United States Patent Office 3,833,721 Patented Sept. 3, 1974

3,833,721

ASTRINGENT COMPOSITIONS

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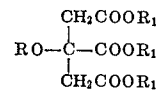
No Drawing. Filed July 14, 1972, Ser. No. 272,044
Int. Cl. A61k 7/00
U.S. Cl. 424—47 9 Claims

ABSTRACT OF THE DISCLOSURE

The present invention is concerned with aerosol spray anti-perspirant compositions of the type in which the astringent material is suspended as a solid in an anhydrous liquid vehicle and dispensed in this form and more particularly with anti-perspirant compositions of this type which have substantially reduced propensity to stain clothing. Generally such improvements are brought about by using as the liquid vehicle for such compositions esters which are miscible with the propellant and which are formed from tri-basic acids and lower aliphatic alcohols.

Aerosol anti-perspirant compositions in which the astringent material, e.g. aluminum chlorhydroxide, is dispensed as a solid suspended in an anhydrous hydrophobic liquid vehicle such as mineral oil, isopropyl myristate or isopropyl palmitate have been widely marketed. Although such compositions are effective in reducing perspiration they have a tendency to impart stains to clothing which (stains) remain subsequent to laundering. The present invention is concerned with providing anti-perspirant compositions of this type which have substantially reduced tendency to stain clothing.

It has been found in the present invention that the staining due to such compositions can be substantially reduced by using as the liquid vehicle for said compositions an ester which is miscible with the propellant and which is selected from the group represented by the formula:



wherein R is a hydrogen atom or a 2 to 3 carbon acyl group, i.e. an acetyl or a propionyl group and each R_1 is the same or different than the other R_1's and is an alkyl radical comprising less than 4 carbon atoms. In especially preferred embodiments of the present invention, each R_1 is an ethyl radical. As examples of compounds within the above formula, mention may be made of triethylcitrate and acetyl triethylcitrate. Especially good results have been obtained with triethylcitrate which has been found to be particularly non-toxic, non-irritating and non-corrosive, has good stability in the compositions and in certain instances actually enhances the fragrance of the perfumes used therein.

It should be understood that when desired, if R is a hydrogen, the hydroxy group may be alkoxylated by a 1 to 3 carbon alkyl group or the alkyl radicals (R_1) may be further substituted by hydroxy or 1 to 2 carbon alkoxy groups provided that the esters remain miscible with the propellant and the number of carbon atoms is commensurate with that set forth above.

Generally the astringent may be selected from any of the materials of this nature which are available, e.g. aluminum sulfate, aluminum chloride, aluminum chlorhydroxides such as $Al(OH)_5Cl$ and $Al_2(OH)_4Cl_2$, aluminum sulfocarbolate, zinc chloride, zinc sulfocarbolate, zinc sulfate, zirconium oxychloride, sodium zirconium lactate, sodium zirconium glycolate, zirconyl hydroxy chloride, zirconium sulfate, physical mixtures of the above, and mixed compounds and complexes comprising 2 or more of the above cations such as a mixed aluminum zirconium chlorhydroxide complex. The preferred astringents for use in the composition of this invention are the aluminum chlorhydroxides. The amount of astringent employed may be varied but in most compositions it will be present in amounts ranging between about 0.5% to about 10% by weight of the total composition including the propellant. In preferred compositions, it will be present in amounts ranging between about 1 to about 7.5%. Further the astringent should be finely ground in order to prevent the valve from clogging. Usually if the particle size is less than 100 microns and preferably less than 60 microns, clogging will be held to a minimum.

The ester is present in amounts such that in combination with the propellant it will be the continuous phase of the dispersion or suspension. As can be appreciated, this amount will vary depending upon the amount of astringent employed. In most instances, the ester will comprise from about 0.5 to about 50% by weight of the total composition including the propellant. In preferred compositions, the ester is present in amounts ranging between about 0.5 to about 15%.

Generally any of the materials which have been employed as propellants in aerosol compositions may be used in the compositions of the present invention; provided of course that they are miscible with the liquid vehicle. As examples of such materials mention may be made of: dichlorodifluoromethane, trichloromonofluoromethane, trichlorotrifluoroethane, tetrafluorodichloroethane, butane, propane, isobutane and mixtures and blends of the above. The propellant will generally be present in amounts which will be sufficient to dispense all of the composition at a moderate velocity. In most instances the compositions will have vapor pressures ranging between 15 and 85 p.s.i.g. and preferably between 20 and 40. Generally the propellant will be present in amounts varying between 50 to 98% by weight of the total composition and preferably between 70 to 98%.

The preferred compositions of the present invention will further include a suspending, dispersing or flocculating agent to prevent the astringent from agglomerating or settling. As examples of such agents, mention may be made of clays, such as bentonite, modified clays, e.g. the reaction product of bentonite and a surface active quaternary salt, silicas such as colloidal silicon dioxide, silicates, polymeric suspending agents such as cellulose and derivates thereof and surfactants such as high molecular weight amides, e.g. lauryl monoethanolamide. If desired, the compositions may further include other ingredients such as perfumes, emollients, talc, starches, anti-bacterials, etc.

The effectiveness of the compositions of the present invention in reducing stain was demonstrated by using the esters disclosed herein on a weight basis in place of isopropyl palmitate in a standard formula and measuring the extent of staining it caused as compared with the composition containing isopropyl palmitate. The standard formula was as follows:

	Percent by weight
Vehicle	6.12
Hexachlorophene	0.04
Aluminum Chlorohydroxide	3.40
Pyrogenic Colloidal Silica	0.35
Perfume	0.35
Propellant mixture: 70% by weight trichlorofluoromethane, 30% by weight dichlorodifluoromethane	89.74

The amount of staining was measured by the following procedure:

(1) Five 6 x 6 inch swatches of virgin, unlaundered cotton T-shirt material were made up for each formulation.

(2) Reflectance readings were taken on virgin, unused, unlaundered material using a Photovolt Model 670 Reflectometer equipped with a 610–T search unit and a green filter. The average of 12 readings was designated as R_0.

(3) The swatches were laundered in an apartment size washer for 15 minutes in 10 liters of hot (about 55° C.) tap water containing 30 g. of an alkyl aryl sulfonate detergent and 100 ml. of a commercial hypochlorite bleach. The swatches were rinsed for two 10 minute cycles in hot tap water and then for a 10 minute cycle in cool distilled water. The swatches were dried for 24 hours at 60° C. in a 220 volt Freas Model 625 forced draft oven.

(4) Five swatches of the fabric were mounted on poster boards and the center portions of each were subjected to three 2-second sprays of the formulation which was being tested. An average of about six grams of the formulation was dispensed over the 6-second period. The swatches were allowed to stand for 30 minutes and then smeared with a spatula to even out irregularities in the application area.

(5) The swatches were laundered and dried in the same manner as set forth in step 3 above.

(6) The Photovolt Reflectometer was warmed up for 30 minutes and three readings were made of the stained area. The cloth was rotated 90° and three additional readings were made. The average of the six readings in the stained area was referred to as R_S.

(7) Three reflectance readings were taken in the edge or non-stained areas and the cloth was rotated 90° and three additional readings were taken. The average of six readings in the non-stain area were referred to as R_E.

(8) The "Stain Index" was calculated for each formulation after each cycle by using the following equation:

$$\text{Stain Index} = 100\,\frac{R_E - R_S}{R_O - R_S}$$

where

R_E=average of six reflectance readings in edge or non-stain region.

R_S=average of six reflectance readings in stain areas.

R_0=reflectance of unused, unwashed, virgin material.

The propensity of the formulation to stain clothing was indicated by an increase in the stain index as the above cycle comprising steps 4 through 7 was continually repeated.

Table No. I, below, summarizes the results of tests 1 through 5 wherein triethyl citrate was tested against isopropylpalmitate. The indices are for the fourth, fifth, and sixth staining cycles.

TABLE I.—STAIN INDICES

Triethyl citrate (TEC) vs. isopropyl palmitate (IPP)

Test number		Staining cycle 4	5	6	Average
1	TEC	0	0	0	
	IPP	58.5	57.5	66.0	60.70
2	TEC	0.5	0	0	0.2
	IPP	62.0	67.5	61.0	63.5
3	TEC	18.5	31.5	17.5	22.5
	IPP	70.5	76.5	69.0	71.8
4	TEC	19.5	21.0	----------	20.3
	IPP	47.0	45.0	----------	46.0
5	TEC	21.5	19.5	----------	20.5
	IPP	50.0	53.5	----------	51.8

NOTE.—Grand average stain indices, 5 tests, 13 cycles—TEC, 11.5; IPP, 60.3.

As can be noted, the triethyl citrate has substantially lower stain indices than the isopropyl palmitate.

Table II summarizes the results of a test in which acetyl triethylcitrate was run against isopropyl palmitate.

TABLE II.—STAIN INDICES

Acetyl triethylcitrate vs. isopropyl palmitate (IPP)

Vehicle	Stain cycle 4	5	6	Average
Acetyl triethylcitrate	3.3	4.6	1.3	3.1
IPP	51.0	45.9	55.8	50.9

The effectiveness of the esters of the present invention in reducing stain *in vivo* was demonstrated in a test wherein:

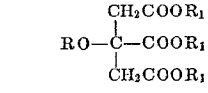
(1) About 100 males were given coded cans of antiperspirants containing parallel triethyl citrate and isopropyl palmitate formulations and new cotton T-shirts. They were instructed to use one product under the right axilla only and the other under the left axilla only. The T-shirt was to be worn for at least four cycles of home laundry. After four weeks, the T-shirts were collected (86 men responded) and evaluated. The T-shirt, underarm areas in contact with the axilla under which triethyl citrate was used consistently showed substantially less stain than that under which isopropyl palmitate had been used. This observation was significant at greater than a 99.5% confidence level.

A similar test was performed on 22 men to whom the formulations were applied by an observer, who then laundered the T-shirts en masse. After four and six cycles of application, use, and laundry, the triethyl citrate side of the T-shirt again showed substantially less staining than the isopropyl palmitate side at a confidence level greater than 99.5%.

In a further test, the triethyl citrate formulation was tested along with an isopropyl palmitate control composition on twenty different synthetic and natural fibers for 1 cycle of the above mentioned stain test. On only one type material (diacetate) was the citrate formulation found to cause more stain than the control.

Having thus described the invention what is claimed is:

1. An aerosol astringent composition having improved antistain properties, said composition comprising 0.5% to 10% by weight of an astringent material selected from the group consisting of aluminum sulfate, aluminum chloride, aluminum chlorohydroxide, aluminum sulfocarbolate, zinc chloride, zinc sulfocarbolate, zinc sulfate, zirconium oxychloride, sodium zirconium lactate, sodium zirconium glycolate, zirconyl hydroxy chloride, zirconium sulfate and aluminum zirconium chlorohydroxide complex, 50 to 98% by weight of a propellant selected from the group consisting of dichlorodifluoromethane, trichloromonofluoromethane, trichlorotrifluorethane, tetrafluorodichloroethane, butane, propane, isobutane and mixtures and blends thereof and 0.5 to 50% by weight of a vehicle, said astringent material being insoluble in both said propellant and said vehicle and said vehicle being miscible with the propellant and being represented by the formula:



wherein R is a hydrogen atom or a 2 to 3 carbon acyl group and each R_1 may be the same or different than the other R_1's and is an alkyl radical comprising less than 4 carbon atoms, said percentages are based on weight of the total composition.

2. A composition as defined in claim 1 wherein each R_1 is an ethyl group.

3. A composition as defined in claim 1 wherein R is a hydrogen atom.

4. A composition as defined in claim 1 wherein R is an acetyl group.

5. A composition as defined in claim 1 wherein said astringent material is aluminum chlorhydroxide.

6. A composition as defined in claim 1 wherein said vehicle is triethyl citrate.

7. A composition as defined in claim 6 wherein said astringent material is aluminum chlorhydroxide.

8. A composition as defined in claim 1 wherein said vehicle is acetyl triethylcitrate.

9. A composition as defined in claim 8 wherein said astringent material is aluminum chlorhydroxide.

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