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THREE-PHASE AEROSOL SPRAYING SYSTEMS

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ABSTRACT OF THE DISCLOSURE

In three-phase aerosol spraying systems comprising, in an aerosol pressure vessel, an aqueous phase to be sprayed which contains as active substance a textile finishing agent, a liquefied organic propellant phase, and the gas phase of the propellant, the improvement of avoiding excessive foam formation and obtaining optimal spray distribution in the sprayed-on zone on the substrate, by providing in the system a lipophilic interface active agent of an HLB value of maximally 6 which is a water-insoluble mono- or di-lower alkyl ether of monoethylene glycol or diethylene glycol and has at least 6 and not more than 12 carbon atoms per molecule; thereby, formation of a foam-causing type emulsion of the liquefied propellant and aqueous phase is avoided, which type of emulsion is usually undesirable in spraying textile finishing agents, and foam formation is suppressed.

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of my pending patent application Ser. No. 391,800, filed Aug. 24, 1964 and now abandoned, which is in turn a continuation-in-part of my abandoned patent application, Ser. No. 267,771, filed Mar. 25, 1963.

DESCRIPTION OF THE INVENTION

This invention relates to improvements in three-phase aerosol spraying systems comprising a pressure vessel and a sprayable mixture contained therein, the system working under pressure.

In technical language, the definition "three-phase aerosol" denotes a mixture which permits the spraying of a liquid phase disposed in a pressure vessel by means of a propellant gas, the difference between these aerosols and other conventional types of aerosols consisting in that the liquefied propellant cannot be mixed with the liquid phase to be sprayed. The three phases of such three-phase aerosols are the following:

(1) The aqueous phase to be sprayed, wherein active substances are dispersed, e.g. dissolved, suspended or emulsified,

(2) The liquefied propellant, and

(3) The gas phase of the propellant.

The liquefied propellant is disposed either above or below the aqueous phase to be sprayed according to its specific weight, the phases not being emulsified, but separated from each other and forming an interface between them, and the gas phase of the propellant is disposed in each case above the two liquid phases. For some purposes, formation of a water-in-oil emulsion has been recommended. For the purposes of the instant invention, this should be avoided.

It is known that normally a very fine spray of water can only be attained when high pressures are applied (of above 10 atm. gauge) with the aid of special spray nozzles, whereas for commercial spray nozzles generally pressures

of up to 5 atm. gauge are used. Consequently the fine spraying of the purely aqueous phase of a three phase aerosol is far from perfect even when so-called rotatory nozzles are used.

For improving the sprayability of the water or the aqueous phase of three-phase aerosols, it has hitherto been necessary to add water-soluble organic liquids, especially mono-hydric lower alkanols, in high quantities. Thus, in three-phase aerosols mixtures of ethanol or isopropanol and water are normally sprayed, the alcohol content of which aqueous mixtures may amount to as high as 70%. The use of ethanol or the like lower alkanols in the aqueous phase, while mainly intended to improve sprayability, also serves to facilitate dissolution of organic active substances in the aqueous phase; however, this use has the disadvantage that such systems are more expensive and are more dangerous on account of the combustibility of the organic components. A further decisive disadvantage of the use of water-miscible organic liquids, such as the aforesaid alcohols, in the aqueous phase to be sprayed, of a three phase aerosol, consists in that these adjuvants have a flocculating action on aqueous colloidal disperse systems. For example, an aqueous starch solution, which is a principal textile finishing agent is coagulated due to the addition of ethanol, and the known device of the addition of water-soluble organic solvents for the improvement of the sprayability of such a system completely fails in this instance. If an improvement of the sprayability of the aqueous phase is attempted by adding normal wetting agents for the purpose of reducing the surface tension, then a fairly substantial intimate intermingling of the liquid aqueous and organic phases occurs in the three-phase aerosols on account of the reduced surface tension, and this leads to an undesired foam formation when the aerosol valve is actuated. Three-phase aerosols, to which conventional wetting agents have been added, cannot be used for most practical purposes on account of this foam formation.

The improved novel system according to the invention contains, in a conventional pressure vessel having a spray valve, a sprayable mixture which consists essentially of an aqueous phase to be sprayed, a liquefied organic propellant phase and the gas phase of the propellant, and the inventive improvement consists more particularly in that said sprayable mixture, contained in the vessel in which said aqueous phase and said liquid propellant are separated from each other forming a common interface between them, i.e. they are not emulsified with each other, is substantially free from monohydric alkanols, and contains above 50% by weight of water, and, as a spray improving agent, a lipophilic interface active agent having an HLB-value according to Griffin of maximally 6 and defined more in detail below, whereby the major portion of said lipophilic interface-active agent is present in said liquefied propellant phase and a minor portion in said aqueous phase, foam causing emulsions are avoided and foam formation is suppressed. This agent is preferably a single lipophilic organic compound but may also be a mixture of different substances.

According to Griffin [see W. C. Griffin, Journal of Soc. Cosm. Chemists, vol. 1, 311, (1949) and vol. 5, 249, (1954)] and an article in "Parfümerie und Kosmetik," vol. 41, 85 (1960), each interface active dipolar substance is correlated with a numerical value in an arbitrarily selected scale which runs from 1–40; these numerical values, the so-called HLB values, represent a measure for the degree of the lipophilic or hydrophilic nature of the respective substances; lipophilic substances have a low HLB number, whereas substances having an increasingly hydrophilic character always have higher HLB values. The boundary value between "lipophilic" and "hydrophilic" is approximately at the HLB number

10. As stated above, in the mixtures according to the invention, substances having an HLB value of 1 to 6 are concentrated in the liquid organic propellant phase on account of their pronounced lipophilic character, whereas they are contained in the aqueous phase to be sprayed in a very small concentration; this distribution is advantageous when sensitive disperse systems are present in the aqueous phase to be sprayed.

A rapid determination of the HLB value of interface-active substances may be made on the basis of the behaviour towards water. Substances having an HLB value of up to 6 are those water-soluble surface-active compounds which cannot or can only be sparingly dispersed when shaken with water and do not give a milky dispersion even after vigorous shaking. This method of determining HLB values of surface-active substances of the most varied classes of compounds is known from the literature already cited and in particular from "Parfümerie und Kosmetik," volume 41, (1960), page 86.

Interface-active substances having an HLB value of up to 6, which are particularly suitable for use in the mixture according to the invention as spray improving interface-active agents, are mono- and diethers of glycols with alcohols, preferably alkanols of 4 to 6 carbon atoms, and especially the mono-alkyl and di-alkyl ethers of ethylene glycol and diethyleneglycol having a total of at least 6 and preferably not more than 12 carbon atoms, for example, ethyleneglycol mono-n-hexyl ether, diethyleneglycol mono-n-hexyl ether, ethyleneglycol di-n-butyl ether, diethyleneglycol di-n-butyl ether, propyleneglycol monobutyl ether, etc. "Allyl" in the most preferred class of these ethers has also from 4 to 6 carbon atoms.

The mixture in the system according to the invention contains as active substance, dissolved or dispersed in the aqueous phase to be sprayed, finishing agents for textiles, because on the one hand the lipophilic interface-active substances having an HLB value of 6 at the mixumum considerably facilitate the hot pressing of the textiles treated with the finishing agent and on the other hand the said spray improvement agents do not exert an adverse effect on the colloidal disperse system of the finishing agent, and do not cause disturbing foam formation or an excessively narrow spray angle and irregular spray density on the sprayed-on area of the textile substrate.

The mixture for finishing textiles may be composed, for example, as follows and may contain the following groups of substances:

(a) Finishing agents: which are dissolved or dispersed in water and which, calculated on the total weight of the mixture to be sprayed amount to 0.5–20% by weight, may belong to the following classes:

natural and modified starches or derivatives thereof,
cellulose derivatives,
polyvinylalcohols,
polyvinylacetates,
polystyrene resins,
polyacrylic resins, etc.

(b) Spray improving agent as defined above, in an amount of 0.1–5% of the total mixture to be sprayed.

(c) Propellants: unhalogenated or halogenated gaseous hydrocarbons or mixtures thereof, which may be liquified under pressure and which have a pressure of at least 0.5 atm. gauge at 20° C. and cannot be mixed with water, for example propane, butane, dichlorodifluoromethane, dichlorotetrafluoroethane, Propane/butane mixtures, especially of a weight ratio in the range of 10:90 to 40:50 give particularly satisfactory results.

The required quantity of propellant is based on the physical behaviour of the propellant, the composition of the aqueous phase to be sprayed of the mixture according to the invention, the type of valve used and the volume of the pressure vessel used; the proportion of propellant in the mixture generally lies between 2 and 30%.

The mixture according to the invention for finishing textiles may also contain the following auxiliary substances as well as the above substances:

(d) Softening agents: in quantities of 0.5 to 5% of the mixture, preferably polyhydric alcohols, for example ethyleneglycol, propyleneglycol, polyethyleneglycol, polypropyleneglycol, glycerol, etc.,

(e) Optical whitening agents: in quantities of 0.01 to 0.5% of the mixture, for example stilbene derivatives, triazole derivatives, benzimidazole derivatives, etc.,

(f) Anti-microbials: in quantities of 0.1 to 5% of the mixture, for example substituted benzoxazolones, substituted salicyclic acid anilides, substituted phenols, organotin-compounds, halogen isocyanuric acid derivatives, etc.,

(g) Perfumes: in quantities of 0.1 to 1% of the mixture, for example essential oils, synthetic perfumes, etc.

The following may be stated on the action of the auxiliary substances:

The softening agents prevent inter alia a blockage of the spray nozzles by reducing the adhesion and the hardness of the films of the finishing agents forming on drying. The aerosol systems according to the invention, therefore, preferably contain such softening agents in the above-stated amounts. The presence of softening agents also assists in completely suppressing foam formation. The optical whitening agents produce on white textiles an intense white effect and the anti-microbials prevent inter alia the formation of odour in textiles soaked with perspiration. The perfumes finally give the product a pleasant smell which is desirable in application and in the treated textiles.

Sprayed from an aerosol bomb equipped with a precision valve having a stem orifice of 2 times 0.020" and a mechanical breakup button at an angle of about 90°, onto a textile fabric over a distance of 20 cm., a spray circle of at least about 8 to 12 cm. and with preferred systems of 12 to 18 cm. diameter is obtained, free from any disturbing foam formation.

The following non-limitative examples explain some preferred embodiments of the mixture according to the invention more fully. Parts therein represent parts by weight. The HLB values of the spray improvement agents used are taken from the table on page 89 of the said publication "Parfümerie und Kosmetik."

EXAMPLE 1

	Parts
Starch derivative soluble in hot water	5.0
Ethylene glycol dibutyl ether [1]	1.5
Propyleneglycol	1.0
Lavender oil	0.3
Water	72.2
Propane/butane (20:80)	20.0

[1] (The formula of this compound is $C_4H_9—O—CH_2CH_2—O—C_4H_9$ it is commercially available as dibutylcellosolve).

The hot water soluble starch derivative is dissolved in hot water, the remaining components of the mixture, apart from the propellant, are added to the starch solution and homogenized in a suitable apparatus. The mixture is treated with propane/butane (20:80) in a pressure container equipped with a precision valve having a stem orifice of 2 times 0.020" and a mechanical breakup button. This preparation may be readily sprayed; sprayed on cotton, it produces after hot pressing an excellent starch effect.

EXAMPLE 2

	Parts
Polyvinyl alcohol	1.50
2-n-hexyloxy-ethanol, commercially	2.00
Available as hexylcellosolve ethyleneglycol	1.00
The sodium salt of 2-(stilbyl-4")-(naphtho-1',2':4, 5) 1,2,3-triazole-2",6'-disulphonic acid	0.05
Orange oil	0.25
Water	92.20
Iso-butane	3.00

The polyvinyl alcohol is dissolved in water, the remaining components of the mixture, with the exception of the propellant, are distributed in the polyvinyl alcohol solution with the aid of a suitable apparatus. The mixture is treated with iso-butane in a pressure container. A readily sprayable preparation is obtained having the same properties as in Example 1, however it gives a distinctive white effect to textiles which are sprayed and then hot pressed.

EXAMPLE 3

	Parts
Polyvinyl acetate-dispersion 50%	4.0
Dibutyl diethyleneglycol ether [1]	1.0
Glycerine	0.5
Dichlorobenzoxazolone	0.5
Water	84.0
Dichlorodifluoromethane	4.0
Dichlorotetrafluorethane	6.0

[1] (This compound is of the formula

$$C_4H_9—O—CH_2—CH_2—O—CH_2—CH_2—O—C_4H_9$$

it is commercially available as dibutylcarbitol.)

The polyvinyl acetate-dispersion is diluted in water, the the remaining components of the mixture, with the exception of the propellant, are added to this dilution and homogenized with a suitable apparatus. This mixture is mixed in a pressure container with the dichlorofluoromethane and the dichlorotetrafluorethane. The finished mixture has equally good sprayability as that mentioned in Example 1: The fabric sprayed therewith and then hot pressed has a good starch effect, which fabric possesses as a result of the dichlorobenzoxazolone content excellent fungistatic and bacteristatic properties.

EXAMPLE 4

	Parts
Polyvinyl alcohol	5.00
Diethyleneglycol dibutyl ether	1.00
Propyleneglycol	1.50
Bis[(tri-n-butyl)-tin]-oxide [1]	0.05
2,2'-disulphonic acid	0.10
Pentachlorophenol, sodium salt	0.50
Water	86.85
Dichlorodifluoromethane	5.00

[1] The sodium salt of 4,4'-bis(2-m-sulphanilino-4-diethanolamino-1,3,5-triazin-6-yl)-diamino-stilbene.

The polyvinyl alcohol is dissolved in water, the remaining components of the mixture, with the exception of the propellant, are added and distributed with the aid of a suitable apparatus. The mixture is treated in a pressure vessel with the dichlorodifluoromethane. A readily sprayable three-phase aerosol is obtained. Sprayed onto cotton, the preparation gives a soil-repellent finish after hot pressing with a good white effect and also with a fungistatic and bacteristatic effect. 1 part of ethyleneglycol monobutyl ether may be used in this instance as spray improving agent instead of the diether employed above.

EXAMPLE 5

	Parts
Starch derivative soluble in hot water	5.0
Diethyleneglycol-mono-n-hexyl ether (HLB value below 6)	1.5
Propyleneglycol	1.0
Lavender oil	0.3
Water	72.2
Propane/butane (20:80)	20.0

The hot water soluble starch derivative is dissolved in hot water, the remaining components of the mixture, apart from the propellant, are added to the starch solution and homogenized in a suitable apparatus. The mixture is

treated with propane/butane (20:80) in a pressure container. This preparation may be readily sprayed; sprayed on cotton, it produces after hot pressing an excellent starch effect.

We claim:

1. In a system comprising a pressure vessel and a sprayable mixture contained in said vessel under pressure, which mixture consists essentially of an aqueous phase to be sprayed, a liquefied organic propellant phase and the gas phase of the propellant, the improvement consisting in combination, in that

(i) said aqueous phase consists essentially of

(a) a water-soluble or water-dispersible textile finishing agent in an amount of from about 0.5 to 20% by weight calculated on the total weight of said mixture,

(b) water in an amount of from 50% to about 93% by weight calculated on the total weight of said mixture, said textile finishing agent being dissolved or dispersed in said water; said aqueous phase and said liquefied propellant phase not being emulsified with each other but being separated from each other forming a common interface; and

(ii) said mixture further contains a spray improving agent selected from a monoether and a diether of a glycol and an alkanol, said ether having at least 6 and not more than 12 carbon atoms, said glycol being selected from ethylene glycol, diethylene glycol, and propylene glycol, said alkanol having from 4 to 6 carbon atoms, and said spray improving agent having an HLB value according to Griffin of maximally 6, in an amount of from about 0.1 to 5% by weight calculated on the total weight of said mixture, the major proportion of said spray improving agent being present in said liquefied propellant phase, and a minor proportion of said spray improving agent being present in said aqueous phase; and

(iii) said mixture is substantially free from monohydric alkanol of from 1 to 5 carbon atoms.

2. The improvement described in claim 1, wherein said textile finishing agent is selected from water-soluble and water-dispersible natural and modified starch, polyvinyl alcohol, polyvinyl acetate, polystyrene resin and polyacrylic resin.

3. The improvement described in claim 1, wherein said spray improving agent is mono-alkyl or di-alkyl ether of monoethylene glycol or di-ethylene glycol, wherein "alkyl" has from 4 to 6 carbon atoms.

4. The improvement as described in claim 1, wherein said mixture further contains not more than 5% of an optical whitening agent derived from stilbene, triazole or benzimidazole.

5. The improvement as described in claim 1, wherein said mixture further contains not more than 5% of an antimicrobially active substance.

6. The improvement as described in claim 2, wherein said textile finishing agent consists of 0.5 to 10% by weight of a natural starch soluble in water.

7. The improvement as described in claim 2, wherein said textile finishing agent consists of 0.5 to 20% by weight of a modified starch derivative soluble in water.

8. The improvement as described in claim 1, wherein said spray improving agent is diethyleneglycol mono-n-hexyl ether.

9. The improvement as described in claim 1, wherein said spray improving agent is diethyleneglycol di-butyl ether.

10. The improvement as described in claim 1, wherein said spray improving agent is ethyleneglycol di-butyl ether.

11. The improvement as described in claim 1, wherein said spray improving agent is ethyleneglycol mono-n-hexyl ether.

12. The improvement described in claim 2 wherein said textile finishing agent is polyvinyl alcohol.

13. The improvement described in claim 2 wherein said textile finishing agent is polyvinyl acetate.

References Cited

UNITED STATES PATENTS

2,524,590	10/1950	Boe	252—305
2,995,278	8/1961	Clapp	252—305
3,066,037	11/1962	Curtin et al.	106—213
3,131,154	4/1964	Klausner	252—305
3,159,535	12/1964	Sesso et al.	167—39
3,211,563	10/1965	Reed	252—305

3,402,056	9/1968	Ehrmantraus	252—305
3,419,658	12/1968	Sanders	252—305

OTHER REFERENCES

Griffin I, Society of Cosmetic Chemist Journal, vol. I, December 1949, pp. 311–321.

Griffin II, Society of Cosmetic Chemist Journal, vol. V, December 1954, pp. 249–256.

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