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SKIN-PROTECTING SUNSCREENING PROCESS

Saul I. Kreps, Cedar Grove, N.J., assignor to Van Dyk & Company, Inc., a corporation of New Jersey

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1 Claim. (Cl. 167—90)

This invention relates to improved sunscreening agents.

As is known, the protection of the human skin from sunburn involves essentially the application to the skin of a substance which effectively absorbs the erythema-producing range of the ultra violet rays of natural or artificial light. This range includes ultra violet radiations of energy equivalent to wave lengths of from 2900 to 3200 angstrom units. A number of well-known sunscreening agents have been employed in the past. These generally comprise the o-aminobenzoic and p-aminobenzoic esters and include such materials as methyl anthranilate (methyl o-aminobenzoate), glyceryl-p-aminobenzoate and ethyl-N-(d-glucosyl) iminobenzoate. Such materials are made up in different types of cosmetic formulations such as lotions, oil emulsions, sun tan creams and the like for application to the skin to provide a protective film of the finely distributed particles of the absorbing agent on the skin.

While these materials have proven to be excellent sunscreening agents they do nevertheless present certain disadvantages particularly with respect to stability during storage. Because of the ester groupings in this class of materials they are subject to hydrolysis. This hydrolysis may be catalyzed particularly by bases and acids which usually are present in the cosmetic formulations and results in the formation of water soluble p-aminobenzoic acids. This hydrolysis is deleterious in that it reduces the efficacy of the cosmetic preparations containing the sunscreening agent. For example, glyceryl-p-aminobenzoate is an effective sunscreening agent at two percent concentration in a cosmetic preparation. But hydrolysis results in the production of p-aminobenzoic acid or a salt of the acid neither of which are effective protection at two percent concentration. This undesirable effect is accentuated upon long storage of the preparations when bottled and placed in distributors' or retailers' stocks; such extended storage may provide time enough for the slow hydrolytic reactions to run to completion.

The prime objective of this invention is to provide novel sunscreen cosmetic preparations containing screening agents which are not only highly effective absorbents of the erythema-producing rays, but also which do not hydrolyze and thus preserve their effectiveness indefinitely.

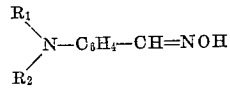
The inherent selective absorption characteristics and the resulting efficiency as screening agents are indicated in spectrophotometric curves of a number of novel screening agents comprehended by the inventor. These curves are a result of the well-known instrumental test of the screening powers of the indicated materials.

As is known, an effective sun tan preparation essentially performs two functions. The first and most important is to protect the user from burning, blistering and injurious effects of prolonged exposure to sunlight: The second function is to permit the most rapid possible development of skin pigmentation, or tan. As noted above the erythemal range from which protection is sought lies between about 2900 and 3200 angstrom units. It is generally agreed that effective, relatively rapid tanning, without painful erythema, results from exposure of the skin to radiations of from about 3200 to about 3750 angstrom units. An effective sun tan preparation is thus one which selectively absorbs or screns the erythemal rays but permits transmission of the tanning range above about 3200 angstrom units. It will be observed

that such a selectivity is generally characteristic of the sunscreening agents of the invention.

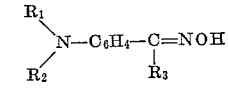
As a result of extensive experimentation and screening evaluations, it has been ascertained that several series of compounds, novel in this field of use, serve as excellent sunscreening agents being characterized by prolonged stability and desirable selective absorption of the erythemal range. These series of compounds include as a class the following types or species.

I. Oximes of o- and p-aminobenzaldehydes having the following characteristic structure:



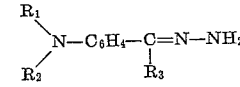
where R_1 and R_2 are hydrogen, alkyl aryl, alkylidine or substituted alkyl, aryl or alkylidine groups.

II. Oximes of o- and p-aminobenzoyl ketones, having the following characteristic structure:

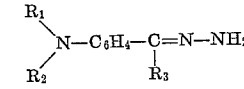


where R_3 is an alkyl group.

III. Hydrazones of o- and p-aminobenzaldehydes having the following characteristic structure:



IV. Hydrazones of o- and p-aminobenzoyl ketones, having the following characteristic structure:



As noted previously a characteristic feature of these compounds is their greatly increased resistance to hydrolysis in alkaline and acid media as compared with the earlier ester-type compounds.

Within the concept of the invention is the utilization as sunscreening agents of compounds of the type described but also derivatives of these; thus substitutions on the amino group such as acetyl, "Shiff" base and the like.

Typical, although by no means exclusive sunscreening compounds within the purview of the art: p-aminobenzaldoxime, p-aminobenzalhydrazone, p-dimethylaminobenzaldoxime, p-dimethylaminobenzalhydrazone, p-aminoacetophenoxime and p-aminoacetophenone hydrazone. It has been ascertained that in general the substitution of an oxime group lowers the absorption maximum by about 400 angstrom units compared to the original aldehyde or ketone. The hydrazone group on the other hand causes a shift to high wave lengths. In formulating any particular cosmetic sunscreen composition various combinations or mixtures of the several compounds may be used to secure the desired screening.

In the course of investigation of the type of compounds described hereinbefore to determine their utility and efficacy as sunscreens it was found that p-aminoacetophenone and p-dimethylaminobenzaldehyde are characterized by a high selective absorption of the erythemal rays which establishes these compounds as effective sunscreening agents.

The novel sunscreening agents described herein may be prepared by methods well-known in the art. In the production of cosmetic sunscreening preparations they may be associated with any suitable cosmetically acceptable vehicles to produce the desired cosmetic product; thus they may be dissolved in aliphatic alcohols to form hydroalcoholic lotions or may be embraced in oily lo-

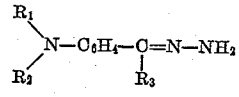
tions, emulsified lotions, sun tan creams and the like. The well-known cream bases may be used. Liquid compositions of the present invention may be packaged in pressure tight containers having a gas under pressure, commonly called aerosols. The gas is preferably a halogenated hydrocarbon, such as chlor-fluor methane (Freon).

The novelty and utility of the described series of compounds will be appreciated; their effective absorption characteristics coupled with their inherent resistance to hydrolysis recommends them as materials of choice in cosmetic sunscreening products.

It will be understood that the invention is not limited to the particular substances described but resides in the concept of modifying the stability of sunscreens having the amino benzoyl-nucleus by introduction of oximido or hydrazono groups to produce eminently efficient and stable sunscreening compositions.

I claim:

A method of treating the human skin to protect it against erythema which comprises applying to the skin a substance taken from the class consisting of compounds represented by the formula—



wherein R_1, R_2 and R_3 are radicals taken from the class consisting of H and CH_3, said compounds being the hydrazones of the class consisting of o- and p-aminobenzaldehydes and o- and p-amindacetophenones.

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