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[54] **DEFOAMER FOR AEROSOL CONCENTRATES**

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[58] **Field of Search** 424/184, 47, 73, 357; 252/305, 321, 90

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[57] **ABSTRACT**

Internal foaming in aerosol containers may be suppressed by adding about 0.001 to 3% of a hydrophobic silica calculated on the basis of the concentrate (that is the ingredients other than the propellant).

10 Claims, No Drawings

DEFOAMER FOR AEROSOL CONCENTRATES

PRIOR ART

Foaming of aqueous liquids is undesirable in many applications and a wide variety of methods are known to overcome these problems. These methods and additives are usually quite specific to each problem. For example, hydrophobic silica has been used to prevent or control foaming in aqueous black liquors in the paper industry and in polymer latices. In shaving creams, U.S. Pat. No. 2,908,605 recognizes the problem of internal foaming of an aqueous concentrate in aerosol containers. It describes changing the type of soap in an attempt to overcome it. The same problem also occurs with many other aerosol products, such as detergents, lotions and food products. We have unexpectedly discovered an effective method of overcoming the problem of internal foam within the containers of shave creams and other foaming products.

THE PROBLEM

Foam formation within aerosol containers has two disadvantages. First, foam reduces the efficiency of the agitation when the container is shaken to disperse the propellent. Secondly, when most of the contents of the aerosol container have been used, foaming reduces the amount of liquid concentrate available for spraying. When internal foaming occurs, the last 10–15% of the contents of the container will foam when shaken and the propellent will escape without dispensing the useful ingredients properly. However, by use of our invention, the dispersion of propellent in the concentrate is improved and also a greater amount of effective material can be sprayed with products which otherwise foam inside aerosol containers.

OUR INVENTION

We have found that internal foaming in aerosol containers can be controlled and suppressed by the addition of small amounts of solid hydrophobic siliceous materials. Especially effective were precipitated silica hydrates made hydrophobic by the application of a silicone coating closely bound to the surface of the silicas as, for instance, by curing. The amount of hydrophobic material may be as low as 0.001%, based on the concentrate, and larger amounts will increase the effectiveness but usually no more than 1 or 2% will be required for suppression of internal foam formation. Amounts as high as 3% or more may be used. The amount will depend on the formulation, the propellent and the hydrophobic agent employed. Although hydrophobic liquids and solids are well known to suppress foaming in liquid systems, we were surprised to find that the hydrophobic materials described herein prevented internal foaming in aerosol containers but had no adverse effect on the external foam or emulsion, such as is formed by a shaving lather, a hair shampoo or a window cleaner, for example.

DETAILED DESCRIPTION

Although we prefer to use a hydrated precipitated silica as the base for the hydrophobic defoamer, we have found that pyrogenic silicas, natural silicas and even siliceous materials such as clay will form hydrophobic defoamers if they are sufficiently finely divided. While we prefer the pH of the base to be from above about

8 to about 11, we have made reasonably satisfactory defoaming agents where the base pH has been as low as 4. There is no reason why a pH as low as about 1 to 2 should not be satisfactory. The ultimate particle of the base is usually stated in terms of the average particle diameter. This should be in the range of 7 to 100 millimicrons. In practice these finely divided silicas exist as agglomerates of ultimate particles. These agglomerates should be 10 microns or below, preferably below 2 microns in average diameter.

The coating may be any material which will make the substrate hydrophobic such as a silicone, silane, alcohol, amine, imidazoline, quaternary amine, silicate ester, isocyanate, etc. As shown in the examples, we obtained satisfactory results with silicone fluid coatings and chlorosilane coatings. We found a cured silicone coating to be especially effective and we prefer to use dimethyl polysiloxane or hydrogen methyl polysiloxane. The base can be coated evenly and cured by known processes, such as by heating or catalysis. Only the hydrophobic solid is effective as determined by flotation on water so that if only 50% of the solid floats, twice as much solid must be used.

The formulation of aerosols and the necessary properties of the propellents are adequately described in the book "Aerosols, Science and Technology," published by Interscience Publishers, Inc. in 1961. The information therein is incorporated herein by reference. Necessary techniques and explanations are all included in this reference.

Any of the ordinary liquefiable propellents may be used as well as combinations of propellents which are often used to achieve a suitable pressure within the container or impart another desired property of the aerosol. We have demonstrated excellent suppression of internal foaming in systems with hydrocarbon and halogenated hydrocarbon propellents as well as combinations thereof.

Among suitable liquefied propellents which may be employed are the alkanes containing up to 5 carbon atoms, such as propane and butane, lower alkyl chlorides and halogenated hydrocarbons. The latter are the fluorinated and fluorochlorinated lower alkanes such as are sold under the trademark "Freon" by the Freon Products Division of E. I. DuPont de Nemours & Co., and "Genetron" sold by General Chemical Division of Allied Chemical Corp. and other manufacturers.

We have also found it preferable to charge the hydrophobic solid defoamer with the concentrate and propellent rather than blending the defoamer and concentrate before charging the container.

GENERAL STATEMENTS

In the packaging field the term "aerosol" refers to pressurized products. The discharge obtained from an aerosol container may be a fine spray or a liquid spray or a foam or an emulsion and, in some cases, dry materials. In many aqueous systems, regardless of the form of the discharge, there is a possibility of foaming within the container. It is only with these systems capable of internal foaming that we are herein concerned. Our invention also is effective in systems where organic solvents are present. These may be included for a variety of reasons, such as to increase compatibility, change the pressure, modify the spray, etc. In a non-aqueous system, a solvophobic solid must be used.

Most of the hydrophobic materials in our examples were made by treating a siliceous base with a silicone oil. The silicone oil, or fluid, L–45, is a dimethylpolysiloxane sold by Union Carbide Corp. It has a viscosity of 50 centistokes and is described in the Union Carbide Silicone Product Bulletin. The L–31 silicone fluid, a hydrogen methyl polysiloxane, also sold and described by Union Carbide Corp., is a clear colorless liquid in which one of the methyl groups of the dimethylpolysiloxane is replaced by hydrogen, except on the termial silicon atoms. It also has a viscosity at 25° C. of 50 centistokes and a specific gravity of 1.01. Similar polysiloxane silicone fluids are sold by a number of companies including the General Electric Co. whose dimethyl silicone oils are known as "SF-96" and "Viscasil." "DF-1040" is General Electric Company's methyl hydrogen silicone fluid. These particular silicone oils are used to illustrate the present discovery and are in no way limiting. Satisfactory results could also be obtained with other silicone fluids and gases.

In our examples, the aerosol formulas were put in glass aerosol bottles so that the internal foaming could be observed. We have found that the defoamers of this invention controlled internal foaming within standard aerosol cans. This was noted by the sound of the liquid swirling when the can containing the formula with defoamer was shaken. Less sound or no sound was produced in a similar can containing the same formula without defoamer on shaking. The defoamers of this invention did not reduce or otherwise change the external foam sprayed from either bottles or cans.

EXAMPLE 1

An aerosol shave cream formula, which foams in the container, was tested with a series of hydrophobic defoamers at a concentration of 0.11% based on the weight of the concentrate. In each case a 2 oz. glass aerosol bottle was charged with 18 parts of a concentrate with the following composition:

Stearic Acid	6%
Coconut fatty acids	2%
Glycerine	10%
Triethanolamine	5%
Water	77%

Then 0.02 parts of defoaming additive was put into the bottle. After capping with a standard aerosol valve, 1.4 parts of "Freon 12/114" (40/60), a blend of 40% "Freon 12" and 60% of "Freon 114" which is sold by E. I. DuPont de Nemours & Co., was charged to the bottle. The level of the liquid contents was marked. There was 50 mm free space above the liquid in the bottles. After shaking the bottle ten times by hand, the foam height above the new liquid level was then recorded as shown in the following table.

After running the test, a portion of each aerosol was sprayed. The external foam was not affected by any of the internal defoaming additives.

In the first group, the additive was prepared by coating the siliceous substrate with 10% of L–45 silicone fluid obtained from Union Carbide Co. and described above. The coated materials were then cured by heating for 16 hours at 300° C., and all or most of each of the coated and cured products floated when shaken in water. The silica coated with 10% L–31 silicone fluid, also described above, was cured for 16 hours at 171° C.

Base Coated with L–45	Properties of Base		Foam Height (mm)
	pH	Area (m^2/g)	
Hydrated precipitated fine silica	8.5	300	0
Hydrated fine silica	5	325	35
Hydrated fine silica	8	130	12
Hydrated fine silica	11	175	7
Pyrogenic silica	4	200	5
Silica gel, J. T. Baker Chemical Co. Reagent grade	6.5	—	15
Kaolin clay, air separated	5	—	17

Bases with other Coatings	Properties of Base		Foam Height (mm)
	pH	Area (m^2/g)	
Pyrogenic silica coated with tetrachlorosilane	4	—	17
Hydrated precipitated fine silica coated with L–31 fluid	4	200	20
Other Defoaming Additives			
None	—	—	50
Hydrated precipitated fine silica coated with 10% L–45, uncured	8.5	300	30
Hydrated precipitated fine silica, no coating	8.5	300	45
L–45, alone	—	—	40

EXAMPLE 2

The same concentrate was used as in Example 1. The same procedure as Example 1 was followed except different concentrations of silicas coated with 10% L–45 fluid and cured were used as the defoaming additive. The following table shows that the defoaming effectiveness after 10 shakes was dependent on the amount of the additive.

Base coated with L–45	Concentration (%)	Foam Height (mm)
Hydrated precipitated fine silica, pH 8.5	0.05	10
Same	0.11	0
Pyrogenic silica, pH 4	0.11	5
Same	0.22	2.5
Same	0.55	0

EXAMPLE 3

The same shave cream concentrate was used as in Example 1. The defoaming additive in each case was 0.11% (based on the weight of the concentrate) hydrated precipitated fine silica coated with 10% L–45 oil and cured. The following table shows that the additive was effective when different propellents were used. The foam heights were measured after 10 shakes.

Defoaming Additive Concentration (%)	Propellant	Foam Height (mm)
0	"Freon 12/114" (40/60)	50
0.1	do.	0
0	Isobutane/Propane (84%/16%)	20
0.1	do.	0

EXAMPLE 4

A foam shampoo was prepared by blending Part A and Part B, below, at 70° C. and stirring until cooled to room temperature.

Part A

Triethanolamine	5.0	parts
Polyvinylpyrrolidone	0.17	do.
Versene*	0.17	do.
Triethanolamine lauryl sulfate (40%)	49.0	do.
Propylene glycol	20.0	do.
Water	16.17	do.

Part B

Stearic acid	3.33	parts
Myristic acid	2.0	do.
Oleic acid	3.33	do.
Lanolin, anhydrous	0.33	do.

*sodium ethylene diamine tetraacetate sold by Dow Chemical Co.

The following table shows that hydrated precipitated fine silica, pH 8.5, coated with 10% L–45 fluid and cured, as in Example 1, controlled the internal foaming in an aerosol container. Two ounce aerosol bottles were charged with 22.7 g. of the above foam shampoo concentrate and the hydrophobic silica. Then, after capping with a standard aerosol valve, 2.5 g. of "Freon 12/114" (40/60) was added. The liquid level was marked and then the bottle was shaken 100 times and the foam height above the new liquid level measured. As in Example 1, the dispensed product was observed after running the test. As before, the defoaming additive had no apparent effect on the sprayed foam.

Defoamer Concentration* (%)	Foam Height (mm)
0	25
0.1	25
0.3	0

*The concentration in this and following examples is calculated on the weight of concentrate.

EXAMPLE 5

A foam hairdressing concentrate was prepared by blending Part A with Part B, below, each at 70° C., and stirring until cooled to room temperature.

Part A

Stearic acid	5.6	parts
Lanolin, anhydrous	0.7	do.
Mixed isopropyl myristate and palmitate	4.5	do.
2-ethylhexanol	0.9	do.
Light mineral oil	2.2	do.

Part B

Polyvinylpyrrolidone	0.2	parts
Triethanolamine	2.7	do.
Water	83.2	do.

To a 2 oz. aerosol bottle was charged 25 g. of the above foam hairdressing concentrate and the same defoaming additive used in Example 4. Then, after capping with a standard aerosol valve, 2.5 g. of "Freon 12/114" (40/60) was added. The liquid level was marked and then the foam height measured after shaking 100 times.

Defoamer Concentration (%)	Foam Height (mm)
0	38
0.33	19
0.55	3

When a bottle containing 25 g. of concentrate plus 0.3% defoamer but no "Freon 12/114" (40/60) was shaken 100 times, the foam height was 32 mm. A bottle containing 25 g. of concentrate plus 0.5% defoamer, but no "Freon 12/114" (40/60) developed 13 mm foam on shaking 100 times.

EXAMPLE 6

A window cleaner concentrate was prepared with 0.2 parts of isopropyl alcohol, 10 parts of Triton X–100, a nonionic surfactant sold by Rohm & Haas Co. and 86.8 parts of water. Two ounce aerosol bottles were charged with 32.3 g. of the above formula and the same defoamer used in Example 4 at the concentration shown in the table below. The bottles were then capped with an aerosol valve and 1.2 g. of a blend of 84% isobutane/16% propane was added. The bottles were shaken by hand 10 times and the foam height measured.

Defoamer Concentration (%)	Foam Height (mm)
0	50
0.55	0

On shaking the bottle containing 0.55% defoamer 100 times, 12 mm foam formed but it broke up rapidly whereas the 50 mm foam which formed in the bottle containing no defoamer did not break up rapidly. After running the test, product was sprayed from each bottle. The defoamer had no apparent effect on the dispensed foam.

EXAMPLE 7

A commercial aerosol bathroom cleaner "Crew," sold by S. C. Johnson Co., was chilled and the propellent was allowed to evaporate at atmospheric pressure leaving a detergent concentrate. To a 2 oz. aerosol bottle was charged 25 g. of this concentrate, the defoamer of Example 4 in amounts shown in the table below and then the bottle was capped with a standard aerosol valve. "Freon 12/114" (40/60), 1.4 g., was then added and the liquid level marked. After shaking 10 times, the foam height above the new liquid level was then measured.

Defoamer Concentration (%)	Foam Height (mm)
0	38
0.11	0
0.33	0

The bottles to which 0.11% and 0.33% defoamer were added were shaken an additional 200 times. No foam formed in either bottle. It was noted that in neither of these aerosols was the dispersed foam affected by the presence of the defoamer.

EXAMPLE 8

The same concentrate as described in Example 1, forming an aerosol shave cream base, was used in the amount of 41.4 g. in a 2 oz. aerosol bottle. The same additive used in Example 4 was charged and the bottle was sealed with a standard aerosol valve and then 4.1 g. of "Freon 12/114" (40/60) was added. The free space, above the liquid, was 38 mm. After marking the liquid level, the bottle was shaken 100 times, and then the foam height measured with the following results.

Defoamer Concentration (%)	Foam Height (mm)
0.1	2
0.05	13
0.01	38

Our invention was also demonstrated with a series of aerosol shave creams, prepared and tested as above except the "Freon 12/114" (40/60) was replaced with an equal weight of "Freon 12/11" (50/50). The following table shows that the hydrophobic silica defoaming agent was even more effective with "Freon 12/11" (50/50) than with "Freon 12/114" (40/60).

Defoamer Concentration (%)	Foam Height (mm)
0	33
0.1	0
0.05	0
0.01	3
0.005	10
0.001	15

EXAMPLE 9

Compositions were made up according to the following table which shows the percentage overall concentration of the contents. Six ounce aerosol shaving cream cans were charged with these compositions.

Components	1	2	3	4	5
Stearic Acid	6.5	6.4	6.3	6.4	6.4
Coconut Fatty Acid	0.7	0.7	0.7	0.7	0.7
Glycerine	9.0	8.8	8.7	8.9	8.8
Triethanolamine	4.5	4.4	4.3	4.5	4.4
Water	69.3	68.2	67.0	68.7	68.2
Freon 12/11 (50/50)	10.0	10.0	10.0	10.0	10.0
Defoamer (a)	—	1.5	3.0	—	—
Base Silica	—	—	—	0.8	1.5
Defoamer (% based on concentrate)	—	1.7	3.3	—	—

(a) The base silica had a pH of 8.5 and an area of 300 meters/gram and with a finely divided precipitated hydrated silica. The defoamer was prepared by coating this base silica with L-45 silicone oil and curing as in Example 1.

The samples which contained hydrophobic silica (defoamer) were found to produce little or no foam inside the container while the uncoated base silica was found to have no depressing effect on the internal foaming. The external foam was unaffected by either the defoamer or the base silica.

More or less specific claims will be presented hereinafter and even though such claims are rather specific in nature, those skilled in the art to which this invention pertains will recognize that there are obvious equivalents for the specific materials recited therein. Some of these obvious equivalents are disclosed herein and other obvious equivalents will immediately occur to one skilled in the art and still other obvious equivalents could be readily ascertained upon rather simple routine noninventive experimentation. Certainly no invention would be involved in substituting one or more of such obvious equivalents for the materials specifically recited in the claims. We intend that all such obvious equivalents be encompassed within the scope of this invention and patent grant in accordance with the well known doctrine of equivalents as well as changed proportions of the ingredients which do not render the composition unsuitable for the disclosed purposes.

What we claim is:

1. In the known type of aerosol unit containing a foamable aqueous liquid concentrate and a propellant, the improvement which comprises including in the aerosol unit a finely divided hydrophobic solid siliceous material in the amount of about 0.001–3% based on the weight of said concentrate, said hydrophobic solid siliceous material is a finely divided silica having a particle

size between about 7 and 100 μ and a pH above about 2 coated with a hydrophobic organic film.

2. An aerosol unit according to claim **1** wherein the organic film is formed by curing a silicone oil adsorbed on the surface of the finely divided silica.

3. An aerosol unit according to claim **1** wherein said silica is a microfine precipitated hydrated silica.

4. An aerosol unit according to claim **1** wherein said siliceous material is a finely divided clay.

5. An aerosol unit according to claim **1** wherein said silica is a finely divided pyrogenic silica.

6. An aerosol unit according to claim **2** wherein the silicone oil is selected from the group consisting of dimethyl polysiloxane and hydrogen methyl polysiloxane.

7. An aerosol unit according to claim **1** in which the propellant is selected from the group consisting of a liquified compressed gas and a mixture of liquified compressed gases.

8. An aerosol unit according to claim **1** wherein the foamable aqueous liquid concentrate is a shave cream composition.

9. An aerosol unit according to claim **1** wherein the foamable aqueous liquid concentrate is a detergent composition.

10. A method for controlling foam formation when charging an aerosol unit with a foamable aqueous concentrate and a propellant, which comprises:

a. charging the aerosol unit with a mixture of the foamable aqueous concentrate and 0.001 to 3.0% of a finely divided hydrophobic solid siliceous material, said hydrophobic solid siliceous material being a hydrated precipitated silica having an ultimate particle size between 7 and 100 μ and a pH between 4 and 11 and a surface coating of a polysiloxane cured in situ, and

b. charging the aerosol unit with a propellant.

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