenyl)hydrazine
 1-methyl-1-(2-bromo-3-carboxyphenyl)hydrazine
 1-methyl-1-(4-bromo-3-carboxyphenyl)hydrazine
 1-methyl-1-(5-bromo-3-carboxyphenyl)hydrazine
 1-methyl-1-(6-bromo-3-carboxyphenyl)hydrazine
 1-methyl-1-(4-methyl-3-carboxyphenyl)hydrazine
 1-methyl-1-(5-methyl-3-carboxyphenyl)hydrazine
 1-methyl-1-(6-methyl-3-carboxyphenyl)hydrazine
 1-methyl-1-(2-chloro-4-carboxyphenyl)hydrazine
 1-methyl-1-(3-chloro-4-carboxyphenyl)hydrazine
 1-methyl-1-(2-bromo-4-carboxyphenyl)hydrazine
 1-methyl-1-(3-bromo-4-carboxyphenyl)hydrazine
 1-methyl-1-(2-methyl-4-carboxyphenyl)hydrazine
 1-methyl-1-(3-methyl-4-carboxyphenyl)hydrazine
 1-hydroxyethyl-1-(2-carboxyphenyl)hydrazine

Accordingly, exemplary compounds falling within the above general formula include such as:



Among the general methods for preparing the hydrazine compounds used in the present invention, mention might be made of nitrosating the N-alkyl aniline, reducing to the hydrazine with zinc in acetic acid and sulfonating with oleum. Alternately, the N-alkyl anilines may be sulfonated first and then nitrosated and reduced. When the N-alkyl aniline contains a para substituent such as alkyl, halogen, cyano, sulfonyl, carbalkoxy and the like, the sulfonation will take place in the ortho position. Where these substituents are ortho or meta, sulfonation will be para. The general reaction and specific compounds and conditions can be found in Halv. Chim. Acta 29, 1965-82 (1942).

The carboxy phenyl hydrazines can be prepared in a similar manner by nitrosating and reducing the corresponding carboxyanilines.

As indicated above, the novel compounds of the present invention are particularly useful as sun-screening

agents in pharmaceutical compositions since the same have the ability to effectively screen out ultraviolet light within the region of 2900 A. to 3500 A., i.e., covering the sun-tanning and sun-screening range of the spectrum.

- 5 Accordingly, the present invention also includes pharmaceutical compositions which contain the sun-screening agents in a minor amount. Such pharmaceutical compositions comprise as a major proportion a pharmaceutically acceptable carrier and the sun-screening agent in an amount effective to screen out the burning and tanning rays of the sun. Generally the sun-screening agent is employed in the pharmaceutical composition in an amount of from about 0.01% to about 5% by weight based on the total weight of the composition. In accordance with the present invention, any suitable pharmaceutical carrier conventionally employed as a vehicle for sun-tanning lotions or creams can be utilized. Thus, the pharmaceutically acceptable carrier can comprise a conventional lotion or cream or may advantageously comprise a detergent bar.
- 20 In this regard the pharmaceutically acceptable carrier employed in accordance with the present invention does not constitute an essential feature of the present invention, it being only necessary that such carrier provide a vehicle by which the sun-tanning agent can be effectively applied to the skin.

The present invention will now be described by reference to the following examples. In such examples all parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

Into a 3-liter flask equipped with a stirrer, thermometer, reflux condenser and heating mantle, there are charged the following ingredients:

- 28.0 g. of 1-methyl-1-phenylhydrazine
- 52.5 g. of sodium salt of 2-sulfobenzaldehyde
- 1200 ml. ethanol and
- 30.6 g. of sodium acetate crystals

- The mixture is stirred for 2½ hours at reflux and thereafter it is cooled to 10° C. in an ice bath. The resultant crystals are filtered and the filter cake washed with 240 ml. cold ethanol. The press-cake is then slurried in 750 ml. water and to the slurry there is added a teaspoon of decolorizing carbon after which the mass is filtered. To the filtrate there is added isopropanol until the formation of crystals is noted. The entire mass is then cooled to 10° C. and then filtered and dried at 40° C. in a vacuum oven. There is obtained a yield of 50 g. product which is identified as 2-methyl-2-phenyl-1-(2 sulfophenyl)hydrazone, sodium salt.

EXAMPLE 2

- Example 1 is repeated employing in place of the sodium salt of 2-sulfobenzaldehyde, the same weight of the sodium salt of 4-sulfobenzaldehyde. The product is 2-methyl-2-phenyl-1-(4 - sulfophenyl) - hydrazone, sodium salt.

EXAMPLE 3

- Example 1 is repeated employing in place of the sodium salt of 2-sulfobenzaldehyde, 62.2 g. of the sodium salt of 6-chloro-3-sulfo-benzaldehyde. The product is 2-methyl-2-phenyl-1-(6-chloro - 3 - sulfophenyl)hydrazone, sodium salt.

EXAMPLE 4

- Example 1 is repeated employing in place of the sodium salt of 2-sulfobenzaldehyde, 29.7 g. benzaldehyde, and in place of the 1-methyl-1-phenylhydrazine, 44.4 g. 1-methyl-1-(4-sulfophenyl)hydrazine, sodium salt. The product is 1-methyl-1-(4-sulfo-phenyl)-2-phenylhydrazone.

EXAMPLE 5

- The product of Example 1 is incorporated into a neutral detergent composition in the form of a bar, and which contains as the main detergent ingredient a cocoanut oil

acid ester of sodium isethionate. The amount of the product of Example 1 which is used is 0.2% by weight based on the total weight of the detergent bar. The bar is then used separately by five individuals in a bathing procedure, and thereafter the five persons are exposed to the afternoon's summer sun for two hours. A similar group of five persons use a similar detergent bar but devoid of the product of Example 1, and these individuals are similarly exposed as the first group. Each of the persons in the second group, after exposure, shows considerable reddening of the skin whereas none of the persons in the first group has any visible evidence of sunburn. This performance demonstrates not only the excellent sunscreen characteristics of the compound of Example 1, but also its outstanding substantivity for human skin from the detergent bar which is used for bathing.

EXAMPLE 6

The procedure of Example 5 is repeated except that in place of a detergent bar, there is used a conventional bar of soap (pH about 10) containing 0.3% of the product of Example 1. Comparable results are obtained as in Example 5.

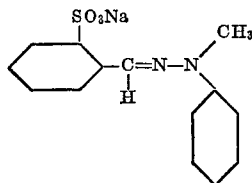
EXAMPLE 7

The product of Example 1 is prepared as a 10% by weight solution in water, and in this solution there is immersed a sample of cellulose textile material which has been previously dyed with a dark red cotton dye. After removal and drying of the sample, it is placed in a fadeometer along with a similarly dyed sample which has not been treated with the product of Example 1. After four hours exposure, the untreated sample shows severe fading whereas the treated goods shows no fading of the dyeing.

EXAMPLE 8

A 3% paste of sun screen formulation is made using:

1 oz.

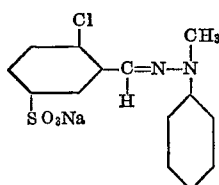


32 oz. polyoxyethylated vegetable oil (Emulphor EL-719), product of GAF Corporation.

The material is mixed to give a clear solution which is applied to the skin. Skin so treated does not develop a burn upon exposure to sunlight.

EXAMPLE 9

A 2% solution of

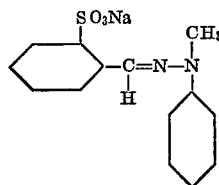


is prepared in 50% by weight alcohol-glycerine mixture. The solution is applied to the skin and allowed to dry. Skin so treated does not develop or burn up exposure to sunlight.

EXAMPLE 10

A 2% paste is made of sunscreen formulation consisting of:

1 oz.



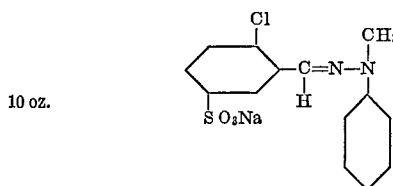
34 oz. isopropyl stearate

15 oz. polyoxyethylated sorbitan monopalmitate (Tween 40')

The material applied as in Example 9 given protection against sunburn.

EXAMPLE 11

A suntan formulation is made consisting of:



2 oz. quinine alkaloid

88 oz. oleic acid USP

The above is mixed with 10 times its weight of corn oil. The resultant product is used as a sun screen agent.

EXAMPLE 12

Into a 3-liter flask equipped with a stirrer, thermometer, reflux condenser and heating mantle, there are charged the following ingredients:

42.3 g. of 1-methyl-1-(p-sulfophenyl) hydrazine (molecular weight 188; $K_{max}=69.2$ at $253 m\mu$)

52.5 g. sodium salt of 2-sulfobenzaldehyde (88.2% pure: molecular weight 186)

1200 ml. of ethanol and

30.6 g. of sodium acetate crystals.

The mixture is stirred for $2\frac{1}{2}$ hours at reflux and thereafter it is cooled to 10° C. in an ice bath. The resultant crystals are filtered and the filter cake washed with 240 ml. of cold ethanol. The press-cake is then slurried in 750 ml. of water and to the slurry there is added a teaspoon of decolorizing carbon after which the mass is filtered. To the filtrate there is added slurry at room temperature, isopropanol until the formation of crystals is noted. The entire mass is then cooled to 10° C. and then filtered and dried at 40° C. in a vacuum oven. There is obtained a yield of 77 g. product which has a K_{max} equal to 70 at $360 m\mu$ and which is identified as 1-methyl-1-(p-sulfophenyl)-2-sulfophenyl hydrazone sodium salt.

EXAMPLE 13

Example 12 is repeated employing in place of the sodium salt of 2-sulfobenzaldehyde, the same weight of 3-sulfobenzaldehyde (i.e., 46.3 g. on a 100% basis). The product is 1-methyl-1-(p-sulfophenyl)-2-sulfophenyl hydrazone sodium salt.

EXAMPLE 14

Example 12 is once again repeated using an equivalent weight on a 100% basis of 2,4-disulfo benzaldehyde sodium salt in place of the sulfobenzaldehyde of Example 12. The product obtained is 1-methyl-1-(2,4-disulfo-phenyl)-2-sulfophenyl hydrazone sodium salt.

EXAMPLE 15

Example 13 is repeated except that in place of the p-sulfonated hydrazine used in that example, there is used an equal weight of the o-sulfonated product. The product obtained is 1-methyl-1-(o-sulfophenyl)-2-sulfophenyl hydrazone sodium salt.

EXAMPLE 16

Example 15 is repeated except that in place of the o-sulfonated hydrazine, there is used an equivalent weight of the o-carboxylated hydrazine. The product obtained is 1-methyl-1-(o-carboxyphenyl)-2-sulfophenyl hydrazone sodium salt.

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EXAMPLE 17

The product of Example 12 is incorporated into a neutral detergent composition in the form of a bar, and which contains as the main detersive ingredient a cocoanut oil acid ester of sodium isethionate. The amount of the product of Example 12 which is used is 0.2% by weight based on the total weight of the detergent bar. The bar is then used separately by five individuals in a bathing procedure, and thereafter the five persons are exposed to the afternoon summer sun for two hours. A similar group of five persons uses a similar detergent bar but devoid of the product of Example 12, and these individuals are similarly exposed as the first group. Each of the persons in the second group, after exposure, shows considerable reddening of the skin whereas none of the persons in the first group has any visible evidence of suburn. This performance demonstrates not only the excellent sun-screen characteristics of the compound of Example 12, but also its outstanding substantively for human skin from the detergent bar which is used for bathing.

EXAMPLE 18

The procedure of Example 17 is repeated except that in place of a detergent bar, there is used a conventional bar of soap (pH about 10) containing 0.3% of the product of Example 12. Comparable results are obtained as in Example 17.

EXAMPLE 19

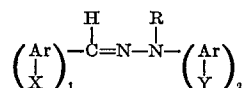
The product of Example 12 is prepared as a 10% by weight solution in water, and to this solution there is immersed a sample of cellulose textile material which has been previously dyed with a dark red cotton dye. After removal and drying of the sample, it is placed in a fadeometer along with a similarly dyed sample which has not been treated with the product of Example 12. After four hours exposure, the untreated sample shows severe fading whereas the treated goods shows no fading of the dyeing.

We claim:

1. A method for protecting the skin against sunlight comprising applying to said skin a sun-screening composition comprising a carrier pharmaceutically acceptable for

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skin application and, in an amount effective to absorb ultraviolet light substantially within the region of 2900 A. and 3500 A., an essentially colorless compound of the formula:



wherein

- (1) (Ar)₁ and (Ar)₂ represent benzene rings,
- (2) X and Y represent hydrogen, a carboxylic acid group, sulfonic acid group or a salt thereof, with the proviso that at least one of X and Y is other than hydrogen, and
- (3) R is an C₁₋₆ alkyl radical.

2. The method of claim 1 wherein R in said formula is methyl.

3. The method of claim 1 wherein one of X and Y in said formula is sulfonic acid.

4. The method of claim 3 wherein the other of X and Y is sulfonic acid.

5. The method of claim 3 wherein the other of X and Y is hydrogen.

6. The method of claim 1 wherein one of X and Y in said formula is carboxylic acid.

7. The method of claim 6 wherein the other X and Y is sulfonic acid.

8. The method of claim 1 wherein said compound is present in an amount of from about 0.01 to 5% by weight based on the weight of said composition.

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SAM ROSEN, Primary Examiner

U.S. Cl. X.R.

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