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PROCESS FOR STABILIZATION OF COMPOSITION COMPRISING CHLOROFLUOROALKANE AND AQUEOUS SOLUTION OF LOWER ALCOHOL

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ABSTRACT OF THE DISCLOSURE

Process for stabilizing an aerosol composition comprising a chlorofluoroalkane and an aqueous solution of a lower alcohol, which comprises adding to said composition (a) at least 0.1% by weight, based on said chlorofluoroalkane, of nitromethane and (b) at least 0.05% by weight, based on said chlorofluoroalkane, of a compound selected from the group consisting of alkali metal phosphates of polyoxyethylene alkyl ethers, phosphoric acid amine salts of polyoxyethylene alkyl ethers, alkali metal phosphates of polyoxyethylene alkylphenol ethers, phosphoric acid amine salts of polyoxyethylene alkylphenol ethers, and alkali metal alkylsulfates.

This invention relates to a process for stabilizing over a long period of time a composition consisting of a chlorofluoroalkane and an aqueous solution of a lower alcohol or a composition consisting of a chlorofluoralkane, an aqueus solution of a lower alcohol and a minor amount of a third component.

As is well known, a composition consisting of a chlorofluoroalkane (especially, chlorofluoromethane or chlorofluoroethane) and an aqueous solution of a lower alcohol (especially, methanol or ethanol) is unstable when in contact with a metal. This unstability is of a considerable degree if the composition contains a third component such as metal halides, acids, aldehydes and organic peroxides. For instance, a typical aerosol composition containing a chlorofluoroalkane, a lower alcohol aqueous solution, perfume composition is difficult to store for a long time because the chlorofluoroalkane decomposes to form an acid in a metal aerosol container and causes corrosion of the container.

Propylene, nitromethane, propyl mercaptan, primary or secondary alkylamines, morpholines or furans have heretofore been known as stabilizers for compositions of this kind. These known stabilizers, however, have not proved to be entirely satisfactory for a number of reasons such as the inability of preventing rust on the inner surface of the metal container which comes into contact with a liquid, or have little or no effect under certain conditions.

An object of the present invention, therefore, is to provide a process for stabilizing a composition comprising a chlorofluoroalkane and an aqueous solution of a lower alcohol, when this composition is enclosed in a metal aerosol container, which prevents the occurrence of rust at the inner surface of the container which is in contact with a liquid and a gas of the composition.

The prior art available indicated that a good stabilizer for an aerosol composition comprising a chlorofluoroalkane and an aqueous solution of a lower alcohol should meet the following requirements.

(1) It should have a function of preventing decomposition of the chlorofluoroalkane by metals or metal oxides.

(2) It should have a function of preventing decomposition of the chlorofluoroalkane by such a material as alcohols, water, acids, aldehydes and organic peroxides.

(3) It should form an adsorption film on the inner surface of the aerosol metal container to prevent contact between the metal and the chlorofluoroalkane.

(4) The aerosol should be colorless, odor-free, and non-toxic because it is in many instances intended for human use.

Extensive research work based on this information has finally led to the discovery that the above-mentioned object of the invention can be achieved by adding to said composition a combination of (a) at least 0.1% by weight, based on chlorofluoroalkane, of nitromethane and (b) at least 0.05% by weight, based on chlorofluoroalkane, of a compound selected from the group consisting of alkali metal phosphates of polyoxyethylene alkyl ethers, phosphoric acid amine salts of polyoxyethylene alkyl ethers, alkali metal phosphates of polyoxyethylene alkylphenol ethers, phosphoric acid amine salts of polyoxyethylene alkyl phenol ethers, and alkali metal alkylsulfates.

The stabilizing effect is minimal if an amount of nitromethane less than 0.1% by weight based on the chlorofluoroalkane is used. There is no critical upper limit for the nitromethane content, but no appreciable improvement in stabilizing effect occurs when the nitromethane is added in an amount of 1% by weight. Preferred compounds (b) to be used with nitromethane are those in which the degree of polymerization of the polyoxyethylene group is 2 to 20, or those in which the alkyl group or alkylphenol group has 8 to 30 carbon atoms. These compounds (b), when added in amounts less than 0.01% by weight based on the chlorofluoroalkane, exhibit hardly any stabilizing effect, and should be added in amounts of at least 0.05% by weight for practical purposes.

The nitromethane (a) by itself shows some anti-corroding effect on both the gas contacting part and the liquid contacting part of the inner surface of an aerosol metal container, but does not completely, prevent the occurrence of rust completely. The compound (b) shows a rust-proof effect by formation of a protective film on the inner wall of the metal container. This effect is however limited to the liquid contacting part, and does not extend to the gas contacting part. The simultaneous use of the nitromethane (a) and the compound (b) in accordance with the present invention completely inhibits the formation of rust on the gas contacting part which has been inhibited to some degree by the nitromethane. In other words, the compound (b) not only inhibits the occurrence of rust on the liquid contacting part, but also facilitates the rust-preventing function of the nitromethane (a) at the gas contacting part.

Of the compounds (b), phosphates, particularly phosphoric acid amine salts, have different stabilizing effects depending upon the degree of polymerization of their polyoxyethylene groups. When the degree of polymerization is lower, a white corrosion tends to be formed on a welding part of a side seam in the aerosol metal container. This is considered to be due to the reaction of the amine salt with a welding metal consisting predominantly of lead. With amine salts in which the polyoxyethylene group has a higher degree of polymerization, such corrosive reaction will occur less. Such a phenomenon arising from the degree of polymerization of the polyoxyethylene group is not seen with respect to alkali metal phosphates. It is supposed to be probably because the alkali metal salts form a protective film on the side seam or corrosive compounds formed by the composition are rendered non-toxic by the alkali metal salts. It is perhaps for the same reason that phosphoric acid amine salts with polyoxyethylene groups having a higher degree of polymerization are less corrosive as mentioned above.

The invention will be specifically described with reference to the following reference example and working examples.

REFERENCE EXAMPLE

This is a preliminary test for determining proper test conditions to be employed in the following working examples.

A number of hair spray aerosol compositions containing a chlorofluoroalkane as a propellant were prepared using six kinds of chlorofluoroalkane, a 95% ethanol aqueous solution, 120 kinds of perfume and polyvinyl pyrrolidone (resin). Each of the resulting compositions was enclosed into a metal container, and allowed to stand for 2 months at 50° C., 2 months at 40° C., 4 months at 40° C. and 12 months at room temperature, respectively. Thereafter, the container was opened, and the occurrence of rust on its inner wall was observed. It was found that samples which had been left to stand for 2 months at 50° C. were subjected to the severest corrosion (about 1.5 times as corrosive as samples which had been allowed to stand for 12 months at room temperature). Some of the results obtained with the samples which had been allowed to stand for 2 months at 50° C. are given in Table 1 below. In Table 1, the state of occurrence of rust was indicated by the symbols defined below. This method is believed to be the most practical one in a test of this kind.

—: no appreciable change
±: appreciable sign of rust

+: rust is generated at a small part (e.g., in the side seam)
++: rust is generated at a part ½ to ⅕ of the entire inner surface of the container; the liquid contained is unusable
+++: rust is generated in almost the entire inner surface of the container, the liquid contained is unusable
*: not tested

TABLE 1

	Perfume	Propellant A	B	C	D	E	F	X
Alcohols	Geraniol	±	±	+	±	±	*	*
	Linalool	*	−	−	−	−	*	−
	α-Tepineol	−	−	±	−	−	−	−
Aldehydes and acetals thereof.	Hydroxy citronellal	±	−	±	−	−	−	±
	Cyclamen aldehyde	++	±	++	±	±	*	−
	Heliotropin	−	*	−	−	−	*	−
Ketones	Methyl acetophenone	+	+	+	+	−	±	−
	Methyl ionone	−	−	−	−	−	−	−
	Maltol	*	±	+++	−	+	±	*
Esters	Benzyl acetate	+	−	±	+	−	*	−
	Isobornyl acetate	−	±	+	+	−	*	−
	Methylheptine carbonate	−	++	+++	+	+	±	*
Phenols	Eugenol	−	−	±	−	−	*	−
	Diphenyl oxide	−	−	±	−	−	*	−
Others	Musk amberette	−	−	−	−	−	+	−
	Rose oxide	−	−	+	−	*	*	−
	Tonalid	−	−	+++	−	*	*	−
Natural perfumes	Bergamot	−	−	−	−	−	*	−
	Lavender	−	−	−	−	−	−	−

NOTE.—A=dichlorodifluoromethane (R-12); B=dichlorotetrafluoroethane (R-14); C=a 50:50 (by weight) mixture of dichlorodifluoromethane (R-12) and trichlorofluoromethane (R-11); D=a 50:50 (by weight) mixture of dichlorodifluoromethane (R-12) and dichlorotetrafluoroethane (R-114); E=a 50:50 (by weight) mixture of dichlorodifluoromethane (R-12) and liquid petroleum gas (LPG); F=liquid petroleum gas (LPG); X=propellant not used.

We could estimate from the foregoing results that the greatest tendency toward rust formation occurs when methylheptine carbonate, cyclamen aldehyde, rose oxide, tonalid or maltol is used as perfume, and trichlorofluoromethane is used as propellant. These perfumes and propellant were therefore used in the following examples.

EXAMPLE 1

A mixture of 75 g. of trichlorofluoromethane and 75 g. of 95% ethanol containing 1%, based on the ethanol, of a perfume was put into a 180 cc. tin-plated aerosol can. The nitromethane (a) and the compound (b) either alone or in combination were added as stabilizers. Each of the obtained aerosol cans was allowed to stand for a month at 50° C. At the end of this period, the can was opened and its inside was examined with the naked eye. The results are shown in Table 2 below. In the table, the "liquid" and "gas" respectively mean a liquid contacting part and a gas contacting part.

TABLE 2

Stabilizer (percent by weight)			Perfume: Methylheptine carbonate		Cyclamen aldehyde		Rose oxide		Tonalid		Maltol	
Compound (b)		Nitromethane (a)	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas
None		None	+++	++	++	++	++	++	+++	++	+++	++
Do		0.3	+	+	++	+	++	+	+	+	+	±
Sodium phosphate of (polyoxyethylene)$_6$ nonylphenol ether.	0.37	None	+	++	++	++	++	++	++	++	+++	++
Do	0.05	0.1	+	+	++	+	±	±	+	±	+++	++
Do	0.05	0.3	±	−	±	±	−	−	−	−	±	±
Do	0.1	0.1	+	−	+	±	−	−	+	±	++	++
Do	0.1	0.3	−	−	−	−	−	−	−	−	−	−
Do	0.3	0.3	−	−	−	−	−	−	−	−	−	−
Sodium phosphate of (polyoxyethylene)$_7$ oleyl-ether.	0.3	None	++	+	++	++	++	++	++	++	++	++
Do	0.05	0.1	+~++	−	−	+	+	+	±	±	+	+
Do	0.05	0.3	−	−	−	−	−	−	−	−	±	±
Do	0.1	0.1	+	−	−	−	−	−	−	−	+	±
Do	0.1	0.3	−	−	−	−	−	−	−	−	−	−
Do	0.3	0.3	−	−	−	−	−	−	−	−	−	−
Phosphoric acid ethanolamine salt of (polyoxyethylene)$_{12}$ nonylphenol ether.	0.3	0.3	−	−	−	−	±	−	−	−	−	−
Phosphoric acid triethanolamine salt of (polyoxyethylene)$_4$ lauryl ether.	0.3	0.3	−	−	−	−	−	−	−	−	−	−
Sodium laurylsulfate	0.3	0.3	−	−	±	−	−	±	−	−	±	−

It is seen from Table 2 that with nitromethane which is now generally used as a stabilizer, even the addition of a 0.3 wt. percent amount does not exhibit a stabilizing effect, while the conjoint use of it with the compound (b) can give rise to almost a complete prevention of rust both at the gas and liquid contacting parts. It has also been found that these salts belonging to compound (b), when used singly, could prevent the occurrence of rust at the liquid contacting part, but not at the gas contacting part.

In this example, the trichlorofluoromethane 95% ethanol mixtures were used. The same tendency was observed in compositions consisting of dichlorodifluoromethane, monochlorodifluoromethane, trichlorotrifluoroethane or dichlorotetrafluoroethane instead of the trichlorofluoromethane and 95% methanol or propanol instead of the 95% ethanol. Also, almost the same tendency is observed when other perfumes than those used in this example are used as a third component.

The following examples illustrate the effects of the compositions according to the invention under severer conditions.

EXAMPLE 2

Hydrochloric acid was added to the same aerosol composition as used in Example 1 to adjust its pH to 3. The composition was put into a can, and allowed to stand for a month at 50° C. At the end of the stated period, the can was opened, and its inside was observed with the naked eye. The results are given in Table 3 below.

TABLE 3

Stabilizers (percent by weight)		Perfume				
Compound (b)	Nitromethane (a)	Methylheptine carbonate	Cyclamen aldehyde	Rose oxide	Tonalid	Maltol
None	None	+++	+++	+++	+++	+++
Do	0.3	++	++	+++	+	++
Sodium phosphate of (polyoxyethylene)$_6$ nonylphenyl ether (0.3).	0.3	−	−	−	−	−
Sodium phosphate of (polyoxyethylene)$_7$ oleyl ether (0.3).	0.3	−	−	−	−	−
Phosphoric acid triethanol amine salt of (polyoxyethylene)$_{12}$ nonylphenol ether (0.3).	0.3	−	−	−	−	−
Phosphoric acid triethanolamine salt of (polyoxyethylene)$_4$ lauryl ether (0.3).	0.3	±	±	±	−	±
Sodium laurylsulfate (0.3)	0.3	−	±	−	−	±

EXAMPLE 3

Sodium hydroxide was added to the same aerosol composition as used in Example 1 to adjust its pH to 10. The composition was put into a can, and allowed to stand for a month at 50° C. At the end of the stated period, the can was opened, and its inside was observed with the naked eye. The results are given in Table 4 below.

TABLE 4

Stabilizers (percent by weight)		Perfume				
Compound (b)	Nitromethane (a)	Methylheptine carbonate	Cyclamen aldehyde	Rose oxide	Tonalid	Maltol
None	None	+++	+++	+++	+++	+++
Do	0.3	+	++	++	+	++
Sodium phosphate of (polyoxyethylene)$_6$ nonylphenyl ether (0.3).	0.3	−	−	−	−	−
Sodium phosphate of (polyoxyethylene)$_7$ oleyl ether (0.3).	0.3	−	−	−	−	−
Phosphoric acid triethanol amine salt of (polyoxyethylene)$_{12}$ nonylphenol ether (0.3).	0.3	−	−	−	−	−
Phosphoric acid triethanolamine salt of (polyoxyethylene)$_4$ lauryl ether (0.3).	0.3	−	±	±	−	±
Sodium laurylsulfate (0.3)	0.3	−	−	−	−	±

It is clear from the results given in Tables 3 and 4 that the stabilizers of the present invention can prevent the occurrence of rust under severe conditions, especially in the presence of an acid. At the end of the stated periods, the pH of each of the compositions was measured. It was found that the composition whose pH had been adjusted to 3 with hydrochloric acid had a pH of 5, and the composition whose pH had been adjusted to 10 with sodium hydroxide had a pH of 8. This means that when the stabilizers according to the invention are used, the liquid inside the can approaches neutrality even after a long time storage.

We claim:

1. A process for stabilizing an aerosol composition for use in an aerosol container subjected to superatmospheric pressures and containing iron or other elements which are easily corroded, said composition consisting essentially of a chlorofluoromethane, a chlorofluoroethane, or mixtures thereof, and an aqueous solution of a lower aliphatic alcohol, comprising adding to said aerosol composition at least 0.1% by weight, based on said chlorofluoro derivatives, of nitromethane, and at least 0.05% by weight, based on said chlorofluoro derivatives of a compound (b) selected from the group consisting of alkali metal phosphates of polyoxyethylene alkyl ethers in which the polyoxyethylene group has a degree of polymerization of 2 to 20 and the alkyl group has 8 to 30 carbon atoms; phosphoric acid amine salts of polyoxyethylene alkyl ethers in which the polyoxyethylene group has a degree of polymerization of 2 to 20 and the alkyl group has 8 to 30 carbon atoms; alkali metal phosphates of polyoxyethylene alkylphenol ethers in which the polyoxyethylene group has a degree of polymerization of 2 to 20 and the alkyl group has 8 to 30 carbon atoms; phosphoric acid amine salts of polyoxyethylene alkylphenol ethers in which the polyoxyethylene group has a degree of polymerization of 2 to 20 and the alkyl group has 8 to 30 carbon atoms; and alkali metal alkylsulfates in which the alkyl group has 8 to 30 carbon atoms.

2. The process according to claim **1** wherein the compound (b) is an alkali metal phosphate of a polyoxyethylene alkylether in which the polyoxyethylene group has a degree of polymerization of 2 to 20, and the alkyl group has 8 to 30 carbon atoms.

3. The process according to claim **1** wherein the compound (b) is a phosphoric acid amine salt of a polyoxyethylene alkyl ether in which the polyoxyethylene group has a degree of polymerization of 2 to 20 and the alkyl group has 8 to 30 carbon atoms.

4. The process according to claim **1** wherein the compound (b) is an alkali metal phosphate of a polyoxyethylene alkylphenol ether in which the polyoxyethylene

group has a degree of polymerization of 2 to 20, and the alkyl group has 8 to 30 carbon atoms.

5. The process according to claim 1 wherein the compound (b) is a phosphoric acid amine salt of a polyoxyethylene alkylphenol ether in which the polyoxyethylene group has a degree of polymerization of 2 to 20 and the alkyl group has 8 to 30 carbon atoms.

6. The process according to claim 1 wherein the compound (b) is an alkali metal alkylsulfate in which the alkyl group has 8 to 30 carbon atoms.

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JOHN D. WELSH, Primary Examiner

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