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HAIR SPRAY COMPRISING TRI-(p-AMINOBENZOYL) ESTERS OF PANTOTHENYL ALCOHOL

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16 Claims. (Cl. 167—87.1)

This application is a division of copending patent application Serial No. 251,752, filed January 16, 1963, now U.S. Patent 3,207,778, granted September 21, 1955.

This invention relates, in general, to improve cosmetic preparations and to methods of preparing and using same. More particularly, the invention relates both to improved aerosol hair sprays and to certain novel esters which have been found to be particularly useful as components thereof.

The expression "aerosol hair spray" will be used herein to denote liquid cosmetic preparations which are intended to be dispensed upon the hair, under pressure, in the form of liquid-gas aerosols. Cosmetic preparations of this nature are well known in the art. Many of the aerosol hair sprays which are now commercially available contain a hair setting component, the function of which is to keep the hair in set position, or to make it manageable when it is combed or coifed. The hair setting action of such sprays is usually attributed to the ability of the hair setting component thereof to form a film on the hair shaft upon evaporation of the solvent vehicle.

Various hair setting components have been used in the formulation of the aerosol hair spray preparations of the prior art. These include, for example, such materials as shellacs, ethyl cellulose, carboxymethyl cellulose, gum arabic, polyvinyl alcohol, copolymers of vinyl acetate and vinylpyrrolidone. In addition, polyvinylpyrrolidone (PVP) has proved, in the past, to be of especial importance as a hair setting component of many commercially successful hair spray compositions.

It is an object of this invention to provide aerosol hair sprays having highly effective hair setting properties.

It is a further object of this invention to provide novel esters which are eminently well suited for use in the formulation of aerosol hair sprays.

It is a more particular object of this invention to provide tri-(p-aminobenzoyl) esters of pantothenyl alcohol as well as mixtures containing substantial quantities of such esters.

Other objects of this invention will be obvious and will in part appear hereinafter.

It has been found that, when a tri-(p-aminobenzoyl) ester of pantothenyl alcohol is used as a component of a hair spray formulation, preparations having greatly improved hair setting properties are obtained. For convenience, pantothenyl alcohol will be referred to, in the present specification and in the claims, merely as panthenol. It is to be understood that, in the practice of this invention, one may employ panthenol either in the racemic or optically active form and that where the word "panthenol" is used herein it includes either and/or both d-panthenol and dl-panthenol. Hence, the expression "tri-(p-aminobenzoyl) esters of panthenol" will be used herein, at various instances, to designate either or both the tri-(p-aminobenzoyl)-d-panthenol and the tri-(p-aminobenzoyl)-dl-panthenol. The esters produced and used in the preferred embodiment of this invention are prepared from dl-panthenol.

Thus, one specific embodiment of the present invention resides in novel panthenol esters, that is, tri-(p-aminobenzoyl)-d-panthenol and tri-(p-aminobenzoyl)-dl-panthenol, and mixtures containing substantial quantities thereof. The method of preparation of such esters, and of mixtures containing such esters, is also included within the scope of the present invention. Another embodiment of the invention resides in novel aerosol hair spray preparations having the novel esters, and mixtures containing same, as an essential component thereof. A further embodiment of the invention resides in the method of setting of hair using such hair spray preparations.

The tri-(p-aminobenzoyl) esters of panthenol which have been found to be useful as the hair setting components of the improved hair spray compositions of this invention are, as indicated heretofore, in and of themselves, novel compounds. These esters, namely, tri-(p-aminobenzoyl)-d-panthenol and tri-(p-aminobenzoyl)-dl-panthenol, are prepared in the following manner: Panthenol, that is, either d-panthenol or dl-panthenol, and p-nitrobenzoyl chloride are charged into, and stirred in, a suitable reaction vessel. A ratio of about 3.0 moles of p-nitrobenzoyl chloride is employed for each mole of panthenol used. The reaction between these reactants is exothermic and it can be initiated merely by mixing same at ordinary room temperatures. However, in the preferred practice of the invention, the reactants are mixed at a temperature which is elevated somewhat above room temperature since this facilitates the start of the reaction. Heating of the reaction mixture to a temperature within the range of from about 30° C. to about 60° C. has been found to be most practical. Higher temperatures can, of course, be utilized, if desired. However, for the most part, no useful purpose will be served by mixing the reactants at a temperature of above about 60° C. Since the reaction between panthenol and p-nitrobenzoyl chloride is exothermic, once it commences, it may be allowed to proceed to substantial completion without further heating. During the course of the reaction, however, the reaction mixture is continuously stirred. When the reaction ceases, the product, thus obtained, is stirred for an additional period of time at a temperature of up to about 90° C. By means of this additional stirring and heating, the reaction is driven to substantial completion. For the present purposes, the reaction may be considered as complete when evolution of hydrogen chloride gas from the reaction mixture ceases. Subsequently, an inert organic solvent is added to the reaction mixture and stirred therewith. In general, any inert organic solvent in which the reaction product is soluble can be used, as, for example, methyl ethyl ketone, dioxane, tetrahydrofuran, etc. The solvent used in the preferred practice of the invention, however, is acetone. The quantity of solvent used in this step of the process is not particularly critical. Thus, for example, one may use a quantity of solvent which is sufficiently large to dissolve completely all of the reaction product. A greater or lesser quantity of solvent can be used, if desired. However, there is no particular advantage in using more solvent than is needed to dissolve the product. On the other hand, it will suffice if the quantity of solvent used is such as to form a workable slurry with the reaction mixture.

After the solvent is added to the reaction mixture, an alkali is introduced in sufficient quantity to neutralize the reaction mixture. Under ordinary circumstances, a ratio of one mole of alkali will be added for each mole of p-nitrobenzoyl chloride employed in the first step of the process. In general, any alkaline earth metal oxide, carbonate or bicarbonate, can be used as the alkali in this step of the process. In the alternative, any alkali metal carbonate or bicarbonate can be used. Thus, suitable alkalis include sodium carbonate, potassium carbonate, calcium carbonate, sodium bicarbonate, potassium bicarbonate and calcium oxide. However, sodium

bicarbonate is employed in the preferred practice of the invention. This step can be carried out at room temperature, or at any temperature up to and including the reflux temperature of the mixture. The mixture is stirred, or stirred and heated, until the evolution of carbon dioxide gas from the mixture ceases. Thereafter, the product is filtered and the insoluble residue is washed with acetone. The filtrate from the original filtration step is combined with the filtrates from the solvent washing steps and the combined filtrate is evaporated to dryness under vacuum.

The residue, remaining after the solvent has been removed by evaporation, is principally a tri-(p-nitrobenzoyl) ester of panthenol. The residue contains also some di-(p-nitrobenzoyl) ester of panthenol and mono-(p-nitrobenzoyl) ester of panthenol. This residue is subsequently dissolved in a suitable solvent. As the solvent one can use a lower aliphatic monohydroxy alcohol, such as methyl alcohol, ethyl alcohol, etc., or a mixture of such alcohols. Alternatively, one can employ a lower fatty acid ester of a lower aliphatic alcohol, such as ethyl acetate, butyl acetate, ethyl propionate, etc., as the solvent. In addition, however, one could, if desired, use any other solvent which does not react, or is not reacted upon, during the subsequent reduction step. Tetrahydrofuran is another example of such a solvent. The product, while dissolved in such solvent, is reduced either by chemical means, for example, using either lithium aluminum hydride or aluminum amalgam as the reducing agent and employing tetrahydrofuran as a solvent, or with hydrogen in the presence of a catalyst, such as platinum, palladium or Raney nickel. In the preferred procedure, reduction is accomplished by reacting the product, while dissolved in a solvent, with hydrogen in the presence of a conventional catalytic quantity of Raney nickel catalyst. Moreover, while in the preferred embodiment of the invention, the reduction is carried out at room temperature and at a hydrogen pressure of about 50 p.s.i., it can be carried out, if desired, at an elevated temperature and/or at under greater or lesser pressure. After the reduction is complete, the reaction mixture is filtered to remove the catalyst.

By the procedure described in the preceding paragraphs, a mixture is obtained containing a substantial quantity of a tri-(p-aminobenzoyl) ester of panthenol. Such mixture comprises at least about 80% by weight of the tri-(p-aminobenzoyl) ester of panthenol and varying quantities of the mono- and of the di-(p-aminobenzoyl) esters of panthenol. Moreover, the mixture can, and generally does, contain a relatively small amount of an alkyl ester of p-aminobenzoic acid, for example, methyl p-aminobenzoate. Additionally, some extraneous compounds may be found in the present products as impurities. The quantities of these impurities normally found in the products do not affect, however, the desired film-forming properties of the tri-(p-aminobenzoyl) esters of panthenol. By a refinement procedure, which will be described hereinafter, an essentially pure tri-(p-aminobenzoyl) ester of panthenol can be obtained. The expression "essentially pure" herein is used to connote a product containing at least about 92% by weight of a tri-(p-aminobenzoyl) ester of panthenol. In general, the product, in its essentially pure form, contains, in addition to the tri-(p-aminobenzoyl) ester of panthenol, relatively small quantities of the mono- and di-(p-aminobenzoyl) esters of panthenol and methyl p-aminobenzoate.

The essentially pure tri-(p-aminobenzoyl) ester of panthenol, which is referred to in the preceding paragraph, may be obtained conveniently by the following method. A ratio of about 3.0 moles of p-nitrobenzoyl chloride and 1.0 mole of panthenol are caused to react in the manner described heretofore. The product, thus obtained, which is a mixture containing a substantial quantity of a tri-(p-nitrobenzoyl) ester of panthenol, is dissolved in a suitable solvent, following which benzene is added thereto. In the case of the ester of dl-panthenol, the solvent preferably employed is chloroform while in the case of the ester of d-panthenol, the solvent preferably used is methanol. Addition of benzene to the solvent solution results eventually in the precipitation of a white crystalline material in either case. Recrystallization of this crystalline product from chloroform- or methanol-benzene mixtures yields the essentially pure benzene adduct of the tri-(p-nitrobenzoyl) ester of panthenol. Upon reduction of this product, in the manner described heretofore, there is obtained an essentially pure tri-(p-aminobenzoyl) ester of panthenol.

It has been found that the film-forming properties of both tri-(p-aminobenzoyl)-d-panthenol and tri-(p-aminobenzoyl)-dl-panthenol are such that these compounds are well suited for use as hair setting components of hair spray preparations. Additionally, however, it has been found that completely suitable hair spray preparations can be prepared by using products, produced as disclosed herein, containing at least about 80% of one of the named tri-(p-aminobenzoyl) esters of panthenol. However, it has been observed that the film-forming properties of the tri-(p-aminobenzoyl) esters of panthenol are somewhat enhanced as the purity of the compound is increased.

The quantities of the side reaction compounds which are present in the products of the invention are widely variable. For example, mono-(p-aminobenzoyl) esters of panthenol, that is, the mono-(p-aminobenzoyl)-d-panthenol or the mono-(p-aminobenzoyl)-dl-panthenol can comprise up to about 7.0% by weight of the products. In most instances, the monoester will comprise from about 0.25% to about 5.0% by weight of the product. A di-(p-aminobenzoyl) ester of panthenol, that is, the di-(p-aminobenzoyl)-dl-panthenol or the di-(p-aminobenzoyl)-dl-panthenol, can comprise up to about 12.0% by weight of the products. Generally, such diester will comprise from about 0.25% to about 10.0% of the weight of the product. Moreover, the products can contain up to about 7.0% by weight of an alkyl ester of p-aminobenzoic acid as, for example, methyl p-aminobenzoate. Ordinarily, however, the products which are produced in the preferred embodiment of the invention will contain from about 0.25% to about 5.0% by weight of the alkyl-p-aminobenzoate. Certain other extraneous compounds may be present, as impurities in the products of the invention. The presence of such impurities does not adversely affect the desired film-forming properties of the tri-(p-aminobenzoyl) esters of panthenol, however, when such impurities do not comprise more than about that 7.0% of the weight of the final products.

As indicated heretofore, the novel compounds of this invention, that is, the tri-(p-aminobenzoyl)-d-panthenol and tri-(p-aminobenzoyl)-dl-panthenol, or the mixtures containing substantial amounts of one of these esters, have been found to be especially well suited for use as the hair setting component of hair spray preparations. These esters, or mixtures containing same, can be used as the sole hair set component of such preparations. Alternatively, these esters, or mixtures containing same, can be used in admixture with prior art materials which perform a similar function. Moreover, these esters can be formulated with any of the adjuvant materials normally used in the production of conventional hair sprays. These adjuvants include, for example, perfumes, antistatic agents, auxiliary hair-conditioning agents, plasticizers, etc. Additionally, the esters, and the mixtures, of this invention are suitable for use in combination with propellants of the type generally employed in the formulation of the conventional hair spray preparations of the art. The preferred hair sprays of our invention, however, contain liquified fluorinated hydrocarbon propellants such as those marketed by E. I. du Pont de Nemours &

Co., Wilmington, Delaware, under the proprietary designation "Freon," or those marketed by Allied Chemical & Dye Corporation, New York, New York, under the proprietary designation "Genetron," or those marketed by Pennsalt Chemicals Corporation, Philadelphia, Pennsylvania, under the proprietary designation "Isotron." Useful propellants are those made by compounding mixtures of various "Freon" products, for example, "Freon" 11 (trichloromonofluoromethane), "Freon" 12 (dichlorodifluoromethane) and "Freon" 114 (symmetrical dichlorotetrafluoromethane). Especially useful are mixtures of "Freon" 11 and "Freon" 12 and of "Freon" 12 and "Freon" 114 in the proportions recommended by the manufacturer for pressure ranges of 12 to 60 p.s.i.g.

The finished hair spray preparations of this invention are readily prepared. The novel panthenol ester hair setting component, the preparation of which has been described heretofore, together with such optional ingredients as the formulator may wish to employ, that is, the perfume, antistatic agent, auxiliary hair-conditioning agent, etc., also referred to heretofore, are dissolved in a suitable solvent to form what will be designated herein as a "concentrate." Preferably, a lower molecular weight aliphatic alcohol, such as ethanol, is used in producing the concentrate. The amount of alcohol used may vary within a rather wide range. Generally, a sufficient quantity of solvent will be used to provide a concentrate containing from about 1.0% to about 10.0% by weight of the novel hair setting component of this invention. A denatured alcohol, for example, the solvent known in the art as "SDA No. 40" alcohol (anhydrous) is used in the preferred embodiment of the invention. Anhydrous solvents are employed to advantage, particularly when corrosion of the container presents a problem. The concentrate and the propellant are then packaged into a suitable dispenser by any known or convenient method.

The ratio of concentrate to propellant in the hair spray compositions of the invention can be varied over a rather wide range. Generally, a weight proportion of about 1.0 part of concentrate for each 2.0 parts of propellant is employed, when such ratio will provide a finished hair spray preparation containing from about 0.25% to about 10.0% by weight of the hair setting component.

The concentrate and the propellant can be packaged, by any known method, in aerosol container-dispensers of the type ordinarily employed in sales to the consumer. For example, the concentrate and the propellant can be packaged by the so-called "cold-fill" method of packaging. In this method, the concentrate is cooled to a temperature of about 0° C., and charged into a suitable aerosol container. The propellant, previously cooled to about −10° C., is then added to the container, following which the container is tightly sealed with a lid having some suitable valve through which the product, in the form of a spray, can be dispensed. The foregoing method of filling the aerosol container is exemplary only, it being fully understood that the present invention is not restricted to this particular method of packaging. For example, if desired, the so-called "pressure-fill" method of packaging can be used.

The novel tri-(p-aminobenzoyl) esters of panthenol, described herein are, in part, characterized by the fact that, in the form of an alcohol solution, they form non-tacky and non-hygroscopic films. These esters are, as indicated heretofore, further characterized by the fact that they are well suited for use as the hair set ingredient of hair spray preparations. In addition to their outstanding hair setting properties, however, certain other advantages accrue from the use of these esters in hair spray preparations. In the first place, hair sprays containing these esters show little or no tendency to flake when applied to the hair. Moreover, these esters have been found to possess sun screen activity and, as a result, the films formed thereby will protect the hair from undesired bleaching by the sun. Moreover, since the films formed by these esters are non-hygroscopic, hair treated therewith tends to be held in place more effectively, particularly under conditions of high humidity. However, the esters can be washed out of the hair readily by means of the use of conventional soaps and shampoos.

The preferred method of making the novel tri-(p-aminobenzoyl) esters of panthenol of this invention is as follows: Panthenol, that is, either d-panthenol or dl-panthenol, is reacted with p-nitrobenzoyl chloride using a ratio of about 3.0 moles of p-nitrobenzoyl chloride for each mole of panthenol. To the reaction product, thus obtained, there is added an inert organic solvent and an alkali, such as an alkaline earth metal carbonate, bicarbonate or oxide or an alkali metal carbonate or bicarbonate. The reaction mixture is filtered, the solid remaining on the filter is washed with solvent, the filtrate and washings are combined and solvent is then removed by evaporation. The residue which remains after the solvent has been removed, said residue comprising predominantly tri-(p-nitrobenzoyl)-d-panthenol or tri-(p-nitrobenzoyl)-dl-panthenol depending upon whether d-panthenol or dl-panthenol was used initially, is subjected to catalytic reduction, by any suitable method, while dissolved in a lower aliphatic alcohol solvent, a lower aliphatic ester or tetrahydrofuran. Optionally, the product may be purified, by way of its benzene adduct, prior to its reduction. The reduction product can be separated from the solvent by any convenient means. By this method, there is obtained a product, non-hygroscopic in nature, which contains a substantial quantity, tha is, 80% by weight or more of the tri-(p-aminobenzoyl)-panthenol. Such ester, or mixture containing such ester, has been found to be well suited for use as a hair set ingredient of a hair spray preparation.

For a fuller understanding of the nature and objects of this invention, reference may be had to the following examples which are given merely as further illustrations of the invention and are not to be construed in a limiting sense. All parts given in the examples are parts by weight unless otherwise indicated.

EXAMPLE 1

In this example, 0.1 mole of d-panthenol and 0.3 mole of p-nitrobenzoyl chloride were charged into a reaction vessel and the mixture was stirred and warmed until the components thereof commenced to react exothermically. The reaction was permitted to proceed, spontaneously, until the exothermic reaction ceased. The reaction product, while being stirred, was then warmed on a steam bath to liberate hydrogen chloride gas. When the hydrogen chloride gas was liberated, the reaction product was dissolved in about 200 cc. of acetone and 0.3 mole of sodium bicarbonate was added to the acetone solution. The reaction mixture was then heated to reflux and it was maintained at reflux temperature for a period of about 30 minutes. The warm solution was filtered and the undissolved material which was retained on the filter was washed with acetone. The filtrate from the first filtration step was combined with the filtrate from the acetone washing step and the solution was, thereafter, evaporated to dryness under vacuum. The residue remaining after the solvent was removed, said residue comprising predominantly tri - (p - nitrobenzoyl)-d-panthenol, was dissolved in ethanol and reduced with hydrogen, at room temperature and using 50 p.s.i. hydrogen pressure, in the presence of Raney nickel catalyst.

When reduction of the product was complete, the reaction mixture was filtered to remove the catalyst. The filtrate was evaporated to dryness to yield the desired product in the form of a non-hygroscopic glass.

The product which was thus obtained was a mixture comprising about 90% by weight of tri-(p-aminobenzoyl) d-panthenol, about 8.0% by weight of di-(p-aminobenzoyl)-d-panthenol and about 1.0% by weight of methyl

p-aminobenzoate. This product was comminuted to a fine powder.

EXAMPLE 2

0.1 mole of dl-panthenol and 0.3 mole of p-nitrobenzoyl chloride were charged into a reaction vessel and the mixture was stirred and warmed until the components thereof commenced to react exothermically. The reaction was permitted to proceed, spontaneously, until the exothermic reaction ceased. The reaction product, while being stirred, was then warmed on a steam bath to liberate hydrogen chloride gas. When the hydrogen chloride gas was liberated, the reaction product was dissolved in about 200 cc. of acetone and 0.3 mole of sodium bicarbonate was added to the acetone solution. The reaction mixture was then heated to reflux and it was maintained at reflux temperature for a period of about 30 minutes. The warm solution was filtered and the undissolved material which was retained on the filter was washed with acetone. The filtrate from the first filtration step was combined with the filtrate from the acetone washing step and the solution was, thereafter, evaporated to dryness under vacuum. The residue remaining after the solvent was removed, said residue comprising predominantly tri-(p-nitrobenzoyl)-dl-panthenol, was dissolved in methanol and reduced with hydrogen, at room temperature and using 50 p.s.i. hydrogen pressure, in the presence of Raney nickel catalyst.

When reduction of the product was complete, the reaction mixture was filtered to remove the catalyst. The filtrate was evaporated to dryness to yield the desired product in the form of a non-hygroscopic glass.

The product which was obtained was a mixture containing a substantial quantity of tri-(p-aminobenzoyl)-dl-panthenol. The mixture was comprised of about 82% by weight of tri-(p-aminobenzoyl)-dl-panthenol, about 10% by weight of di - (p - aminobenzoyl)-dl-panthenol, about 0.5% by weight of mono-(p-aminobenzoyl)-dl-panthenol and about 2.0% by weight of methyl p-aminobenzoate. This product was non-hygroscopic in nature and alcoholic solutions thereof, when sprayed in a thin layer, formed non-tacky films.

EXAMPLE 3

In this example, 30.6 grams (0.15 mole) of dl-panthenol and 84.0 grams (0.45 mole) of p-nitrobenzoyl chloride was gently warmed on a steam bath until a vigorous reaction was initiated during which heat and hydrogen chloride gas were evolved. Once the reaction began, the application of external heat was discontinued. The reaction mixture was allowed to react until the spontaneous reaction began to subside. Thereafter, the reaction mixture was heated to a temperature of about 90° C., with stirring. Such heating and attendant stirring was continued until the evolution of the gaseous hydrogen chloride ceased. To insure that the reaction had gone to completion, the clear, viscous reaction product was dissolved in 300 cc. of acetone and 35.0 grams of sodium bicarbonate was added to that solution. The mixture, thus obtained, was stirred until no carbon dioxide was evolved. The mixture was filtered, the insoluble salt was washed with acetone and the filtrate and the acetone washings were combined. The combined filtrate and acetone washings were then heated under vacuum to remove the solvent. A viscous residue was obtained which, on cooling, set to a soft glass which could not be crystallized and was only slightly soluble in methanol. Infra-red analysis, showing a secondary amide, nitro and ester functions, but no hydroxy groups, was interpreted as indicating that the product was comprised substantially of tri-(p-nitrobenzoyl)-dl-panthenol. This ester was dissolved in a minimum of chloroform, following which benzene was added to the solution. Addition of the benzene caused the precipitation of a white, crystalline material which, upon crystallization from chloroform-benzene mixtures, formed crystal clusters, melting, with decomposition, at 148°–150° C., corrected. The crystalline product, thus obtained, was predominantly the benzene adduct of tri-(p-nitrobenzoyl)-dl-panthenol.

Analysis.—Calculated for $C_{30}H_{28}N_4O_{13}\cdot C_6H_6$, molecular weight 731: Theory: C, 59.1%; H, 4.7%; N, 7.7%. Found: C, 59.2%; H, 4.4%; N, 7.5%.

The foregoing procedure was repeated several times and the products obtained were examined by thin-layer chromatography on silica gel G, using a heptane-ethyl acetate system in a volume of 4:6, with the following results:

Table I

Batch	Percent Tri-(p-nitrobenzoyl)-dl-panthenol-Benzene Adduct-(Rf 0.6)	Percent Di-(nitrobenzoyl)-dl-panthenol-Benzene Adduct-(Rf 0.3)	Percent Unidentified (Rf 0.0; 0.5; 0.7)
A	92.5	5	2.5
B	99.5	0.5	0
C	98.5	1.0	0.5

The substantially pure, crystalline benzene adduct of tri - (p - nitrobenzoyl) - dl - panthenol, melting at 148°–150° C., corrected, produced in this example (14.6 grams) was partially dissolved in 150 cc. of ethyl acetate and it was reduced with hydrogen using Raney nickel catalyst. Hydrogen uptake ceased and reduction was complete in about thirty minutes. The catalyst was filtered off and the solvent was removed under vacuum to yield 11.0 grams of product,

$E^{1\%}_{cm.}$ max. 294/5 mμ=1111

in the form of a snow-white non-crystalline froth. Elemental analysis indicated the product to be substantially pure tri-(p-aminobenzoyl)-dl-panthenol.

Calculated for $C_{30}H_{34}N_4O_7$, molecular weight 562: Theory: C, 64.0%; H, 6.1%; N, 10%. Found: C, 63.5%, 63.5%; H, 6.4%, 6.5%; N, 9.3%, 9.4%.

The foregoing procedure was repeated several times and the products obtained were examined by thin-layer chromatography on silica gel G, using a chloroform-methanol system in a volume ratio of 6:1. The results were as follows:

Table II

Batch	I	II	III	IV	V
A	92	5	0.5	0.5	2
B	97	1	0.5	0.5	1
C	94.5	2	0.5	2	1

In Table II:

Column I represents percent tri-(p-aminobenzoyl)-dl-panthenol (R*f* 0.6)

Column II represent percent di-(p-aminobenzoyl)-dl-panthenol (R*f* 0.7)

Column III represents percent mono-(p-aminobenzoyl)-dl-panthenol (R*f* 0.4)

Column IV represents percent methyl p-aminobenzoate (R*f* 0.9)

Column V represents percent other (unidentified impurities) (R*f* 0.0; 0.1; 0.8)

Each of the products identified in Table II were comminuted to a fine powder.

EXAMPLE 4

A mixture was prepared using 0.5 part by weight of the product produced in Example 1 and 0.2 part by weight of a perfume oil. A concentrate was prepared by dissolving this mixture in 32.3 parts by weight of "SDA No. 40" alcohol (anhydrous).

A propellant was prepared by mixing 60.0 parts by

weight of "Freon" 11 and 40.0 parts by weight of "Freon" 12.

The propellant and the concentrate were then packaged in an aerosol container-dispenser. The container-dispenser employed comprised: (a) a conventional aerosol can, 6 oz. capacity, side seam lead soldered outside, round dome top with 1" curled opening, concave bottom, half pound electrolytic tin plate throughout, no internal coating; (b) an assembled cup-type valve (e.g. Model NN, Precision Valve Corporation, Yonkers, New York), including a polyethylene, mechanical break-up press button and polyethylene dip tube; and (c) a protective dome (e.g. Model 5, Precision Valve Corporation, supra). A suitable form of container-dispenser is that shown diagrammatically in Figure 7 at page 800 of "Cosmetics Science and Technology" (ed. Edward Sagarin), published by Interscience Publishers, Inc., New York, N.Y., 1957.

The filling method employed was the so-called "cold-fill" method of packaging. The concentrate was cooled to 0° C. and 33.0 parts by weight thereof charged into the aerosol container-dispenser. Thereafter, 67.0 parts by weight of the propellant, previously cooled to a temperature of about −10° C., were then added to the container-dispenser. Valves were inserted into the filled cans and these were crimped on. The hair spray preparation, thus obtained, was evaluated by the following method: Hair swatches were wetted with water and put into curlers. The hair swatches were subsequently dried and then sprayed with the hair spray preparation produced as disclosed herein. Each swatch was sprayed six times from a distance of about eight inches.

Evaluation of the product by this method proved it to have highly effective hair setting properties.

EXAMPLE 5

A mixture was prepared using 1.0 part by weight of the product produced as described in Example 2 and 0.2 part by weight of a perfume oil. A concentrate was prepared by dissolving the mixture, thus obtained, in 31.8 parts by weight of "SDA No. 40" alcohol (anhydrous).

The propellant was prepared by mixing 60.0 parts by weight of "Freon" 11 and 40.0 parts by weight of "Freon" 12.

The propellant, in the amount of 67.0 parts by weight, and the concentrate, in the amount of 33.0 parts by weight, were packaged in an aerosol container-dispenser by the "cold-fill" method described in Example 3.

The product of this example was evaluated as a hair spray by the method described in Example 3. By this method of evaluation, the preparation was found to possess highly effective hair setting properties.

EXAMPLE 6

A mixture was prepared using 2.0 parts by weight of the product produced as described in Example 2 and 0.2 part by weight of perfume oil. A concentrate was prepared by dissolving this mixture in 30.8 parts by weight of "SDA No. 40" alcohol (anhydrous).

A propellant was prepared by mixing 60.0 parts by weight of "Freon" 11 and 40.0 parts by weight of "Freon" 12.

Thereafter, 33.0 parts by weight of the concentrate and 67.0 parts by weight of the propellant were packaged in an aerosol container-dispenser by the "cold-fill" method described in Example 4.

The hair spray preparation, thus obtained, was evaluated by the method described in Example 4. By this method of evaluation, the preparation was found to possess highly effective hair setting properties.

EXAMPLE 7

In this example, 0.2 part by weight of a perfume oil was added to, and mixed with, each of the three tri-(p-aminobenzoyl)-dl-panthenol esters described in Table II of Example 3. In each instance, the perfume was added to 2.0 parts by weight of tri-ester. Separate concentrates were prepared by dissolving each of the three mixtures in 30.8 parts by weight of "SDA No. 40" alcohol (anhydrous).

A propellant was prepared by mixing 60.0 parts by weight of "Freon" 11 and 40.0 parts by weight of "Freon" 12.

Thereafter, 33.0 parts by weight of each of the concentrates, previously described, and 67.0 parts by weight of the propellant, were packaged in each of three aerosol container-dispensers by the "cold-fill" method described in Example 4.

The hair spray preparations, thus obtained, were evaluated by the method described in Example 4. By this method of evaluation, the preparations were found to possess highly effective hair setting properties.

I claim:

1. A non-hygroscopic mixture comprising tri-(p-aminobenzoyl-d-panthenol, di-(p-aminobenzoyl)-d-panthenol, mono - (p - aminobenzoyl) - d - panthenol and a methyl ester of p-aminobenzoic acid, said tri-(p-aminobenzoyl)-d-panthenol comprising at least about 80% by weight of said mixture.

2. A non-hygroscopic mixture comprising tri-(p-aminobenzoyl) - dl - panthenol, di - (p - aminobenzoyl)-dl-panthenol, mono-(p-aminobenzoyl)-dl-panthenol and a methyl ester of p-aminobenzoic acid, said tri-(p-aminobenzoyl)-dl-panthenol comprising at least about 80% by weight of said mixture.

3. A liquid composition, for dispensing on the hair under pressure as an aerosol, comprising a concentrate containing a lower aliphatic alcohol, tri-(p-aminobenzoyl)-d-panthenol and a gas propellant.

4. A liquid composition, for dispensing on the hair under pressure as an aerosol, comprising a concentrate containing a lower aliphatic alcohol and tri-(p-aminobenzoyl)-dl-panthenol and a gas propellant.

5. A liquid composition, for dispensing on the hair under pressure as an aerosol, comprising (1) a concentrate containing (a) a lower aliphatic alcohol and (b) a mixture containing tri-(p-aminobenzoyl)-d-panthenol and (2) a gas propellant, said mixture (b) comprising tri-(p-aminobenzoyl)-d-panthenol, d-(p-aminobenzoyl)-d-panthenol, mono-(p-aminobenzoyl)-d-panthenol and methyl-p-aminobenzoate, said tri-(p-aminobenzoyl)-d-panthenol comprising at least about 80% by weight of said mixture.

6. A liquid composition, for dispensing on the hair under presseure as an aerosol, comprising (1) a concentrate containing (a) a lower aliphatic alcohol and (b) a mixture containing tri-(p-aminobenzoyl)-dl-panthenol and (2) a gas propellant, said mixture (b) comprising tri-(p-aminobenzoyl) - dl - panthenol, di - (p - aminobenzoyl)-dl-panthenol, mono-(p-aminobenzoyl)-dl-panthenol and methyl p-aminobenzoate, said tri-(p-aminobenzoyl)-dl-panthenol comprising at least about 80% by weight of said mixture.

7. An aerosol hair spray composition comprising a ratio of about 1.0 part by weight of (1) a concentrate comprising a lower aliphatic alcohol having dissolved therein a tri-(p-aminobenzoyl) ester of panthenol and about 2.0 parts by weight of (2) a liquified fluorinated hydrocarbon gas propellant material selected from the group consisting of trichloromonofluoromethane, dichlorodifluoromethane, symmetrical dichlorotetrafluoroethane and mixtures thereof, said aerosol hair spray composition containing from about 0.25% to about 10.0% by weight of the tri-(p-aminobenzoyl) ester of panthenol.

8. An aerosol hair spray composition comprising a ratio of about 1.0 part by weight of (1) a concentrate comprising a lower aliphatic alcohol having dissolved therein tri-(p-aminobenzoyl)-d-panthenol and about 2.0 parts by weight of (2) a liquified fluorinated hydrocarbon gas propellant material selected from the group consisting of trichloromonofluoromethane, dichlorodifluoromethane, symmetrical dichlorotetrafluoroethane and mixtures thereof, said aerosol hair spray composition containing from

about 0.25% to about 10.0% by weight of the tri-(p-aminobenzoyl)-d-panthenol.

9. An aerosol hair spray composition comprising a ratio of about 1.0 part by weight of (1) a concentrate comprising a lower aliphatic alcohol having dissolved therein tri-(p-aminobenzoyl)-dl-panthenol and about 2.0 parts by weight of (2) a liquified fluorinated hydrocarbon gas propellant material selected from the group consisting of trichloromonofluoromethane, dichlorodifluoromethane, symmetrical dichlorotetrafluoroethane and mixtures thereof, said aerosol hair spray composition containing from about 0.25% to about 10.0% by weight of tri-(p-aminobenzoyl)-dl-panthenol.

10. The product of claim **8** wherein the alcohol solvent is ethanol and wherein the propellant is a mixture of trichloromonofluoromethane and dichlorodifluoromethane.

11. The product of claim **9** wherein the alcohol solvent is ethanol and wherein the propellant is a mixture of trichloromonofluoromethane and dichlorodifluoromethane.

12. The product of claim **7** wherein the alcohol solvent is ethanol and wherein the propellant is a mixture of trichloromonofluoromethane and dichlorodifluoromethane.

13. A method of setting hair on the human head which comprises applying to the hair an aerosol which contains, as the disperse phase, a tri-(p-aminobenzoyl) ester of panthenol dissolved in a lower aliphatic alcohol as the film-forming component.

14. A method of setting hair on the human head which comprises applying to the hair an aerosol which contains, as the disperse phase, tri-(p-aminobenzoyl)-d-panthenol dissolved in a lower aliphatic alcohol as the film-forming component.

15. A method of setting hair on the human head which comprises applying to the hair an aerosol which contains, as the disperse phase, tri-(p-aminobenzoyl)-dl-panthenol dissolved in a lower aliphatic alcohol as the film-forming component.

16. A package comprising a pressure-tight container in the form of a tin plate aerosol can dispenser having a valve-controlled opening and containing a hair spray composition comprising (1) a concentrate comprising a tri-(p-aminobenzoyl) ester of panthenol dissolved in a lower aliphatic alcohol, as the film-forming ingredient, and (2) a liquefied fluorinated hydrocarbon propellant gas, said composition being confined in the container under the vapor pressure of the propellant.

No references cited.

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