United States Patent Office 3,403,207
Patented Sept. 24, 1968

3,403,207

METHOD OF AND COMPOSITION FOR SCREENING ERYTHEMA INDUCING ULTRAVIOLET BANDS

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No Drawing. Continuation of application Ser. No. 463,352, June 11, 1965, which is a continuation-in-part of application Ser. No. 135,442, Sept. 1, 1961. This application Nov. 14, 1966, Ser. No. 594,261

11 Claims. (Cl. 424—60)

ABSTRACT OF THE DISCLOSURE

A method of controlling sunburn, comprising application to the skin of a cosmetic carrier containing esters of paradimethylaminobenzoate with monohydric alcohols having 5 to 18 carbon atoms.

This application is a continuation of application Ser. No. 463,352, filed June 11, 1965 which in turn is a continuation-in-part of application Ser. No. 135,442, filed Sept. 1, 1961 and now both abandoned.

The present invention is directed to products and compositions adapted for application to the human skin for protection against erythema producing radiation. More particularly, it is directed to substances which have ideal properties for such and other applications.

Extensive studies have been made of the ultraviolet radiation of sunlight and skylight reaching the surface of the earth and the effects of such radiation on the human skin. It has been established that the radiation between 2900 Au and 3150 AU produces substantially all of the erythemal energy and a substantial portion of the tanning energy, while that between 3150 AU and 4000 AU promotes incident tanning. The differing intensities and the erythemal and tanning effectiveness of the various wave lengths within these ranges have been established and methods have been determined for calculating accurately their effects on normal untanned skin.

Normal untanned and unprotected skin may be exposed safely to noon-time summer sunlight only for a comparatively limited period. Ultraviolet screens are provided for the purpose of extending that exposure time and are generally evaluated on a basis of an exposure time of four hours. The total erythemal flux of noon-day summer sun during such four-hour period is limited by the ultraviolet screen to provide the desired degree of protection and tanning with safety.

To provide quick tanning with a minimum protection only approximately 15% of the total erythemal flux of sunlight and skylight should reach the skin in the four hour period; for normal protection and tanning on average skin, 8–10%; for sensitive skin, 3–5%; for sun-allergic skin, 1% maximum. Indeed some doctors advocate a degree of protection which would permit transmission of but a small fraction of 1% of the total erythemal flux during the standard four-hour period.

Approximately 76% of the physiological tanning potential of sunlight is found in the ultraviolet range between 2900 AU and 3150 AU, the so-called erythema area; the balance is found in the range between 3150 AU and 4000 AU, the so-called tanning area. The erythemal limitations necessarily control the amount of tanning which may be obtained from ultraviolet in the erythemal area, but there is no limitation on the availability of tanning from the ultraviolet in the incident tanning area since it has no appreciable erythemal effect. Thus, it is apparent that ultraviolet screens can be utilized to furnish any desired amount of protection and/or tanning, by the adjustment of the percentage of such screen used. However, two other characteristics of an ultraviolet absorbing screen determine whether it is a commercially practical, all purpose, sun screen for human use: solubility and stability.

For human application, ultraviolet screens are incorporated in various media: hydroalcoholic lotions, oily solutions, gels and water and oil lotions and creams. Additionally a material, such as dihydroxyacetone may be incorporated in the medium to provide an artificial "tanning" with ultraviolet protection, i.e. pigmentation of the skin which resembles natural melanin pigmentation in appearance only.

Therefore, a practical, all-purpose ultraviolet screen should:

Provide high screening efficiency in the erythemal area coupled with high transmission of incident tanning energy;

Be capable of being readily incorporated in the various media used to apply them to human skin, and remain stable, effective and cosmetically acceptable therein under all conditions normally encountered in commercial use;

Form a thin, continuous, long-lasting protective film on thes kin;

Be resistant to oxidation by air and stable on exposure to both ultraviolet and visible radiation under all normal conditions of storage, application and use.

The principal objective of this invention is to provide a series of new and improved compositions capable of satisfying all of the requirements for a modern, all purpose, commercially acceptable ultraviolet screen for application to the human skin.

It has been known that various amino benzoic acid derivatives have sun screening properties. In particular, it was known that such derivatives of the paraaminobenzoic acids and esters thereof with methyl, ethyl or propyl alcohols have valuable sun-screening effects. Also known were the methyl and ethyl esters of dimethylamino benzoic acids. Such compounds, while having desirable properties were not ideal for the purpose. They lacked one or more of such desirable characteristics as insolubility in water, non-staining of fabrics, stability on storage, stability on exposure to ultraviolet or visible radiation, resistance to oxidation by air, solubility in cosmetic carriers at low temperatures and high screening efficiency coupled with high transmission of incident tanning energy.

Particularly, they lacked stability on exposure to ultraviolet radiation, especially when spread in thin films on the skin, in contact with air. Furthermore, they did not have sufficiently low melting points so as to be liquid at skin temperatures, were not self-plasticizing, and were not compatible with common ingredients of suntan lotions, such as dihydroxyacetone.

The present invention is intended and adapted to improve sun screening substances of the above type, it being among the objects thereof to provide compositions which have high screening efficiency, which are transparent to the tanning rays, have marked solubility in or miscibility with such materials as lower alcohols, mineral, vegetable and animal oils, and are stable on exposure in thin films to both air and light simultaneously.

It is further among the objects of the invention to provide substances for the above purpose which are stable on storage, which do not stain fabrics, which are non-reactive with constituents of cosmetic carriers, which have low melting points an are self plasticizing, and which have little tendency to crystallize from compositions used as sun screening preparations.

The present invention is based upon the use of one

or a combination of the esters of para-dimethylamino benzoic acid with alcohols having at least five carbon atoms, such as amyl, hexyl, octyl, or higher alcohols. These esters additionally are combined with stabilizing agents or antioxidants, such as nordihydroguiaretic acid, butylated hydroxy anisole, butylated hydroxytoluene, ascorbic acid, citric acid, hydroquinone and dilaurylthiodipropionate.

One preferred form of this invention comprises the use of a mixture of 100 parts of isoamyl p-dimethylaminobenzoate with three ten thousandths of one part of hydroquinone. Another preferred form of this invention comprises the use of a mixture of 60 parts of the n-amyl ester, 20 parts of the isopentyl ester, 20 parts of the 2-methylbutyl ester combined with one one-thousandth of one part of butylated hydroxyanisole. Still another preferred form is the use of a mixture of fifty parts of isoamyl-p-dimethylaminobenzoate with fifty parts of n-amyl-p-dimethylaminobenzoate and five thousandths of one part of asborbic acid. A fourth typical embodiment of this invention comprises the use of 80 parts of isoamyl-p-dimethylaminobenzoate, 20 parts of 2-ethyl-hexyl-p-dimethylaminobenzoate and one ten thousandth of one part of nordihydroguiaretic acid.

All of the present alkyl and substituted alkyl esters of the p-aminobenzoic and p-dimethylaminobenzoic acids have highly selective absorption powers for radiation of wavelengths between 2900 AU and 3150 AU, which range of radiation causes the onset of erythema on the human integument. Applicants' p-dimethylaminobenzoate esters are somewhat more effective in this than are the p-aminobenzoic esters. Thus lesser amounts of the p-dimethylamino esters may be employed to offer protection from erythema equivalent to that provided by larger amounts of the p-aminobenzoic acid esters. The amounts which are to be used can be determined by the degree of protection which is desirable in a particular preparation. For example, the protection afforded by a 2 percent aqueous alcoholic solution of ethyl-p-aminobenzoate is also afforded by an alcoholic solution containing no more than 1.2 percent of the isoamyl-p-dimethylaminobenzoate.

The ability to provide the desired protection using a smaller percentage of the ultraviolet screen immediately presents the possibility of a reduction of the solubility problems which may be encountered in use on the human skin. Additionally, the superior stability of the dimethylaminobenzoate esters, in storage and in use, demonstrates specific advantages to be found in such compounds.

A preparation containing the ethyl-p-aminobenzoate will react with residual air in the container and will turn yellow, particularly near the surface of the preparation. In the case of white emulsified creams or lotions, the darkening to be observed on storage is marked, and a dark brown layer soon becomes visible at the surface of the otherwise white cream. Such a preparation is rendered unsalable, and it is therefore undesirable. The oxidation which results in the development of the undesirable and unsightly discoloration is avoided by replacing the highly reactive p-amino (primary amino) group by the relatively unreactive p-dimethylamino (tertiary amino) group. This change in structure of the sun screening material also prevents the development of stains on clothing of the user which is one of the chief drawbacks of the p-aminobenzoic acid esters, in use.

Thus, when a cream or lotion containing about 2 percent of an ester such as glyceryl-p-aminobenzoate may be spilled on clothing, such as a shirt or a bathing suit, and the impregnated cloth is exposed to air and light, oxidation of the p-aminobenzoate ester results in the development of an unsightly stain which is difficult or impossible to remove completely from the cloth by either washing or dry cleaning. On the other hand, a lotion containing 2 percent or more of the isoamyl-p-dimethylaminobenzoic acid ester, in a similar occurrence, produces no staining of the cloth which is not fully and easily removed therefrom by simple laundering or dry cleaning procedures.

Again, a typical group of sun screening preparations contain compounds such as dihydroxyacetone. The latter material is designed to react with free amino groupings in the skin protein, producing a tan to brown coloration on the surface of the skin. When materials such as the aforementioned dihydroxyacetone are combined with p-aminobenzoic acid esters, the reaction immediately takes place between the dihydroxyacetone and the free primary amine group of the sun screening material. This produces a brown coloration in the lotion or cream, renders both the dihydroxyacetone and the sun screening p-aminobenzoate ester ineffective and completely destroys the utility of the preparation for its design purposes. The replacement of the reactive primary amino group with the tertiary amino group completely prevents such reaction and thereby prevents both discoloration of the lotion or cream and the destruction of the skin-protective and skin-colorant function of the suntan preparation.

The esters of p-dimethylaminobenzoic acid are definitely superior to the esters of p-aminobenzoic acid not only in ultraviolet absorption but also in being less reactive when incorporated in the usual type of cosmetic formulations for application to the human skin. However, not all of the esters of the tertiary amino group possess all of the qualities required of a good ultraviolet screen for human use.

Sun screening preparations are generally used in hot weather and at beaches where people enjoy bathing. Thus, it is essential that the thin layer of protective coating on the skin not be appreciably affected by water or perspiration. Yet, the lower esters of p-dimethylaminobenzoic acid, i.e., methy, ethyl, propyl and butyl are appreciably soluble in water. When these materials are applied to the skin in a thin film, they may easily be removed from the skin during bathing or through solution in perspiration of the user. For example, the methyl ester has more than ten times the solubility in water of the amyl ester. As the molecular weight of the alcohol-derived portion of the esters is increased, this tendency of the esters to dissolve in water is progressively decreased, rendering the sun-protective films more permanent on the skin, and providing thereby longer and better protection against erythema.

An ultraviolet absorber for personal use must be capable of screening out at least 85 percent of the erythemal energy of sunlight and as much as 99 plus percent of such energy. The desired results can be obtained by adjusting the percentage of the ultraviolet absorber used In the case of the esters of p-dimethylaminobenzoic acid, this percentage could range from as little as 0.1–0.5 percent to a maximum of 10% or more of the material. The solubility of the sun screening ester in the desired percentage concentrations is a controlling factor in incorporating such esters in the cosmetically acceptable media for application to the skin.

For example, none of the esters of p-aminobenzoic acid are appreciably soluble in mineral, vegetable or animal oils at ordinary temperatures. The esters of p-dimethylaminobenzoic acid with the lower aliphatic alcohols also are appreciably insoluble in these oils. Thus, even in a one percent concentration in mineral oil the methyl, ethyl and propyl esters separate out immediately at room temperature, while the butyl ester separates from the oily vehicle within 24 hours and slowly crystalizes.

Amyl, hexyl and higher esters of p-dimethylaminobenzoic acid are miscible with mineral, vegetable and animal oils. Solutions containing as much as from seven to ten percent by weight of these esters in mineral oil remain completely homogeneous on storage for prolonged periods of time at various atmospheric temperatures. This permanent solubility in oils at required concentra-

tions is especially important when the vehicle is not only the oil, but when an emulsified cream or lotion is desired. This may be illustrated by the following typical example:

An emulsified lotion is made up by combining

	Parts
Ester of p-dimethylaminobenzoic acid	3.0
Cetyl alcohol	1.0
Glyceryl monostearate	2.0
Polyethylene glycol laurate	5.0
Stearic acid	2.0
Peanut oil	4.0
with	
Triethanolamine	0.5
Urea	2.0
Propylene glycol	6.0
Water	74.5

When the ester employed is the methyl, ethyl or propyl ester, said ester is insoluble in the oily phase and is dispersed in the aqueous phase instead. Such esters, because of their water-solubility, are readily removed from the skin and do not provide long-enduring protection against erythema. If the ester employed is the butyl ester, it is insufficiently soluble in the oily phase and separates therefrom as either an oily or a crystalline third phase within a short time, usually 24 hours. Since this ester at this concentration is relatively insoluble in water, it eventually separates as a third phase and settles to the bottom of the preparation. As a result of such separations, the emulsion rapidly separates and is rendered unusable, and ineffective for its design purpose.

When the sun screening compound used is the amyl, hexyl, heptyl or octyl esters, its ester is completely miscible with the oily phase, and the emulsion formed is completely stable in storage for periods in excess of two years. The use of the amyl or higher esters thus renders the sun tan emulsified lotion or cream usable for long periods of time, an effect which cannot be achieved by the use of the methyl to butyl esters of p-dimethylaminobenzoic acid.

In order to obtain the ultimate in protection in a sun screening preparation, as much as ten percent or more of the ester of dimethylaminobenzoic acid will be required to achieve the desired results. At these higher levels of concentration, even the use of the amyl, hexyl and higher esters may result in separation from the vehicle, over an extended period of time. This posibility is overcome by incorporating in the preparation a mixture of the amyl, hexyl or higher esters. Such mixtures remain soluble in oils and emulsified creams and lotions indefinitely, at the maximum concentrations required. An example of such an oily sun-screen lotion is:

	Parts
Isoamyl-p-dimethylaminobenzoate	8.0
2-ethylhexyl-p-dimethylaminobenzoate	2.0
Mineral oil (U.S.P.)	46.0
Peanut oil	44.0

Such a clear oily lotion remains completely homogeneous in storage over a long period of time and during transportation even at temperatures as low as zero degrees Fahrenheit. These mixtures of the higher esters have been found to remain soluble in the oils indefinitely at concentrations as high as thirty percent. As a result, when incorporated in an emulsified cream or lotion in the comparatively very high concentrations required for the ultimate in erythemal protection, the creams and lotions exhibit complete stability over extended periods of storage and at all temperature conditions normally experienced. On the contrary, the methyl to butyl esters would be practically useless for cosmetic application in such high concentrations and eventual instability may be experienced even with the pure amyl, hexyl or higher esters used singly in such concentrations, depending, of course, on the percentage of the particular ester used.

Another typical vehicle in which ultraviolet absorbers are incorporated is the aqueous alcoholic lotion. A typical example of such a lotion is

	Parts
Ester of p-dimethylaminobenzoic acid	2.0
Ethyl alcohol	68.0
Water	30.0

In such a preparation, when the ester of p-dimethylaminobenzoic acid used is the methyl, ethyl, propyl or butyl, the resulting preparation is not ideally suited to the purpose for which it is intended, namely, protection of the user against sun-induced erythema. When the volatile vehicle evaporates from the skin, the sun screening compound rapidly crystallizes on the skin, and the continuity of the film, which is so essential for protection, is destroyed. These esters, which are all normally crystalline solids at skin temperature, form a powder of small crystals on the skin which not only do not cover and protect the entire surface of the skin, but rapidly dust off the skin, or are removed therefrom by the motion of the user, by contact with the clothing of the user, or by abrasion and erosion by sand or water. The protection offered by these unplasticized, particulate powders is inferior to that provided by an adherent, continuous liquid film on the skin.

On the other hand, when the esters employed are the amyl, hexyl, heptyl, octyl or higher esters, and especially mixtures of these esters, after evaporation of the volatile aqueous alcoholic medium, there is left on the skin a continuous oily film. Such film provides complete and long-lasting protection against sun-induced erythema, and is not easily removed by exercise, abrasion or washing.

It is known, for example, that the methyl-p-dimethylaminobenzoate melts at 102° C., the ethyl ester at 67–68° C. and the isobutyl p-dimethylaminobenzoate has been reported by Gregoire, Girard and Barbaud (Ann. pharm. franc. 9, 493–513 (1951)) to melt at 245° C. Such compounds will crystallize at skin temperatures. Compared to these esters, the n-amyl p-dimethylaminobenzoate melts at −170° C. and 2-methylbutyl p-dimethylaminobenzoate at −35° C. A mixture of these esters such as 60 parts of n-amyl, 20 parts of isoamyl and 20 parts of 2-methylbutyl p-dimethylaminobenzoate melts at −80° C. A mixture of 50 parts n-amyl and 50 parts 2-ethylhexyl p-dimethylaminobenzoate melts at −56° C. These very low melting mixtures, even in the absence of extraneous plasticizers, remain liquid on the skin, and adhere strongly to it, providing the desired complete protection against sun-induced erythema.

The esters of p-dimethylaminobenzoic acid have much greater stability than the esters of p-aminobenzoic acid and as a result do not discolor on exposure to light and air, either initially or in finished formulations, and further could be safely incorporated with a material such as dihydroxyacetone. It would be expected that the tertiary amino group would be completely stable on exposure to light and air. However, it has been found that this is not true. For example, a sample of isoamyl p-dimethylaminobenzoate on storage in a clear glass or plastic bottle develops an odor which is repulsive and undesirable.

This was found to be typical of all the p-dimethylaminobenzoates, that in bodies of these esters which are exposed to light and air simultaneously there are formed traces of decomposition products. Indeed, trace amounts of these decomposition products can be found immediately upon completion of manufacture. It was further found that these decomposition products have a self-catalytic effect so that the presence of just a few parts per million in a p-dimethylaminobenzoate exposed to light and air in storage, results in major decomposition of the product. The decomposition is further accelerated when the p-dimethylaminobenzoate is incorporated into a typical cos-

metic vehicle such as an aqueous alcoholic or oily lotion or an emulsified lotion or cream.

The formation of decomposition products in the applicants' otherwise highly desirable esters and mixtures of esters of p-dimethylaminobenzoic acid makes their use as sun screens for application to human skin highly questionable. Firstly, the decomposition products impart to the esters and to any vehicle in which they may be incorporated for such use, the penetrating and repulsive odor of dimethylamine. Secondly, and more importantly, the catalytic reaction of such decomposition products can seriously impair the sun screening potential of such esters. For example, in accelerated testing, the entire absorption potential of p-dimethylbenzoic acid in the erythemal range of the ultraviolet spectrum has been completely destroyed by oxidation. The decomposition products, caused by oxidation in the presence of light and readily recognizable both in the ester and the cosmetic vehicle by their undesirable odor, seriously detract from the utility of the p-dimethylaminobenzoate as a sun screen and present a serious disadvantage as to their use on the human skin.

To overcome this, there should be incorporated in the esters, and mixtures of esters, otherwise well suited for use as sun screens, a relatively minor portion of a material which will inhibit the formation of the catalytic traces of decomposition products. These inhibitory materials include nordihydroguiaretic acid, citric acid, ascorbic acid, hydroquinone, butylated hydroxy anisole, butylated hydroxytoluene and any other type of antioxidant, and mixtures of one or more of such inhibitory materials. The amounts of these inhibitory materials which are required range from one part of inhibitor to ten thousand parts of the p-dimethylaminobenzoic acid ester to five parts of inhibitor in one thousand parts of the ester.

Moreover, it is essential that the required amount of the inhibitor be incorporated as part of the manufacturing procedure by which the particular ester, or mixture of esters, of p-dimethylaminobenzoic acid is produced. If this it not done and the catalytically active traces of decomposition products are formed, subsequent additions of the inhibitory materials, say at the stage of manufacture of the finished cosmetic solution or lotion, will not prevent the continued and undesirable decomposition of the sun screening esters, as described above. The catalytic action of any minute traces of decomposition materials resulting from the manufacture itself or immediately thereafter from exposure to light and air, must be and can be completely inhibited to prevent a serious decomposition of the p-dimethylaminobenzoic acid ester or mixture of esters.

For example, in all of the examples in this disclosure, if the ester, or mixture of esters, of p-dimethylaminobenzoic acid employed does not contain the required amounts of the inhibitory material, the finished lotions shortly develop the undesirable odor of dimethylamine. In use on the skin, the esters, or mixture of esters, from such lotions are exposed to the action of light and air in extremely thin layers. Under such conditions, although the odor which may be developed while on the skin is inappreciable because the amine formed is very volatile, the film of screen loses its efficiency to provide protection against sun-induced erythema, and the user may not be protected. On the other hand, if the ester, or mixture of esters, employed in these aforementioned preparations, as part of manufacturing procedure, are combined with the relatively minor amounts required of one or more of the inhibitory materials, the preparation does not develop any odor of dimethylamine even on long term exposure to light and air during storage, nor does it lose any of its protective activity when spread in this film on the skin of the user. As stated previously, if the inhibitory material is not incorporated immediately, the later addition of an inhibitory material, even in the cosmetic vehicle, will not sufficiently prevent the catalytic action of the decomposition materials to avoid the odor problem or the reduction of the absorbtive properties of the sun screen.

The new and improved compositions of matter encompassed by this invention, therefore fulfill all of the requirements for use in screening the ultraviolet of sunlight and skylight from human skin. They include the amyl and higher esters, and mixtures of the amyl and higher esters, of p-dimethylaminobenzoic acid in which there is initially incorporated a small percentage of oxidation inhibitor. They are designed to safely provide any desired erythemal protection and/or sun tanning. They may be incorporated in all types of cosmetically acceptable stable solutions and emulsions. They are stable during extended periods of storage and under all normally experienced temperature conditions. They provide the required, long-lasting, complete skin coverage necessary for safe exposure to the effects of sunlight and skylight over a minimum of four hours duration. They may be used with other materials which may be incorporated in suntan products and will not damage clothing or other materials with which they may come in contact.

The higher esters may be derived from mono-alcohols having up to 16 and 18 carbon atoms and still be highly effective for the present purposes.

What is claimed is:

1. A method of protecting the human skin from the effects of erythema inducing ultraviolet radiation which comprises applying to said skin a film of a composition of a cosmetic carrier containing distributed therein from a sufficient amount to the limit of solubility therein of an alkyl ester or mixture of such esters of p-dimethylaminobenzoic acid wherein the esterifying radical is of a monohydric alcohol having from 5 to 18 carbon atoms, said esters having a sufficiently low melting point as to be liquid at skin temperatures, said esters being miscible in said carrier at said temperatures.

2. A method of protecting the human skin from the effects of erythema inducing radiation according to claim **1** wherein said cosmetic carrier is taken from the class consisting of water-alcohol mixtures, water and oil creams, oil based lotions, and oils.

3. A method according to claim **2** wherein said carrier is a lower monohydric alcohol.

4. A method according to claim **2** wherein carrier is an oil selected from the group of glycerin-fatty acid esters and petroleum oils.

5. A method according to claim **2** wherein said carrier is a cosmetic lotion or cream.

6. A method according to claim **2** wherein said composition contains also an antioxidant sufficient in amount to prevent decomposition of said ester.

7. A method according to claim **2** wherein said ester is selected from the group consisting of amyl, hexyl, heptyl and octyl, and mixtures thereof.

8. A composition adapted for application to the human skin comprising a cosmetic carrier containing distributed therein from a sufficient amount to the limit of solubility therein of an alkyl ester or mixture of such esters of p-dimethylaminobenzoic acid, wherein the esterifying radical is of monohydric alcohol having from 5 to 18 carbon atoms, said esters having a sufficiently low melting point as to be liquid at skin temperatures, said esters being miscible in said carrier at said temperatures, to provide substantial protection against erythemal radiation.

9. A composition according to claim **8** wherein said cosmetic carrier is taken from the class consisting of water-alcohol mixtures, water and oil creams, oil based lotions, and oils.

10. A composition according to claim **9** wherein said ester is selected from the group consisting of the amyl, hexyl, heptyl and octyl esters, and mixtures thereof.

11. A composition according to claim **9** wherein an antioxidant is also contained therein.

(References on following page)

References Cited

UNITED STATES PATENTS

2,202,865	6/1940	Piggott et al.	260—471
2,853,423	9/1958	La Via	167—90

OTHER REFERENCES

Hackh's Chemical Dictionary, 3rd ed., The Blakiston Co., Philadelphia, Pa. (1944), p. 381.

Greenberg et al.: Handbook of Cosmetic Materials, Interscience Publishers, N.Y. (1954), p. 189.

Sagarin: Cosmetics, Science and Technology, Interscience Publishers, N.Y. (1952), pp. 197–203.

Merck Index, 7th Ed., Merck & Co. Inc., Rahway, N.J.

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U.S. DEPARTMENT OF COMMERCE

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,403,207 September 24, 1968

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It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading to the printed specification, lines 5 to 7, "Saul I. Kreps, 40 Catherine Court, Cedar Grove, N. J. 07009, and Ernst Ohlsson, 2 Oak Knoll Road, Summit, N. J. 07901" should read -- Saul I. Kreps, Cedar Grove, and Ernst Ohlsson, Summit, N. J., assignors to Van Dyk & Company, Inc., a corporation of New Jersey --.

Signed and sealed this 21st day of October 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

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Commissioner of Patents