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3,840,465

AEROSOL FOAM COMPOSITION

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No Drawing. Continuation-in-part of application Ser. No. 90,815, Nov. 18, 1970, which is a continuation-in-part of application Ser. No. 696,681, Dec. 19, 1967, both now abandoned. This application Sept. 14, 1972, Ser. No. 289,189

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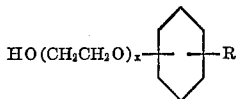
U.S. Cl. 252-90

12 Claims

ABSTRACT OF THE DISCLOSURE

A foam producing composition packaged in a pressurized container, said composition comprising an aqueous solution of a foam producing surfactant containing a liquid propellant dispersed therein by a propellant soluble, water insoluble surfactant selected from the group consisting of compounds having the general formula

(a)



wherein R is a hydrocarbyl radical containing from about 3 to 12 carbon atoms and x is an integer from 1 to 6, and

(b)



wherein R₁ is an alkyl radical containing from 10 to 13 carbon atoms, and y is an integer from 2 to 6 and mixtures thereof.

This application is a continuation-in-part application of application Ser. No. 90,815, filed Nov. 18, 1970, now abandoned which, in turn, is a continuation-in-part application of application Ser. No. 696,681, filed Dec. 19, 1967, now abandoned.

The present invention relates to improved foam producing liquid soap compositions and more particularly to micellar dispersions of an aqueous soap composition and a hydrocarbon or halogenated hydrocarbon propellant in a pressurized aerosol container.

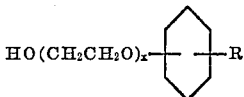
It is known from Spitzer et al., U.S. Pat. 2,655,480, that an aqueous soap solution in a pressurized type container containing a foam-producing propellant such as the chlorofluoromethanes and chlorofluoroethanes will produce a fine textured foam when discharged from the container. The propellant is insoluble in the soap solution and forms a liquid-liquid emulsion in the soap solution upon shaking before use.

A disadvantage of this type of composition is that, because of the insolubility of the propellant in the soap solution, it is necessary to shake the container before releasing the pressure therein to effect mixing of the components for subsequent formation of the foam.

By the present invention this disadvantage has been overcome and one is now able to obtain a voluminous foam from aqueous soap compositions in pressurized containers without prolonged shaking of the container before discharging the contents thereof.

The present invention resides in a foam producing composition packaged in a suitable container, the composition comprising a micellar dispersion or microemulsion of a hydrocarbon or halocarbon propellant in an aqueous solution of a foam-producing surfactant and containing a propellant soluble, water insoluble surfactant selected from the group consisting of a compound having the general formula

(a)



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wherein R is a hydrocarbyl radical containing from about 3 to 12 carbon atoms and x is an integer from 1 to 6 and

(b) $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_y \text{---} \text{R}_1$

wherein R₁ is an alkyl radical containing from 10 to 13 carbon atoms and y is an integer from 2 to 6 or mixtures thereof.

The propellant soluble surfactants described by the general formulae are further characterized by such substantially insoluble in water, but readily soluble in the propellant. Also, they produce little or no foam in contact with water.

By the term "micellar dispersion" as used in the specification and claims, is meant transparent dispersions of the hydrocarbon or halocarbon propellant in the aqueous surfactant solution. These systems are sometimes also referred to as microemulsions.

The foam-forming component of the aqueous surfactant concentrate may comprise the alkali metal and amine salts of the alkyl sulfuric or phosphoric acids, alkylnaphthalene sulfonates, diamylsulfosuccinates, ethanalaminecaprate, sulfated fatty acids such as sulfated stearic acid, palmitic acid, oleic acid, coconut fatty acids and the like as well as alkali metal salts of fatty acids such as capric, lauric, oleic, and mixtures. Also suitable are the water-soluble highly ethoxylated alkyl phenols, amines, amides, alcohols, glyceryl esters, sorbitan esters and mixtures.

The aqueous surfactant concentrate is used in an amount of from about 5 to 35% by weight of surfactant in water with amounts between 10 and 25% being preferred to provide a very persistent foam.

The water insoluble, propellant soluble surfactant component of the composition of the present invention can be an omega-hydroxyethoxyalkylbenzene, an omega-hydroxypolyethoxyalkylbenzene, containing up to six ethylene oxide groups and the alkyl group containing 3-12 carbon atoms; or an omega-hydroxypolyethoxyalkane containing up to six ethylene oxide groups, or mixtures thereof. Representative compounds include omega-hydroxyhexaethoxynonylbenzene, omega-hydroxyethoxypropylbenzene, omega-hydroxytetraethoxynonylbenzene, omega-hydroxytriethoxydecane, omega-hydroxytriethoxytridecane and the like. The surfactants are not appreciably soluble in water and produce little or no foam. They are miscible with the propellants in the ratios used. They disperse the water-insoluble propellant in the aqueous surfactant solution.

The propellant-soluble surfactant is preferably a hexal ethoxylated nonylphenol or triethoxylated tridecanol.

The propellant soluble surfactant component is employed in an amount of about 1 to 20% by volume of the composition, preferably about 4-8% for most satisfactory results.

Suitable propellants include aliphatic hydrocarbons and halogenated derivatives thereof having vapor pressures of from about 5 to about 300 p.s.i.g. and preferably between about 10 to 100 p.s.i.g. at about room temperature. Representative propellants include propane, butane, isobutane, mixtures thereof, halogenated aliphatic hydrocarbon derivatives such as

trichloromonofluoromethane,
dichlorodifluoromethane,
monochlorotrifluoromethane,
carbon tetrafluoride,
dichloromonofluoromethane,
monochlorodifluoromethane,
monobromotrifluoromethane,
dibromodifluoromethane,
trifluoromethane,
tetrachlorodifluoroethane,
trichlorotrifluoroethane,
dichlorotetrafluoroethane,

dibromomonochlorotrifluoroethane,
dibromotetrafluoroethane,
monochloropentafluoroethane,
ethylidene fluoride,
1,1,1-difluorochloroethane,
difluoroethane and

mixtures thereof as well as mixtures of these halogenated aliphatic hydrocarbons and aliphatic hydrocarbons. Propane or dichlorodifluoromethane are preferred as the sole propellant with a mixture of 20% by weight of dichlorodifluoromethane and 80% by weight of dichlorotetrafluoroethane being preferred as the mixed propellant. The propellant is employed in an amount of from 1 to 20%, preferably 4 to 10%, on a volume basis.

The composition of the present invention is in a closed pressure vessel such as an aerosol type container of any suitable size fitted with a conventional foam dispensing head from which it is dispensed in the form of foam as desired. A suitable head is described in further detail in U.S. 2,678,147 and this patent is incorporated herein by reference. Pressures in the container are conventional, i.e. from about 10 to about 120 p.s.i.g. at room temperature.

The order of addition of the components of the composition is not critical. One may add to the container the aqueous soap solution and propellant soluble, water insoluble surfactant separately or together, followed by the propellant or all components can be admixed together before being introduced into the container. It is desirable when introducing the propellant separately into the container to do so at a pressure above its vapor pressure so as to maintain the propellant in the liquid phase in the container except for a minor portion thereof that vaporizes to fill the void space in the container.

The composition of the present invention has an unexpected advantage over present day containered compositions for foam production. As the volume of the composition of the present invention in the container decreases with use, the dispersion is still maintained until essentially no more foam is produced therefrom. This is in contrast to conventional compositions on the market which sputter and produce a foamy liquid as the final portion of the contents of the can are used up. Furthermore, if protected against extremes of temperature, the compositions of the present invention do not require shaking before use whereas the conventional foam producing compositions have to be shaken before each use. Failure to do so with the conventional compositions may result in premature loss of the propellant.

Following is a description by way of example of a method of carrying out the present invention.

The test apparatus consists of a vertical cylindrical brass tube measuring approximately 7.5 inches in length, 1.25 inches in inside diameter, having a $\frac{3}{16}$ " wall thickness. It contains matching pairs of elongated viewing apertures approximately 2.5 inches in length on opposite sides thereof and adjacent the top and bottom of the tube. The lower end of the brass tube is joined to a brass base member. The other or upper end is closed by a threaded closure means or cap provided with inside gasket sealing means.

A thick walled, open mouthed glass tube 1.25 inches in outside diameter and 7.25 inches long is disposed inside the brass tube and rests on a shock-absorbent material such as rubber or styrofoam which is held in position in the closed end of the brass tube. The mouth of the glass tube is in contact with gasket sealing means when the cap is threadably engaged for closure with the upper threaded end of the brass tube.

The cap is provided with two openings therein to receive the inlet and discharge tubing which are 0.25 inch diameter high pressure copper tubes. The lower end of the inlet tubing extends below the mouth of the glass tube a distance of about 1.5 inches and the other end is connected to a propellant supply means having a regulating

valve. The lower end of the discharge tubing terminates approximately at the same level as the mouth of the glass tube while the other end of the discharge tubing is fitted with a pressure gauge and is connected also to a bleed-off tube having a regulating valve therein.

The test apparatus is used in the following manner. The aqueous soap concentrate and surfactant of prescribed type are externally mixed with stirring and are then poured into the glass tube. The cap is screwed on the brass tube and the valve in the bleed-off tube is closed. The regulating valve on the propellant supply is opened and the propellant gas is introduced into the sealed glass tube through the inlet tubing. After the desired amount of propellant gas has passed into the glass tube the open valve is closed. The test apparatus is then shaken by hand for a minute or so to permit rapid formation of the micellar dispersion (propellant in the soap solution). If the composition has been properly formulated the liquid in the glass tube will be seen to be clear and transparent. In the absence of unusual temperature variations (above about 150° F. or below 32° F.) the solution will remain clear indefinitely. The apparatus can now be inverted and foam drawn off by opening the draw-up valve slightly.

EXAMPLE I

A mixture consisting of 30 ml. of a 30% by weight aqueous solution of ethanalamine caprate and 6 ml. of a surfactant sold by the trade name Surfonic N-40 (reaction product of 4 moles of ethylene oxide and nonylphenol) was stirred in a glass container until homogeneous. There was then added 30 ml. of water with continued stirring. A clear solution resulted. The solution was introduced into the glass test tube in the test apparatus. The cap was screwed on the brass tube and 6 ml. of (liq.) propane was passed into the test tube through the propellant line at a pressure of 125-130 p.s.i.g.

The valve in propellant charge line was closed and the apparatus shaken thoroughly by hand. A transparent micellar dispersion of propane in the aqueous solution in the glass test tube was seen through the longitudinal slots in the brass tube.

The apparatus was permitted to remain undisturbed for 1.5 hours.

The apparatus was inverted, the valve in the discharge line opened slightly and the dispersion allowed to discharge therethrough as a uniform foam. About 1000 ml. of persistent foam were collected in a glass receiver.

COMPARATIVE EXAMPLE A

Example I was repeated except that no propellant-soluble surfactant was used. Visual observations of the contents of the glass test tube indicated the propane propellant separated out as an upper layer even after prolonged shaking. On discharge from the glass tube, only about 500 ml. non-persistent foam were obtained.

EXAMPLE II

Example I was repeated using 6 ml. dichlorodifluoromethane (Freon 12) as the propellant. About 800 ml. persistent foam were collected.

COMPARATIVE EXAMPLE B

Example II was repeated except no surfactant Surfonic N-40 was present. Observation of the contents of the glass tube showed the propellant as a separate bottom layer therein even after vigorous shaking. About 700 ml. of foam were obtained.

EXAMPLE III

Example I was repeated using a 30% by weight aqueous solution of potassium laurate. A clear solution was formed. About 800 ml. of foam was obtained which persisted for 240 minutes.

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COMPARATIVE EXAMPLE C

Example III was repeated omitting Surfonic N-40. A non-homogeneous mixture was obtained on shaking. About 500 ml. of foam were collected.

EXAMPLE IV

Example I was repeated using a 30% by weight aqueous solution of sodium diamylsulfosuccinate (Aerosol AY). A clear solution was obtained after shaking. About 600 ml. of foam were collected which persisted for 135 minutes.

COMPARATIVE EXAMPLE D

Example IV was repeated using 36 ml. of the aqueous soap solution but no surfactant Surfonic N-40. A non-homogeneous mixture was obtained after vigorous shaking. There was collected about 700 ml. of foam which persisted only for 40 minutes.

EXAMPLE V

A 22% by weight aqueous solution of sodium alkyl naphthalene sulfonate was mixed with 6.25% (basis 22% by weight of soap) of a surfactant sold under the trade name Surfonic TD-30 (reaction product of 3 mols of ethylene oxide and tridecanol) with stirring until a clear solution was obtained. A 66 ml. portion of this solution was introduced into the glass tube and the threaded cap screwed on the brass tube. The glass tube was pressurized with 6 ml. of propane and the apparatus shaken by hand. A clear dispersion was observed through the slots in the brass tube. There was collected 850 ml. of foam which persisted for 60 minutes.

COMPARATIVE EXAMPLE E

Example V was repeated omitting the surfactant Surfonic TD-30. A non homogeneous mixture was observed after pressuring with propane. About 900 ml. of foam were collected which persisted only for 40 minutes.

EXAMPLE VI

45 ml. of 10% potassium oleate solution was mixed with 10 ml. of a mixture of 75% (vol.) of Formula 30 alcohol and 25% of a material sold under the trade name Surfonic N-60 (formed from 6 moles of ethylene oxide nad nonylphenol). To this clear solution in the pressure vessel was added 5 ml. propane. After shaking, the contents of the glass tube were clear and homogeneous. The vessel was inverted and 200 ml. of foam were removed. At the end of 5 days the remaining solution was still clear. Approximately 600 cc. more foam were removed.

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COMPARATIVE EXAMPLE F

47.5 ml. of a 10% potassium oleate solution was mixed with 7.5 ml. of Formula 30 alcohol and charged to the pressure vessel. To this clear solution was added 5 ml. propane and the vessel was thoroughly shaken. The propane rose to the top of the aqueous solution after a short period of standing. Initially, 30 ml. of non-persistent foam were withdrawn and again after 2 days. After 6 days without shaking, 350 ml. of additional non-persistent foam were withdrawn for a total of 410 cc. The final 50 ml. were somewhat fluid.

EXAMPLE VII

50 ml. of a 15% aqueous solution of a material known as Surfonic N-300 (adduct of 30 moles of ethylene oxide and nonyl phenol) were mixed with 4 ml. Surfonic N-60 to give a clear solution. The mixture was charged to the pressure vessel and 4 ml. Freon-12 were added. After vigorous shaking the contents of the glass tube were clear, with no Freon layer on the bottom. After 24 hours standing, the liquid in the tube was still clear and 60 ml. thick foam were withdrawn. After 48 hours without shaking 30 ml. more foam were withdrawn and after 72 hours, 400 ml. more foam.

COMPARATIVE EXAMPLE G

55 ml. of a 15% aqueous solution of Surfonic N-300 were charged to the pressure vessel and 4 cc. Freon 12 were added. After vigorous shaking the Freon settled out rapidly. After 15 min. standing, 30 ml. of foamy liquid were withdrawn and after 24 hours with no shaking 140 ml. foamy liquid were removed, exhausting the contents of the pressure vessel. No significant amount of thick foam, such as was obtained in Example VII, was obtained.

The above Example I-VII demonstrate that a clear micellar dispersion can be formed with an aqueous solution of a soluble foam producing surfactant and a propellant provided the solutions contain a propellant soluble, water insoluble surfactant of the prescribed type and the resulting dispersion yields a persistent foam. In contrast as shown by Comparative Examples A-G, non-homogeneous solutions are formed in the absence of the prescribed propellant-soluble surfactant and the resulting foams are not as persistent or as voluminous.

In another series of tests the compositions were prepared in the following manner.

The components were added to a 100 ml. stoppered graduate and shaken by hand approximately 25 times. The results of observation of the shaken graduate were recorded. The following table shows the compositions and observations.

TABLE

Example	Type	Aqueous surfactant		Propellant		Water-insoluble surfactant		Water (ml.)	Micellar dispersion
		Amount (ml.)	Type	Amount (ml.)	Type	Amount (ml.)	Type		
VIII.....	30% wt. ethanolamine caprate.....	30	Freon 113 ⁹ ..	6	Surfonic N-40...	6	30	Yes.	
H.....do.....	30do.....	6do.....	6	51	No.	
I.....	30% wt. ethanolamine caprate.....	30do.....	6do.....	6	30	No.	
IX.....	30% wt. Potassium laurate.....	30do.....	6	Surfonic N-40...	6	30	Yes.	
J.....do.....	30do.....	6do.....	6	30	No.	
X.....	30% wt. Aerosol A Y (sodium diamyl sulfo-succinate)...	30do.....	6	Surfonic N-40...	6	30	Yes.	
K.....do.....	30do.....	6do.....	6	30	No.	
XI.....	15% wt. Surfonic N-300.....	50do.....	4	Surfonic N-60...	2	0	Yes.	
L.....do.....	50do.....	4do.....	2	0	No.	
XII.....	40% wt. Primene 81 R phosphate ¹	20do.....	6	Surfonic N-40...	6	30	Yes.	
XIII.....	20% wt. Primene JMT acetate ²	30do.....	6do.....	6	30	Yes.	
XIV.....	30% wt. Ethomeen C/25 ³	30do.....	8do.....	4	30	Yes.	
XV.....	30% wt. Priminox R-15 ⁴	20do.....	8	Surfonic N-60...	4	30	Yes.	
XVI.....	30% wt. Ethofat 242-25 ⁵	24do.....	8	Surfonic N-40...	4	30	Yes.	
XVII.....	40% wt. triethanolamine dodecylbenzenesulfonate.....	30do.....	6	Surfonic N-60...	6	30	Yes.	
XVIII.....	30% wt. Sipex L-12 ⁶	30do.....	8	Surfonic N-40...	4	30	Yes.	
XIX.....	30% wt. Tween 20 ⁷	20do.....	8	Surfonic N-60...	4	30	Yes.	
XX.....	30% wt. Tween 80 ⁸	20do.....	8do.....	4	30	Yes.	
XXI.....	40% wt. triethanolamine lauryl sulfate.....	30do.....	8	Surfonic N-40...	4	30	Yes.	

¹ Primene 81 R phosphate=Alkyl ammonium salt of phosphoric acid where the alkyl group is a mixture of 11-14 carbon atoms.

² Primene JMT Acetate=Alkyl ammonium salt of acetic acid where the alkyl group is a mixture of 18-22 carbon atoms.

³ Ethomeen C/25=Coconut fatty acid amines ethoxylated with 15 moles of ethylene oxide.

⁴ Priminox R-15=Reaction product of t-alkyl primary aliphatic amines of 12-14 carbon atoms and 15 moles of ethylene oxide.

⁵ Ethofat 242-25=Tall oil fatty acids ethoxylated with 15 moles of ethylene oxide.

⁶ Sipex L-12=Polyethoxylated dodecyl alcohol.

⁷ Tween 20=Sorbitan monolaurate ethoxylated with 20 moles of ethylene oxide.

⁸ Tween 80=Sorbitan monooleate ethoxylated with 20 moles of ethylene oxide.

⁹ Freon 113=Trichlorotrifluoroethane.

The data in the above table show that in the absence of the water soluble surfactant (Example H) or the water insoluble surfactant (Examples I, J, and L) no micellar dispersion is formed. The Table shows that when both surfactants are present one obtains a micellar dispersion (Example VIII-XXI).

The foam producing composition of the present invention is useful as a shampoo, a shaving soap, a tire cleaner, a rug or upholstery cleaner and the like.

In addition to the ingredients heretofore described, it should be understood that other minor components currently used in aerosol foam technology to improve the utility of the foam may be used, for example, odorants, alcohols, mineral oils, glycerol and glycols.

We claim:

1. A persistent foam-producing composition packaged in a pressurized container which consists essentially of an aqueous solution of a foam forming water soluble surfactant selected from the group consisting of the alkali metal and amine salts of alkyl sulfuric acids, alkylphosphoric acids, alkylphosphonic acids, diamylsulfosuccinates, ethanolamine-caprate, sulfated fatty acids, alkali metal salts of fatty acids, water-soluble highly ethoxylated alkyl phenols, amines, amides, alcohols, glyceryl esters, sorbitan esters and mixtures, containing a liquid propellant selected from the group consisting of aliphatic hydrocarbons, halogenated derivatives of aliphatic hydrocarbons and mixtures thereof, said propellant having a vapor pressure of from about 5 to about 300 p.s.i.g. at about room temperature, dispersed therein by a propellant soluble, water insoluble surfactant selected from the group consisting of omega - hydroxy - tetraethoxy - nonylbenzene, omega - hydroxy-hexaethoxy-nonylbenzene, and omega-hydroxy-triethoxy-tridecane, said foam forming surfactant being present in the aqueous solution in an amount of from 5 to 35% by weight, said liquid propellant being present in the composition in an amount of from about 1 to 20% by volume, and said water insoluble surfactant being present in the composition in an amount from about 1 to 20% by volume, said composition being a transparent micellar dispersion of said propellant in the aqueous solution.

2. A composition as claimed in Claim 1 wherein said liquid propellant is propane.

3. A composition as claimed in Claim 1 wherein said liquid propellant is dichlorodifluoromethane.

4. A composition as claimed in Claim 1 wherein said propellant soluble, water insoluble surfactant is omega-hydroxy-tetraethoxy-nonylbenzene.

5. A composition as claimed in Claim 1 wherein said propellant soluble, water insoluble surfactant is omega-hydroxy-hexaethoxy-nonylbenzene.

6. A composition as claimed in Claim 1 wherein said propellant soluble, water insoluble surfactant is omega-hydroxy-triethoxy-tridecane.

7. A composition as claimed in Claim 1 wherein said liquid propellant is trichlorotrifluoroethane.

8. A persistent foam-producing composition for use in a pressure container consisting essentially of an aqueous solution of a foam-forming water soluble surfactant se-

lected from the group consisting of the alkali metal and amine salts of alkyl sulfuric acids, alkylphosphoric acids, alkylphosphonic acids, diamylsulfosuccinates, ethanolamine-caprate, sulfated fatty acids, alkali metal salts of fatty acids, water-soluble highly ethoxylated alkyl phenols, amines, amides, alcohols, glyceryl esters, sorbitan esters and mixtures which is present in an amount of from about 5 to about 35% by weight of said solution, a water insoluble liquid propellant selected from the group consisting of aliphatic hydrocarbons, halogenated derivatives of aliphatic hydrocarbons and mixtures thereof, said propellant having a vapor pressure of from about 5 to about 300 p.s.i.g. at about room temperature, dispersed in said aqueous solution in an amount in the range of from about 1 to 20% by volume, by from 1 to 20% volume of a propellant soluble, water insoluble surfactant selected from the group consisting of omega-hydroxy-tetraethoxy-nonylbenzene, omega-hydroxy-hexaethoxy-nonylbenzene, and omega-hydroxy-triethoxy-tridecane, said composition being a transparent, micellar dispersion of said propellant in said aqueous solution.

9. A composition as claimed in Claim 8 wherein said foam-forming water soluble surfactant is present in said aqueous solution in an amount of from about 10 to 25% by weight thereof, said propellant is present in an amount of 4 to 10% by volume, and said propellant soluble surfactant is present in an amount of from 4 to 8% by volume.

10. A composition as claimed in Claim 8 wherein said foam-forming surfactant is ethanolamine caprate.

11. A composition as claimed in Claim 8 wherein said foam-forming surfactant is potassium laurate.

12. A composition as claimed in Claim 8 wherein said foam-forming surfactant is potassium oleate.

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