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Wahl

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[54] COLOR AND ODOR STABILIZED DRY AEROSOL ANTIPERSPIRANT

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[58] **Field of Search**.....424/47, 45, 68, 69, 46

[56] **References Cited**

UNITED STATES PATENTS

3,088,874 5/1963 Geary et al. 424/47

FOREIGN PATENTS OR APPLICATIONS

987,301 3/1965 Great Britain.....424/68

OTHER PUBLICATIONS

Lester et al., Handbook of Cosmetic Materials, 1954, pp. 96.

Sagarin, Cosmetics Science and Technology, 1957, pp. 1,035, 1,053 and 1,067.

Winter, Handbuch Der Gesamten Parfumerie Und Kosmetik, 1952, pp. 156 and 675.

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[57] **ABSTRACT**

Dry aerosol antiperspirant compositions containing hexachlorophene and/or perfumes which are subject to deterioration and are stabilized by the incorporation of a small amount of citric acid.

1 Claim, No Drawings

COLOR AND ODOR STABILIZED DRY AEROSOL ANTIPERSPIRANT

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to aerosol antiperspirant compositions of the type which are essentially anhydrous, i.e., containing only a small amount of water. Specifically, this invention relates to such compositions containing materials such as hexachlorophene and perfumes which tend to deteriorate during storage.

2. Prior Art

Combinations of hexachlorophene and citric acid in solid detergent compositions are disclosed in British Pat. No. 786,285. It is also known that dicarboxylic acids such as oxalic, sebacic, adipic and malonic acids are useful in preventing the color degradation of bar soaps containing hexachlorophene upon exposure to light; see, e.g., U.S. Pat. No. 3,085,066. Salts of citric acid have also been disclosed for this same purpose; see e.g., U.S. Pat. No. 2,970,917 which discloses dihydrazinium and monohydrazinium citrates in soap bars containing hexachlorophene. Antiperspirant compositions have been disclosed containing astringent salts, hexachlorophene, a perfume, and tartaric acid; see, e.g., U.S. Pat. No. 3,509,253. Citric acid has been disclosed as a metal scavenger to protect vitamins and other oxygen-sensitive materials.

SUMMARY OF THE INVENTION

This invention relates to dry aerosol antiperspirant compositions consisting essentially of:

A. From about 1 percent to about 12 percent by weight of a finely divided astringent comprising an acidic, metallic salt that is insoluble in the composition;

B. From about 0.1 percent to about 5 percent by weight of a suspending agent for the astringent;

C. From about 1 percent to about 15 percent by weight of a carrier liquid of low volatility;

D. From about 0.1 percent to about 1.5 percent by weight of hexachlorophene;

E. From about 0.005 percent to about 0.5 percent by weight of citric acid;

F. A solvent for the citric acid in an amount sufficient to dissolve at least a portion of the citric acid; and

G. The balance, an anhydrous liquefiable propellant in an amount sufficient to produce an aerosol spray.

THE ASTRINGENT SALT

Suitable antiperspirant compounds for use in this invention can be any of those well known in the art that are insoluble in the aerosol composition as a whole. Generally, these are acidic, metallic salts, often of aluminum, zirconium or zinc. Most preferably, aluminum chlorhydroxide (ACH) is used, although other astringent salts are also suitable. Examples of other salts are aluminum chloride, aluminum sulfate, aluminum oxychloride, aluminum oxysulfate, zirconyl chloride, zirconyl hydroxychloride, zirconium oxychloride, zinc sulfate and zinc sulfocarbolate. Many inorganic-organic mixtures and complexes are also known in addition to the simple antiperspirant salts. Examples of these are zirconium salt/ amine/ and amino acid complexes as taught by Siegal in U.S. Pat. No. 3,407,254 (Oct. 22, 1968); zirconium salt/aluminum chlorhydroxide/glycol complexes as taught by Jones et al. in U.S. Pat. No. 3,405,153 (Oct. 8, 1968); and aluminum chlorhydroxide/ glycol complexes as taught by Jones et al. in U.S. Pat No. 3,402,932 (Jan. 7, 1969). Other complexes which can be used include those aluminum chlorhydroxide/zirconyl hydroxychloride complexes disclosed in the co-pending application of Raymond E. Bolich, Jr., Ser. No. 59,690, and the aluminum hydroxide/zirconyl hydroxychloride/amino acid complexes disclosed in the co-pending application of Wilmer L. Luedders, Ser. No. 59,693, said applications being filed concurrently herewith. The latter application is now abandoned. These applications and patents are incorporated herein by reference.

Commercial availability of the above astringent salts is widespread, and the choice of the desired antiperspirant compound is limited only by factors well known to those skilled in the art. As heretofore discussed, the above-mentioned aluminum salts are preferred, and for the purposes of the present invention, aluminum chlorhydroxide and the complexes described in the applications of Bolich and Luedders filed concurrently herewith, are especially preferred,

In dry aerosol antiperspirant compositions, the antiperspirant active is dispersed as a finely divided powder. The powder must be in the form of a uniform size particle and must be small enough to remain suspended in the composition within the aerosol container and to pass through the valve without clogging. The particle size must also be such that the antiperspirant is adequately dispersed on the skin and reacts rapidly enough with the moisture of the skin and air to convert the antiperspirant compound in dry powder form into the ionic state which is needed for effectiveness in suppressing perspiration. In this connection, the emollient-carrier of the present invention which will be discussed in more detail hereinafter is also a very important part of this mechanism.

Particle sizes smaller than about 100 microns have been found to be suitable for the practice of the present invention. Preferably, particles averaging from about 10 microns to about 26 microns are desirable. Normally, from about 1 percent to about 12 percent by weight of the composition is a desirable amount for perspiration control. Below about 2 percent, the antiperspirant effectiveness drops off, while above about 12 percent is not practical because the antiperspirant effectiveness does not increase commensurate with the additional quantities used, and in addition, the viscosity of the product increases so that handling is more difficult and atomization is less satisfactory. The most preferred range is from about 2.5 percent to about 6 percent.

THE SUSPENDING AGENT

The suspending agent can be any of those which have been disclosed in the prior art. Suitable examples include: a colloidal silica such as Cab-O-Sil, a pyrogenic silica having a particle diameter between about 0.001 and 0.03 microns as disclosed in British Pat. No. 987,301, and British Pat. No. 1,167,173; finely divided hydrophobic clays such as a reaction product of a clay

such as Bentonite and dimethyldistearyl ammonium chloride (Bentone 34 or Bentone 38) as disclosed in British Pat. No. 1,167,173; those nonionic suspending agents disclosed in U.S. Pat. No. 3,014,844; those suspending agents disclosed in U.S. Pat. No. 3,218,262; those aliphatic monoalkylol amides ($C_{12} - C_{20}$ acyl; $C_2 - C_3$ alkylol) disclosed in the co-pending application of Douglas L. Dannemann and Jerry J. Yetter, Ser. No. 888,958, filed Dec. 29, 1969, now abandoned; and those primary aliphatic amines ($C_{12} - C_{20}$) disclosed in the co-pending application of Charles L. Scripps and Jerry J. Yetter, Ser. No. 888,959, now abandoned filed Dec. 29, 1969. All of the above patents and applications are specifically incorporated herein by reference. The preferred suspending agent is Bentone in an amount from about 0.1 percent to about 1.5 percent, preferably in an amount from about 0.3 percent to about 0.75 percent, and most preferably from about 0.4 percent to about 0.6 percent.

THE CARRIER LIQUID

A carrier liquid of low volatility is used in the instant invention so that the stream issuing from the aerosol container is a moist spray rather than a gritty, dusty cloud. This imparts a cosmetic feeling to the skin when applied thereto an reduces the likelihood of breathing the otherwise dry powder. The carrier liquid also aids efficacy be keeping the antiperspirant compound in contact with the skin so that it does not flake off or wash off. Thus, the carrier liquid is needed for practical use of the instant invention though it is not required per se for purposes of preparing a dry powder antiperspirant composition in stable form. The carrier liquid also decreases the vapor pressure of the propellant mixture which is desirable.

Any of the carrier liquids that are known in the art are suitable for the compositions of the instant invention. Examples are carboxylic esters like isopropyl myristate and isopropyl palmitate; hydrocarbons like mineral oil and tetradecane; alcohols such as lauryl alcohol, hexadecyl alcohol, and oleyl alcohol; carboxylic acids such as lauric and oleic acid; lanolin and its derivatives such as acetylated lanolin; and silicone oils such as dimethylpolysiloxane. Other operable carrier liquids are more hydrophilic than the above-mentioned compounds, for example, organic compounds containing multiple ester groups. This includes, but is not limited to, diesters of dibasic organic acids. Examples of compounds containing multiple ester groups that are suitable for the instant invention are di-n-octyl-n-decyl phthalate, di-n-octyl phthalate, di-n-hexyl phthalate, di-n-butyl phthalate, diethyl sebacate, diisopropyl adipate, and ethyl ethylcarbomethyl phthalate [ortho C_2H_5OOC-ϕ-$COOCH_2COOC_2H_5$].

Still other operable carrier liquids are even more hydrophilic than these esters. Among them are polyethylene glycol monolaurate and butoxy-polyoxyethylene oxypropylene glycols [the Ucon 50 HB series; Trade Mark — Union Carbide].

Among these various carrier liquids, carboxylic esters having from about 12 to about 26 carbon atoms are preferred. As described supra, they can be either aliphatic or aromatic and can contain either one ester group or multiple ester groups. Especially preferred are di-n-butyl phthalate, diethyl sebacate, diisopropyl adipate, and ethyl ethylcarbomethyl phthalate.

Any of the carrier liquids described supra can be used in amounts from about 1 percent to about 15 percent. Below about 2 percent, the carrier liquid is insufficient to form a moist spray and the spray is, therefore, undesirably dusty and gritty and does not adhere well to the skin. Above about 15 percent, the composition deposited upon the skin feels undesirably oily and greasy. Amounts of carrier liquid from about 6 percent to about 10 percent are preferred.

THE HEXACHLOROPHENE

2,2'-dihydroxy-3,5,6,3'-,5', 6'-hexachlorodiphenylmethane (hexachlorophene) is a well-known antibacterial agent. Recently, hexachlorophene has been incorporated in small amounts in dry aerosol antiperspirant compositions of the type disclosed herein. When it is incorporated in such antiperspirant compositions, it forms a pink color upon aging. The reason for this result is unobvious in view of the fact that previous discoloration problems with hexachlorophene took place in light; and these aerosol compositions are not exposed to light. It is, of course, undesirable to have an antiperspirant composition colored pink, since it tends to discolor clothing and skin. It is not known what causes this pink color, but is is theorized that some kind of complex is forming between the hexachlorophene and ferric ions. Preferably, the amount of hexachlorophene is at least about 0.05 percent and most preferably, from about 0.1 percent to about 0.5 percent.

PERFUME

Perfumes are common ingredients of aerosol compositions; and many common perfume ingredients such as aldehydes, cyclic materials, ketones, etc., tend to undergo reactions in the presence of, e.g., metal ions, such as ferric and copper ions. This is undesirable since small amounts of perfume ingredients can cause a very large change in the overall odor impact of the perfume. It is believed that the citric acid also stabilizes the perfume. The amount of perfume is preferably at least about 0.1 percent and is most preferably from about 0.2 'percent to about 0.9 percent.

THE CITRIC ACID

The hexachlorophene and the perfume are stabilized in dry aerosol compositions by the inclusion of a very small amount of citric acid as described hereinbefore. Preferably, there is from 0.01 percent to about 0.5 percent citric acid present. A preferred range is from about 0.01 percent to about 0.04 percent. This range is preferred since excessive amounts of citric acid can actually cause a worse odor grade than the smaller amounts from about 0.01 percent to about 0.04 percent, although the odor grade is still better than if no citric acid were present.

It is surprising that the citric acid is effective in an essentially anhydrous system and in such small amounts despite the presence of large amounts of the astringent, etc. It is believed that citric acid is unique in this respect.

Citric acid monohydrate is preferred, since it dissolves more readily.

The solvent for the citric acid is preferably ethanol in an amount from about 0.25 percent to about 2.0 per-

cent. Other solvents such as methanol, isopropanol, propanol, etc., can be substituted in substantially equivalent amounts. The solvent is used to predissolve the citric acid before it is mixed into the composition.

THE PROPELLANT

Any liquefiable propellant can be used in the compositions of this invention. Examples of materials that are suitable for use as propellants are trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, monochlorodifluoromethane, trichlorotrifluoroethane, propane, butane, and isobutane, used singly or admixed. Trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, and isobutane, used singly or admixed, are preferred.

The amount of the propellant gas is governed by normal factors as well known in the aerosol art. It is satisfactory to consider the propellant as constituting the balance of the composition of the instant invention that is not accounted by the other components as detailed herein. The preferred limits of propellant are therefore from about 70.7 percent to about 93.9 percent. Especially preferred limits are from about 80 percent to about 92 percent.

All parts, percentages, and ratios herein are by weight unless otherwise specified.

The following examples illustrate the invention.

EXAMPLE I

An aerosol antiperspirant composition is prepared containing 3.5 percent of powdered aluminum hydroxychloride which will pass through a 325 mesh screen. The composition also contains:

8.00% — Isopropyl myristate;
0.60% — Bentone 38;
0.10% — Hexachlorophene;
0.40% — Perfume;
0.27% — Ethanol/H_2O (95:5);
0.01% — Citric acid monohydrate; and
1.50% — SDA No. 40 (anhydrous denatured ethanol)

and the balance being a propellant mixture comprising 60 percent trichlorofluoromethane and 40 percent dichlorodifluoromethane.

The above composition is prepared by dissolving the hexachlorophene in the isopropyl myristate using a high speed mixer at a temperature of about 70°F. The aluminum hydroxychloride is then added to the batch and mixed for about 5 minutes at a temperature of about 70°F. The Bentone 38 is next added and mixed. Then the 95 percent ethanol is added and mixed. While the mixing continues, the temperature is slowly increased at the rate of 2° to 3°F. per minute, until a temperature of from about 130° to 150°F. is attained. The mixture is subsequently cooled to a temperature of about 110°F. while the mixing continues. The citric acid is dissolved in the SDA No. 40 and then added to the mixture and mixed. The perfume is then added. The mixing is continued at a temperature of from about 100°F. to about 110°F. until the mixture becomes homogeneous. The mixture is then allowed to cool to room temperature and is subsequently charged into an aerosol container. The propellant mixture is then added to the container, a standard three-piece tin plated aerosol can, using an under-the-cap filler.

The result is a highly effective powder aerosol antiperspirant composition for use on the skin stabilized as to color and odor as compared with a similar composition which does not contain the citric acid.

EXAMPLE II

All of the following compositions were prepared by the process of Example I.

Composition I

Aluminum chloride	7.0%	
Isopropyl palmitate	10.0	
Cab-O-Sil	0.6	
Trifluoromethylcarbanilide	.2	
Perfume	.3	
Hexachlorophene	0.3%	
Citric acid, monohydrate	0.02	
SDA No. 40		1.2
Propellant consisting of: 20% trichlorofluoromethane; 8% dichlorodifluoromethane; 17% n-butane; and the balance dichlorotetrafluoroethane		balance

Composition II

A mixture of aluminum sulfate, zinc sulfate, and zirconyl chloride (1:1:1)	7.0%
A mixture of di-n-butyl phthalate, and diisopropyl adipate (1:1)	14.0
Octadecyl monoethanol amide	0.75
A mixture of trichlorocarbanilide, trifluoromethylcarbanilide, and tribromosalicylanilide (3:2:1)	0.2
Perfume	0.8
Hexachlorophene	0.3
Citric acid, anhydrous	0.02
SDA No. 40	1.5
A mixture of 26% trichlorofluoromethane, 7% dichlorodifluoromethane, 22% n-butane, and the balance dichlorotetrafluoroethane	balance

Composition III

A mixture of aluminum oxychloride, aluminum oxysulfate, and zirconium oxychloride (2:1:1)	7.0%	
A mixture of dimethylpolysiloxane, lauric acid, and oleic acid (1:1:1)	10.0	
A mixture of lauryl amine, hexadecyl amine, octadecyl amine, and eicosyl amine (1:1:1:1)	1.5	
Cab-O-Sil	0.6	
Trifluoromethylcarbanilide	.2	
Perfume	.3	
Hexachlorophene	0.3	
Citric acid monohydrate	0.03	
Propyl alcohol	1.2	
Propellant consisting of: 20% trichlorofluoromethane; 8% dichlorodifluoromethane; 17% n-butane; and the balance dichlorotetrafluoroethane		balance

Composition IV

A mixture of zirconyl hydroxychloride, aluminum chlorhydroxide and zinc sulfocarbolate (1:1:1)	10.0 %	
A mixture of mineral oil and tetradecane (1:1)	15.0	
A mixture of Cab-O-Sil and Bentone 38 (1:1)	0.75	
Hexachlorophene	0.3	
Citric acid monohydrate	0.08	
95% Ethanol	0.17	
SDA No. 40	2.0	
Perfume		0.9%
A mixture of: 10% dichlorodifluoromethane; 20% isobutane; 20% trichlorofluoromethane; and the balance dichlorotetrafluoroethane		balance

Composition V

Aluminum chlorhydroxide	8.0 %
Isopropyl myristate	10.0
Bentone	0.7
Hexachlorophene	0.1
Citric acid monohydrate	0.1
95% Ethyl alcohol	0.3
Perfume	0.37
Isopropyl alcohol	1.50
A mixture of: 17.15% trichlorofluoromethane; 8.58% dichlorodifluoromethane; 17.15% n-butane; and 42.88% dichlorotetrafluoroethane	balance

Composition VI

A complex prepared by heating and agitating 7.5:4.6 mixture of aluminum hydroxychloride, and zirconyl hydroxychloride, and agitating it according to the process of the co-pending application of Raymond E. Bolich, Jr., Ser. No. 59,690 filed concurrently herewith	8.0 %
Isopropyl myristate	10.0
Cab-O-Sil	0.7
Hexachlorophene	0.1
Citric acid	0.1
Methanol	0.4
Perfume	0.37
A mixture of: 17.15% trichlorofluoromethane; 8.58% dichlorodifluoromethane; 17.15% n-butane; and 42.88% dichlorotetrafluoroethane	balance

Composition VII

A 1:1 mixture of aluminum hydroxychloride and the complex of Example I of U.S. Pat. No. 3,407,254	6.0 %
The complex of Example I of the co-pending application of Wilmer L. Luedders, Ser. No. 59,693 filed concurrently herewith	
Isopropyl myristate	10.0
Bentone	0.7
Hexachlorophene	0.1
Citric acid monohydrate	0.01
SDA No. 40	0.3
95% Ethyl alcohol	04.%
Perfume	0.37
A mixture of: 17.15% trichlorofluoromethane; 8.58% dichlorodifluoromethane; 17.15% n-butane; and 42.88% dichlorotetrafluoroethane	balance

All of the above compositions are desirable, effective antiperspirant compositions stabilized against odor and color changes as compared with similar compositions without citric acid.

EXAMPLE III

All of the following compositions were prepared according to the process of Example I.

Percent by Weight

Component	I	II	III	IV
Aluminum hydroxychloride	3.50	3.50	3.50	3.50
Isopropyl myristate	8.00	8.00	8.00	
Alon[1]			0.6	
Bentone 38	0.60	0.60		0.60
EtOH/H_2O 95/5% wt.	0.27	0.27	0.4	0.27
Trichlorocarbanilide	0.10			
Geigy CH 3565[2]		0.10		
Hexachlorophene	0.2	0.2	0.10	0.10
Citric Acid	0.04	0.02	0.4	0.1
Dibutyl phthalate				8.00
SDA No. 40	1.50	1.00	2.00	0.25
Perfume	0.40	0.40	0.40	0.40
Propellant[3] q.s.	100%	100%	100%	100%

1. Fumed aluminum oxide Al_2O_3.
2. 2,4,4',-trichloro-2'-hydroxydiphenyl ether.
3. CCl_3F:CCL_2F_2 (60/40) by weight.

Each of the above compositions is a highly effective dry aerosol powder antiperspirant for use on the skin, which is stabilized with respect to color and odor in comparison with similar compositions without the citric acid.

What is claimed is:

1. A dry aerosol antiperspirant composition consisting essentially of:

A. from about 2.5 percent to about 6 percent by weight of finely divided aluminum hydroxychloride;

B. from about 0.3 percent to about 0.75 percent by weight of a reaction product of Bentonite and dimethyldistearylammonium chloride;

C. from about 0.1 percent to about 0.5 percent by weight of hexachlorophene;

D. from about 0.01 percent to about 0.04 percent by weight of citric acid;

E. from about 0.25 percent to about 2 percent by weight of a solvent for the citric acid selected from the group consisting of methanol, ethanol, propanol and isopropanol;

F. from about 6 percent to about 10 percent by weight of a carrier liquid of low volatility selected from the group consisting of isopropyl myristate, isopropyl palmitate, di-n-butyl phthalate, diethyl sebacate, disopropyl adipate, and ethyl ethylcarbomethyl phthalate; and

G. the balance, an anhydrous, liquefiable propellant selected from the group consisting of trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, isobutane, and mixtures thereof in an amount of from about 70.7 percent to about 93.9 percent.

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