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ANTIPERSPIRANT COMPOSITION CONTAINING ALUMINUM HYDROXYCHLORIDE

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5 Claims

ABSTRACT OF THE DISCLOSURE

A liquid antiperspirant composition suitable for canning in aerosol cans without undue corrosion of the can, and the method of making the composition. The effective astringent is aluminum hydroxy chloride which is dissolved in anhydrous ethanol by aging, e.g., in the aerosol can, over an extended period of time, e.g., two weeks in the substantial absence of water. The composition can contain hexachlorophene bacteriostat and lanolin emollient among other non-aqueous ingredients, and is canned with about an equal amount of propellant 11 and/or propellant 12 as an aerosol.

THE DISCLOSURE

The present application is a continuation-in-part of the application of Donald R. Virzi, Ser. No. 489,744, filed Sept. 23, 1965.

This invention relates to antiperspirant compositions suitable for use in aerosol spray cans. The invention further relates to the method of manufacture of such compositions.

With the development and refinement of aerosol cans and the increasing availability of such cans on the market, many items, especially in the cosmetic field, have been prepared for marketing in such cans. The aerosol spray can has received outstanding consumer acceptance. One such cosmetic item which has received acceptance is the deodorant.

Antiperspirant preparations are available in various forms as, for example, creams, lotions, sticks, pads and powders. However, to date an acceptable liquid antiperspirant product has not been provided which can be marketed in an aerosol can or other metal container.

An antiperspirant differs from a deodorant basically in that an antiperspirant contains an astringent. The astringent functions by inhibiting the flow of perspiration, apparently by reacting with proteins of the skin to cause swelling and blocking of the openings of sweat glands to reduce the flow of perspiration. Among the materials which have astringent properties are the salts of such metals as aluminum, zinc, zirconium, iron, chromium, lead and mercury. The salts of aluminum and zinc find most frequent use. The metal ion of the salt apparently functions to cause at least part of the reaction with the skin tissue and some coagulation of skin protein. However, astringency also appears to be dependent somewhat on the anion and many such anions are effective, e.g. sulfate, chloride, hydroxychloride, phenolsulfonate, formate, acetate, lactate, sulfamate and alums. In most common use are the sulfates, chlorides, hydroxychlorides and phenolsulfonates. Most of the salts which show good astringent properties have a low pH, e.g. in the range of 2.5 to 4.0. Many other metal salts have been used as astringents and are known in the art.

Each of the presently accepted astringents is a highly acidic material. When antiperspirants are packaged in cans, the acidity attacks the metal of the can. Although slight corrosion, e.g. slight de-tinning, may be tolerated

in a canned antiperspirant, such extensive corrosion as rust, enamel lifting, pitting and perforations cannot be tolerated. A shelf life of at least one year is highly desirable, and corrosion, rusting and pitting of metal by the antiperspirant cause failure of metal cans within a much shorter period of time, e.g., a few months or less.

In order to overcome the corrosion problem, antiperspirant compositions have been marketed in either glass or plastic bottles. However, the glass bottles are susceptible to breakage and the plastic bottles either permit desirable ingredients to escape through the bottle walls or the formulation deteriorates the plastic so that the formulation must be tailored to the bottle by selecting ingredients which will not deteriorate the plastic or pass through the wall, unduly limiting the product formulator. Another suggested solution has been to line cans with plastic lining materials or coat the can interiors with enamel. However, although such linings or coatings cover almost all of the interior contact surfaces of the cans, corrosion is still initiated at uncoated or thinly coated sites and the corrosive properties of the antiperspirant are sufficient to pit the coatings or linings and eventually cause can failure.

Attempts have also been made to neutralize the acidic effect of the astringent by incorporating such buffering agents as urea and similar amides for counteracting corrosive action. However, it has been found that such agents generally render the preparation materially less effective as an antiperspirant.

So far as is known, an effective amount of astringent has not yet been incorporated into a liquid cosmetic composition suitable for packaging in a metal container or can and having acceptable canned shelf life.

It is a general object of this invention to overcome or minimize the problem of corrosion of metals normally caused by an astringent in a cosmetic formulation.

Another object of this invention is to provide a new and useful antiperspirant composition suitable for packaging in aerosol spray cans.

A further object of this invention is to provide a new and useful method for manufacturing the compositions of the foregoing objects.

Still other objects will be apparent from the description of the invention herein.

While the present invention is susceptible of embodiment in many different forms, there will be described embodiments and examples of the invention with the understanding that the invention is not intended to be limited to such embodiments or examples. Suitable variations will be evident to those in the art. For example, it is common to use bacteriostats, emollients, fumigants, perfumes, and the like, and these may be selected by those skilled in the art. Additionally, the astringency action of many compounds has been well established and reference to the art may be had for astringents useful in the compositions of this invention.

The compositions of this invention include a solution of astringent in an anhydrous volatile solvent. The astringent, examples of which have been given above, is a metal salt of an acidic component and the salt is dissociable by hydrolysis with water to form the acid component. For example, aluminum hydroxy chloride is a compound which dissociates to form hydrochloric acid which can attack and corrode the walls and other metal portions of aerosol cans.

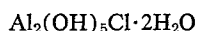
In the method for preparing the compositions, the astringent, e.g. aluminum hydroxy chloride, is dissolved in a suitable anhydrous volatile solvent, advantageously ethanol. The solvent is sufficiently anhydrous to prevent appreciable dissociation of the astringent salt, e.g. less than 1% water content and preferably no more than

500 to 600 p.p.m. water. The solvent is sufficiently volatile to vaporize under ambient conditions within a short period of time after the composition has been applied to the skin.

In formulating the preferred compositions, aluminum hydroxy chloride is mixed with ethanol and the mixture is aged until the aluminum hydroxy chloride is solubilized in the ethanol, e.g. by permitting the mixture to stand. Heretofore it has been understood in the antiperspirant art that astringents such as aluminum hydroxy chloride are completely insoluble in ethanol. However, I have discovered that aluminum hydroxy chloride can be solubilized in the ethanol. The preferred procedure for solubilizing the aluminum hydroxy chloride is to permit a mixture of the aluminum hydroxy chloride and ethanol to stand or age for an extended period of time until a true solution appears to form.

In one experiment, when 5% aluminum hydroxy chloride was added to ethanol, initially the aluminum hydroxy chloride was present as a precipitate. After a period of six to eight days a jelly-like mass appeared to form and after a period of about twelve to fourteen days a true solution appears to form. Thus, the proper aging time can be determined by visual observation of the formation of the solution. The temperature is not critical but the solvent is retained in the liquid state. The amount of salt useable, based on solvent, is limited only by its solubility in the solvent after aging. In one advantageous procedure, the amount of salt is slightly above its solubility level as evidenced by the presence of a small amount of undissolved salt in the solution. The total concentration of astringent salt in the solvent is such as to provide effective astringent action to the antiperspirant formulation.

Aluminum hydroxy chloride is sometimes referred to as aluminum chlorhydrat or aluminum chlorhydroxide and is reported as having the empirical formula:



The following examples are offered for purposes of illustrating the invention and are not intended as a limitation on the invention.

EXAMPLE I

In this example, an antiperspirant concentrate is prepared from the following ingredients in the following amounts:

Ingredient:	Amount, wt. percent
Aluminum hydroxy chloride	5
Lanolin	2
Propylene glycol	2
Hexachlorophene	0.4
Felton Aphrosia	0.1
Ethanol (200 proof)	90.5

In the preparation of an aerosol antiperspirant formulation containing the concentrate of Example I, the ingredients of the formulation were mixed. The mixture or concentrate was then introduced into an aerosol can together with an equal volume of a 50/50 volume mixture of propellant 11 and propellant 12 and the can was capped with a valving cap. The can was then permitted to stand until the aluminum hydroxy chloride was completely dissolved in the ethanol, about two weeks.

A portion of the formulation was placed in a glass aerosol bottle in lieu of the can so that the dissolution of the aluminum hydroxy chloride could be observed visually. The jelly formed at about seven days and the solution was apparently complete at about thirteen days. The composition could be readily sprayed from either the aerosol can or the aerosol bottle and used as an effective antiperspirant.

The lanolin in the above composition functions as an emollient and is especially preferred since it gives excellent soothing qualities to the composition. Propylene glycol is used as a humectant; hexachlorophene is used as a bacteriostat as is common in cosmetic preparations;

the Felton Aphrosia is a perfume to give the formulation a more pleasant odor. Emollients, humectants, bacteriostats and perfumes are commonly used in the deodorant compositions and their presence in the compositions is preferred although not necessary or critical. These can be selected by those in the art as desired.

The antiperspirant compositions, when packaged in an aerosol container, includes a propellant as is normal for aerosol products. Any of the usual propellants can be used in conventional amounts, although most often the propellant will probably be a halohydrocarbon or other non-flammable volatile material. Of the specific propellants used in the examples herein, propellant 11 is trichlorofluoromethane and propellant 12 is dichlorodifluoromethane.

The ethanol included in the above formulation is 200 proof, i.e. anhydrous ethanol. The particular ethanol of the above composition was obtained under the trade name USI-SDA 40, as marketed by U.S. Industrial Chemicals Company. Such commercial anhydrous ethanol is usually denatured by addition of small amounts of other ingredients, which ingredients do not materially affect the properties of the present compositions. The anhydrous ethanol will pick up water from the atmosphere and some water can be tolerated in the present compositions, i.e., less than about 1% based on ethanol. Usually, care should be taken to store the ethanol under anhydrous conditions if the ethanol is to be stored for a prolonged period of time.

EXAMPLE II

An antiperspirant concentrate was formed by mixing the aluminum hydroxy chloride of the following formulation with the remaining ingredients:

Ingredient:	Weight percent
Aluminum hydroxy chloride	5
SDA 40 (200 proof)	90.6
Lanolin	2
Propylene glycol	2
Hexachlorophene	.3
Perfume	.1

The resulting concentrate was mixed with an equal volume of the 50/50 mixture of propellant 11 and propellant 12. The mixture of concentrate and propellant was sealed in 24 cans of each of a number of container varieties including plain aerosol tinned cans, aerosol cans having an interior single epoxy coating, and aerosol cans having an interior double epoxy coating. The packaged cans were stored at about 100° F. After 14 days, a can of each of the can varieties containing the composition of Example II was opened, and it was noted that in the plain cans, there was slight to moderate de-tinning over-all on the interior but no pitting or rust or excessive corrosion and in the cans with interior coatings there was only slight de-tinning at lap edges. Other cans of each variety were checked at the end of 30 days with results similar to those of the 14-day check.

The aerosol formulation of Example II was also placed in clear glass aerosol bottles so that the formulation could be observed visually. Also placed in each bottle was a strip of tin plate so that the effect of metal corrosion could also be followed visually. After 33 days of storage at room temperature, no corrosion, pitting or rust was noted on the strips. In these tests it was further noted that when the bottles were initially packed the formulation was very cloudy. The aluminum hydroxy chloride settled to the bottom in a white powder within several hours leaving a clear liquid. After a few days, the white crystalline powder became a translucent gel and after 2 weeks the gel went into solution.

The concentrate of Example II was also tested by a tin plate corrosion test. According to the tin plate corrosion test procedure, a strip of tin plate is abraded to expose the base steel and the strip is then partially immersed in a test tube filled with the concentrate. The test tubes are

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sealed with a cork and stored at room temperature. Within a test period of 30 days, the concentrate of Example II did not pit or rust the strip.

The following preparations were also made and tested:

Preparation I

Ingredient:	Weight percent
Aluminum hydroxy chloride -----	5
Water -----	5
SDA 40 (200 proof) -----	85.6
Propylene glycol -----	2
Lanolin -----	2
Perfume -----	.2
Hexachlorophene -----	.2

Preparation II

Ingredient:	Weight percent
Aluminum hydroxy chloride -----	5
Water -----	10
Lanolin -----	2
Propylene glycol -----	2
Perfume -----	.2
SDA 40 -----	80.6
Hexachlorophene -----	.2

The concentrates of Preparations I and II were mixed with an equal volume of the 50/50 mixture of propellants 11 and 12 and were introduced into cans as in Example II and stored at 100° F. After 22 days' storage of Preparation I and 21 days' storage of Preparation II, samples of each can were opened and examined, and it was found that all cans showed extreme corrosion, rust, pitting, and enamel blistering of metal cans and detinning, rust, and corrosion of tin cans. After 50 days' storage of Preparation I and 49 days' storage of Preparation II, more samples of the cans were opened, and it was noted that the containers showed severe de-tinning and rust to the extent where the test had to be discontinued. The product in these cans was discolored red. The interior coatings of the enamel cans were pitted and perforated.

The concentrates of Preparations I and II were also tested by the tin strip corrosion test. At the end of three hours in the tin strips has started to rust. At the end of 24 hours the liquid concentrate had assumed a red color and at the end of 30 days the strips were badly rusted and pitted and the concentrates were of a red wine color, thick and syrupy, resulting from a high content of products of rust.

As a guide for a suitable formulation, the astringent is included in the solvent in a solubilizable amount as can be observed by testing various amounts and determining the limit of solubility. Usually an amount of astringent in the range of 0.01 to 20 weight percent, more often 1 to 10 weight percent and preferably 3 to 7 weight percent, based on ethanol, is used. Humectants and emollient oils are included in amounts sufficient to give the desirable humectant and emollient functions but not sufficient to provide a sticky composition after application to the skin. Usually less than 5% to 10% should be used. The bacteriostat is used in an amount sufficient to check bacteria growth, and the perfume is included in an amount sufficient to give the desired perfuming or masking effect. After mixing the ingredients of the formulation and charging them to the aerosol container, together with an amount of propellant sufficient to propel the formulation from the container, the

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containers are then stored under ambient conditions for two to three weeks prior to shipment. The composition is a physical mixture and its preparation apparently involves no chemical reactions.

It is apparent from the foregoing that I have provided a new and useful formulation and method of making the same which advantageously permits the use of corrosive astringents in antiperspirant compositions which can conveniently be packaged in aerosol cans while permitting extended shelf life.

All percent given herein are percents by weight unless otherwise indicated.

I claim:

1. The method of producing a liquid antiperspirant composition comprising: preparing in a container a mixture of from 0.01 to 20 weight percent aluminum hydroxychloride with a quantity of anhydrous ethanol, the quantity of anhydrous ethanol and of aluminum hydroxychloride being sufficient for dissolving an effective astringent amount of aluminum hydroxychloride into the anhydrous ethanol, and aging the mixture so that said amount of aluminum hydroxychloride forms a gel within the anhydrous ethanol, and then further aging the mixture containing the gel until the gel is dissolved in the anhydrous ethanol to form the liquid antiperspirant composition.

2. The method of claim 1 wherein the aluminum hydroxychloride in said mixture is between about 1 and about 10 weight percent based on ethanol.

3. The method of claim 1 wherein the aluminum hydroxychloride in said mixture is between about 3 and about 7 weight percent based on ethanol.

4. The method of producing a liquid antiperspirant composition comprising: placing in a container a mixture of from about 1 to about 10 weight percent aluminum hydroxychloride with a quantity of anhydrous ethanol, the quantity of anhydrous ethanol and of aluminum hydroxychloride being sufficient for dissolving an effective astringent amount of aluminum hydroxychloride into the anhydrous ethanol, adding an aerosol propellant to the mixture in the container to pressurize said mixture confining the pressurized mixture in the container with a valving cap, and aging the pressurized mixture so that said amount of aluminum hydroxychloride forms a gel within the anhydrous ethanol, and then further aging the pressurized mixture containing the gel until the gel is dissolved in the anhydrous ethanol to form the liquid antiperspirant composition.

5. The product produced by the method of claim 2.

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