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CLEAR AEROSOL SOAPS

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2 Sheets-Sheet 1

FIG. 1.

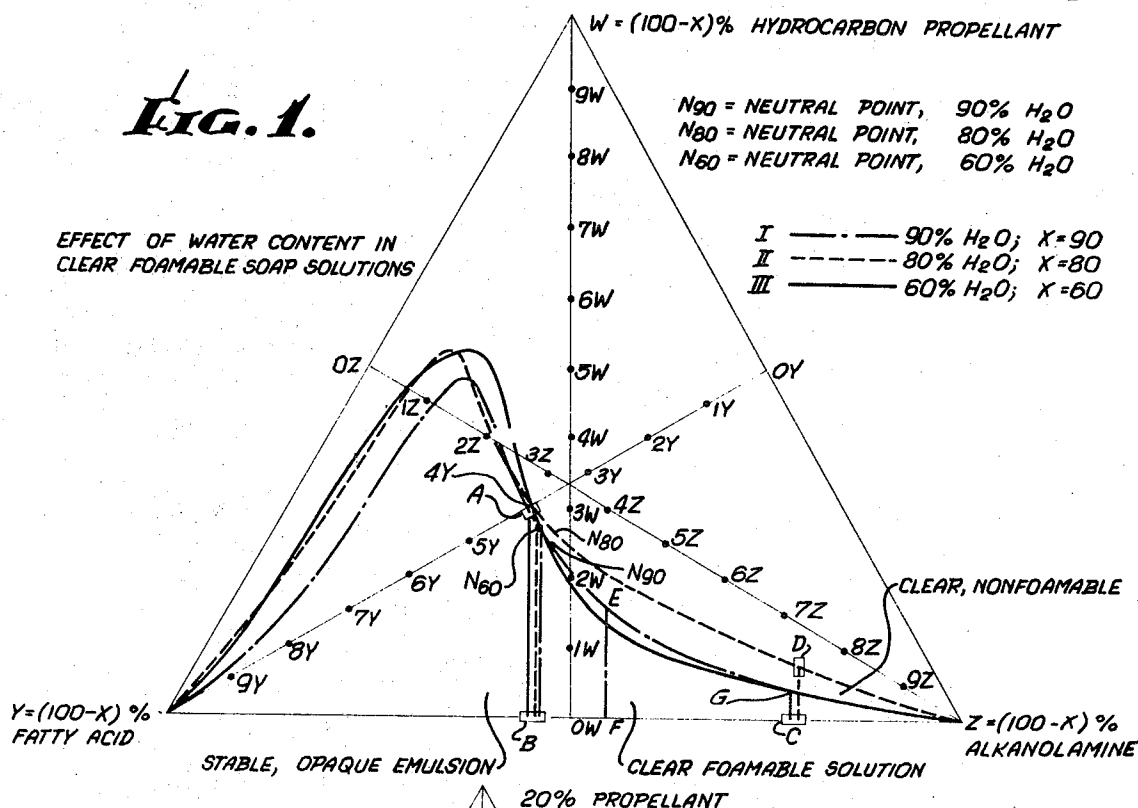
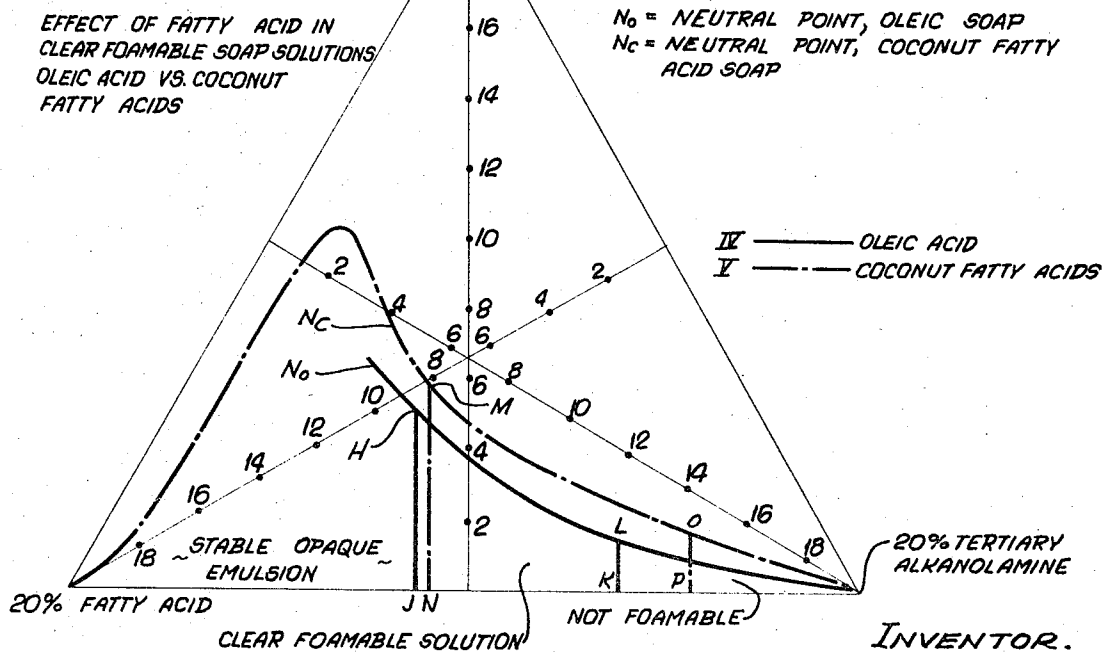


FIG. 2.



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2 Sheets-Sheet 2

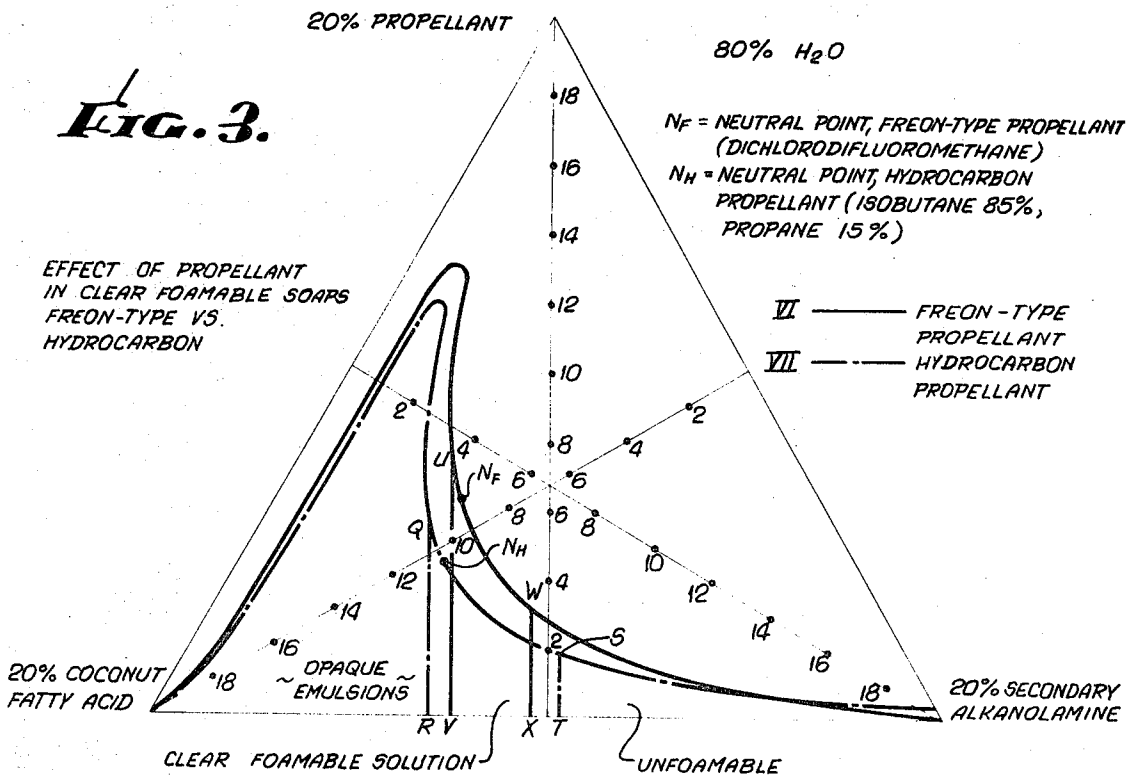
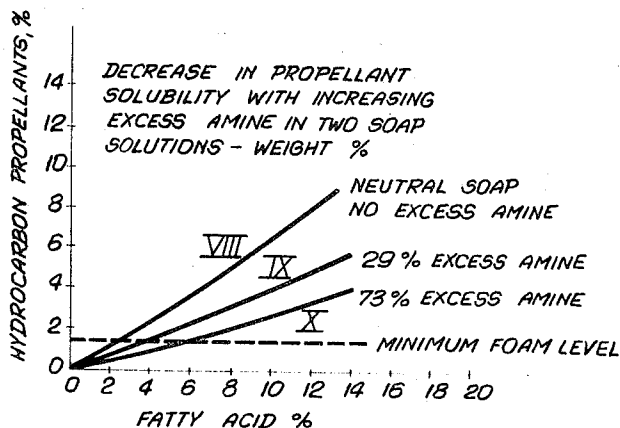
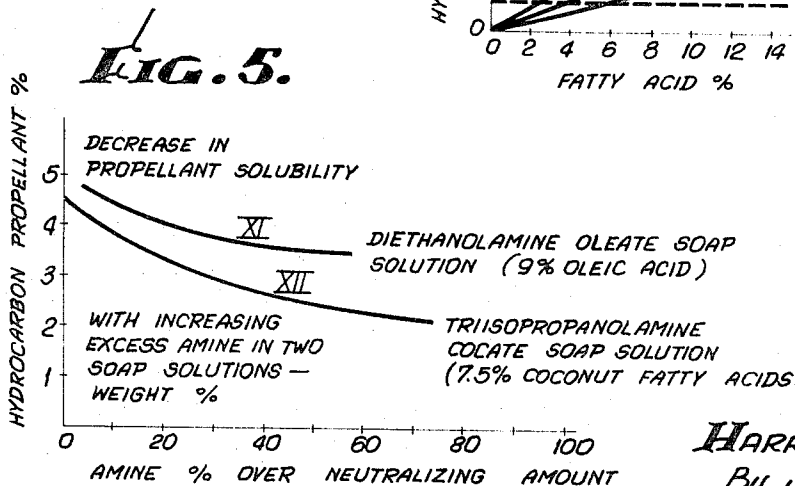


FIG. 4.



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CLEAR AEROSOL SOAPS

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14 Claims

ABSTRACT OF THE DISCLOSURE

A clear, homogeneous and single phase soap composition which foams on release to normal pressure conditions and thus is useful in aerosol dispensers the location or size of which makes pre-use agitation inconvenient. The soap composition includes a fluid mutual solution of a major weight amount of water, a water insoluble liquid phase normally gaseous propellant the presence of which tends to lower the solubility of the soap and thus cause precipitation of fatty acid in the solution, and a water soluble soap prepared from a water insoluble, but propellant soluble fatty acid and a water soluble, aliphatic amine which is present in the solution in an amount sufficient to solubilize fatty acid precipitated and not dissolved in the solution by the propellant.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention has to do with foamable soap compositions which are visually clear. Such compositions find particular utility in the aerosol package field for dispensing as foams e.g. as a shaving lather.

(2) Prior art

Foamy soap has been obtainable from aerosol packages in the past. In U.S. Pat. 2,655,480 to Spitzer compositions of water soap and a propellant are taught which when released from a pressurized container burst into a foam on the vaporization of the propellant within the soap solution. The Spitzer compositions contain a liquefied, and emulsified, water insoluble propellant. Others, e.g. U.S. Pat. 2,995,278 and U.S. Pat. 3,289,949 to Roth, have taught foamable compositions which are aqueous solutions intimately mixed with a propellant immediately before discharge through the dispensing nozzle of the aerosol package.

It will be observed from a consideration of presently available foamy soap dispensing packages that an emulsion of propellant and soap solution is required or an arrangement of ports and tubes constituting a form of valve is needed to ensure adequate mixing of these materials for satisfactory foaming. In the case of propellant emulsions, it is advisable to shake the aerosol package well prior to use to reestablish the emulsion or propellant dispersion. With valve arrangements the angle of holding the package may have a material effect on quality of output foam.

Certain applications for aerosol dispensed soap conveniently employ a fixed container, e.g. one secured to a wall adjacent a sink with the valve conveniently placed for use. Such packages obviously cannot be shaken to restore propellant dispersion levels. In these applications the liquid product/propellant mixture is desirably stable and intimate, in a manner typical of a solution.

A further desirable property of foamable soaps is visual transparency both from an aesthetic and a sales promotion standpoint. This property too requires an intimacy of mixture found only in solutions.

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Propellants are generally hydrocarbons or halogen, i.e. chloro- and fluoro- substituted hydrocarbons and are water insoluble. Soap solutions of course are water based. The addition of propellants to aqueous soap formulations tends to decrease the solubility of the soap in the solution. This decreased solubility causes separation from the solution of the water insoluble portion of the soap, the fatty acid portion. A curd results which is unattractive and the product loses some performance properties.

SUMMARY OF THE INVENTION

It is a major objective of the present invention to provide foamable soap solutions which are visually clear, effective foam formers, and stable on storage. More particular objectives are the provision of foamable soap compositions the components of which are soluble in the combination so as to provide a single phase, homogeneous foamable mixture and the provision of a foamable soap composition which does not require pre-use agitation or special valving for dispensing as a useful foam.

Foamable soap compositions have now been found which, through the use of particular amines in defined amounts, achieve homogeneity and thus visual clarity, and are stable to storage and dispensable to uniform foams without agitation. In particular, clear, homogeneous and foamable soap compositions have been discovered which consist essentially of a fluid, mutual solution of a major weight amount of water, a water insoluble, liquid phase, normally gaseous propellant composed of carbon atoms substituted with hydrogen, chlorine or fluorine atoms or combinations thereof having a tendency to lower the solubility of soaps in the water and thus to cause precipitation of soap-forming fatty acids in the solution, and a water soluble soap of a water insoluble and propellant soluble fatty acid and a water soluble, aliphatic amine containing from 2 to 9 carbon atoms with no more than 4 carbon atoms in a single chain, said amine being present in said solution in an amount sufficient to solubilize fatty acids precipitated and not dissolved in the solution by the propellant.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a ternary diagram showing the range of fatty acid, alkanolamine and hydrocarbon propellant providing clear foamable soap solutions at varying concentrations of water;

FIG. 2 is a ternary diagram showing proportion of oleic acid and coconut fatty acids producing clear foamable solutions at fixed concentrations of water and propellant;

FIG. 3 is a ternary diagram showing the effect of hydrocarbon and haloalkylpropellants on an aqueous soap solution;

FIG. 4 is a graph showing the effect of different concentrations of amine on propellant solubility at different fatty acid concentrations; and

FIG. 5 is a graph showing the effect on propellant solubility of different concentrations of amine in two aqueous soap solutions.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The single phase foamable soap solutions of the present invention may be packaged in the conventional aerosol package in the usual way. Thus a pressure resistant vessel having a valve dispenser and charged with gaseous propellant may be used to store the foamable compositions herein disclosed for use. Glass or other transparent containers will be particularly attractive because of the pleasing visual aspect of these novel compositions. In certain preferred embodiments the clear soap

solution will be present in a pressure resistant container as the lowermost of three phases with a second or intermediate phase of liquefied but undissolved propellant thereabove and a gaseous phase propellant as the uppermost layer in phase equilibrium with the layer of liquefied propellant.

The major weight portion, i.e. 50 percent by weight and above of the soap compositions of the present invention, is made up of water. Preferably, water levels will range between 60 and 90 weight percent because of the greater tolerance of these solutions for variations in the quantity and quality of other composition components. Use of 80 weight percent and less water provides optimum formulating flexibility in terms of useful ranges of propellants and soap components and, therefore, this level of water content will most frequently be used.

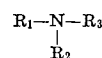
The propellants useful in the present formulation are volatile organic materials, generally boiling below 40° F., which exist normally therefore as a gas but which may be liquefied at mildly elevated pressures and normal temperatures. In addition, suitable propellants when liquefied will be insoluble in water, soluble in aqueous soap solutions and be solvents for fatty acids. Among the materials satisfying these criteria are saturated aliphatic hydrocarbons having up to 4 carbon atoms. Therefore such materials as methane, propane, isopropane, n-butane, isobutane and cyclobutane may be used. A second class of propellant includes the halohydrocarbons, materials having chloro and/or fluoro groups substituted for one, up to all of the hydrogens on aliphatic saturated hydrocarbon backbones. Many of these materials are generally classified as Freon-type propellants. Specific illustrations are dichlorodifluoromethane, 1,1 - difluoroethane, monochlorodifluoromethane and trichlorotrifluoroethane. Most suitable halogen substituted propellants are within the class of compounds characterized by having from 1 to 2 carbon atoms inclusive and at least two halogen substituents selected from chloro- and fluoro- groups up to a maximum of such substituents equal to the number of replaceable hydrogens on the compound. Preferred members of the class will contain both fluoro and chloro groups, and optimally in equal number. In general above about 1.5% by weight of hydrocarbon propellant and 3.0% by weight of halogenated hydrocarbon propellant is required for adequate foaming of the present soap solutions. The maximum amount of propellant is limited by solubility in the soap solution and by practical considerations of foam quality.

The soaps herein are generally termed "amine soaps" and are produced by the association of certain amines, to be described, and fatty acids. The soap solutions herein will contain from 7.5 to about 30 weight percent soap, the sum of the fatty acid and amine components establishing the soap concentrations.

As the fatty acid component of these soaps there is employed one or more members of the class of unsubstituted, saturated and unsaturated straight or branch chain monocarboxylic primary fatty acids, containing major amounts of C₁₂ to C₁₈ chain length acids. These acids are neutralized in the known manner with particular amines to produce soaps useful herein. Specific acids include coconut fatty (lauric) acids and stearic acid, particularly, and myristic, palmitic, oleic, linoleic and linolenic acids as well.

Useful amines are water soluble and are saturated aliphatic amines containing from 2 to 9 carbon atoms and in which no chain contains more than 4 carbon atoms. These amines may be primary, secondary or tertiary and preferably hydroxy-substituted. Specific examples of suitable amines include hydroxylated and nonhydroxylated amines such as butyl amine and pentyl amine, among the primary amines, secondary amines having preferably 4 to 6 carbon atoms such as methyl butyl amine and ethylpropyl amine and dipropyl amine, and tertiary amines having preferably 6 to 9 carbon atoms such as

triethylamine, tripropylamine and methyl-pentylpropyl amine. Preferably these amines have a single hydroxyl substituent and particularly one hydroxy group per branch e.g. as in ethylethanolamine or diethanolamine and triethanolamine but no more than one hydroxyl group for each two carbon atoms of the amine. It will be seen then that amines used for forming soaps in the present composition have the general structure



in which R₁ is an alkyl group or hydroxyalkyl group containing up to 4 carbon atoms, R₂ is a hydrogen atom or an alkyl or hydroxy alkyl group containing up to 4 carbon atoms and R₃ is a hydrogen atom or an alkyl group or hydroxyl alkyl group containing up to 4 carbon atoms with the proviso that the sum of the carbon atoms in R₁, R₂ and R₃ is always at least 2 and is less than 7 and preferably 5 or 6 when R₃ is hydrogen and less than 10 and preferably 6, 7, 8 or 9 when R₃ is an alkyl group or hydroxyalkyl group. Reference is made to Table III for a listing of additional suitable amines.

The compositions of the present invention may include in addition to water, propellant, amine and fatty acid other compatible, i.e. mutually soluble in the composition, materials for various purposes and in small, effective amounts. Thus colorants, dyes, thickeners and solubilizers, such as the polyols e.g. glycerine and alkylene glycols such as propylene glycol may be included in the composition. In addition water soluble fatty acid amides of various of the above amines e.g. of the fatty acids above listed may be added to facilitate achievement of a single phase system e.g. such materials as the coconut (or lauric) fatty acid amide of diethanolamine.

These additive materials have an effect on propellant solubility as illustrated in Tables I and II following.

In Table I aqueous solutions of various fatty acids at 4 weight percent neutralized with a 50 weight percent excess of diethanolamine were measured for propellant solubilizing properties with and without the addition of 2 weight percent of an amide additive, diethanolamine cocate 1-1 amide.

TABLE I
[Weight percent]

Fatty acid (4%)	Amine	Propellant	
		Without Amide	With amide
Stearic (98% C ₁₈)	2.25	1.40	3.54
Oleic (72% C ₁₈)	2.25	1.40	2.41
Stearic (50% C ₁₈)	2.35	1.38	2.03
Palmitic (20% C ₁₆)	2.50	1.15	1.82
Coconut	3.03	0.92	1.71

It will be observed that propellant solubility for soaps of all acids was increased by the use of the amide.

Various other additives typical of aerosol soap formulations have differing effects on propellant solubility. In Table II a neutral soap solution comprising in water 7.5 weight percent fatty acid and 6.8 weight percent triisopropanolamine is shown with various additives in typical concentrations and the weight percent hydrocarbon propellant soluble in the resulting solutions is given.

TABLE II
[Weight percent]

Additive	Additive	Propellant solubility
None		4.65
Lauryl dimethyl amine oxide	0.6	6.00
The 5 mole ethylene oxide adduct of lauric acid amide	5.0	4.92
Diethanolamine amide of Coconut fatty acid, 1-1 ratio	5.0	5.4
Propylene glycol	10.0	4.3
Glycerine	10.0	3.9

It will be observed that the diethanolamine amide and amine oxide additives increased propellant solubility while the ethylene oxide amide decreased propellant solubility somewhat and the polyols glycerine and propylene glycol further decreased propellant solubility.

The invention will be further described in conjunction with the attached drawings. In general FIGS. 1-3 illustrate that within the various possible combinations of amine, propellant and fatty acid certain combinations afford clear, homogeneous compositions in water. It is surprising, in view of teachings previously in the art that these component materials form emulsions, e.g. U.S. Pat. 2,655,480 referred to above, to find a limited zone within a ternary graph in which all materials are mutually soluble. From the FIGS. 1-3, it is apparent that the zone of mutual compatibility lies on the amine side of the neutral point (N) and at less than one-half the possible propellant concentration. A considerably larger area of mixture lies on the acid side of the neutral point but this is the emulsion area as indicated and is apparently the area in which previous formulations have worked. The emulsions obtained are stable and opaque but foamable.

The compositions of interest in this invention are those to the right of the neutral point, those having no greater than an amine neutralizing amount of acid and indeed often substantially less than an amine neutralizing amount of acid. It has been found that the excess of amine should be that sufficient to dissolve solid fatty acid in the composition.

While not wishing to be bound to any particular theory, fatty acid free and solid in the composition is believed to be the result of the propellant, on being added to the aqueous soap solution, lowering the dielectric constant of the solution and thus lowering the solubility of polar substances such as amines in the solution and reducing the ionization level of the amine. While this dielectric constant lowering increases the solubility of the acid in the solution the improvement is too small to be of any practical significance. Thus with reduced amine solubilization the fatty acid which was previously solubilized by association with amine prepipitates from the solution. In general the propellants contemplated herein are solvents for fatty acids, so as the fatty acids precipitate they may be immediately resolubilized by the propellant present. It may happen, however, that not all of the precipitated acid is thus resolubilized. In this event if solution clarity is to be maintained an excess of amine must be added over that normally, in the absence of propellant, required to neutralize the acid. It is true as FIGS. 4 and 5 reveal that additional amine lowers the solubility of the propellant in the solution, so too great an excess of amine must be avoided. The consequences of lowering propellant solubility can range from production of a separate phase of propellant in the composition as e.g. a supernatant layer thus eliminating most of the propellants from the composition, to the point of insufficient propellant for foaming on release from the pressurized container, unless shaken just before using.

With particular reference to FIG. 1 the effect of water concentration in the composition is shown. Line I contains 90% water, Line II 80% and Line III 60%, by weight. Otherwise than in proportions the composition is the same, a soap of an alkanolamine (e.g. triethanolamine) and a fatty acid (e.g. C₁₂) and a hydrocarbon propellant (propane-isobutane mixture). In each case the proportions affording clear soaps include at least substantially, a neutralizing amount of amine. At 60% water, line III (solid), the area ABCG is a single phase homogeneous and foamable soap composition. An increase in the water level to 80%, line II (dotted) enables clear solutions in the area ABCD and it will be noted a considerably greater compatibility zone of propellant and amine, for improved foaming characteristics. Further increases in water content to 90%, line I (dot-dash) reduces the area of complete compatibility to that indicated as ABFE. 75

FIG. 1 is arranged so that the amount of amine, Z, acid, Y, and propellant, X, is calculable once the percent amount of water is known.

In FIG. 2 it is shown that different acids will provide slightly different areas of mutual solution. Compare Area HJKL (oleic) and Area MNOP (coconut fatty acids). Line IV, oleic acid, is shown thus to be generally less variably formulable with hydrocarbon propellant and tertiary alkanol amine than coconut fatty acid, Line V.

In FIG. 3 the effect of using a Freon type propellant, (halogenated alkane e.g. dichlorodifluoromethane) line VI is compared with a hydrocarbon propellant, a mixture of isobutane and propane, line VII. It is shown that the area of compatibility is smaller with the Freon type propellants. Compare areas QRST (hydrocarbon) and UVWX (Freon-type).

In FIG. 4 the neutral points for a number of fatty acid-amine soap solutions are shown in line VIII against percent propellant soluble in the soap solution. It is evident that an increase in amine above the neutralizing amount relative to the fatty acid lowers the solubility of the propellant in the soap solution. Line IX indicates propellant solubility at 29 weight percent excess amine acid, line X propellant solubility at 73 weight percent excess amine. The dotted line in FIG. 4 is drawn along the threshold of foamable levels of propellant concentration. Compositions below the dotted line are not satisfactory in foaming characteristics, owing to too little propellant content.

In FIG. 5, the effect of excess amine in two specific soap solutions on propellant solubilities is shown. Line XI is drawn for a diethanolamine oleate soap solution. Addition of quantities of amine above the neutralizing amount (0 on the base) lowers solubility of the hydrocarbon propellant from 4.75% to about 3.6% in adding up to 60 weight percent excess amine. Line XII is drawn for a triisopropanolamine cocate soap solution. In this case the effect of excess amine is greater in lowering propellant solubility from about 4.5% in the neutral soap to about 2% at 70 weight percent excess amine.

The limitation on propellant solubility effected by the presence of excess amine may be used to advantage where it is desired to maintain within an aerosol container a layer of liquefied and undissolved propellant. Such a layer, if not agitated to emulsion with the soap solution, will be between the soap solution and the gaseous propellant in the head space and, as product is drawn from the container, the layer will vaporize with the accompanying enlargement of the head space volume to maintain pressure there without use of propellant from within the soap solution. In this manner uniform foams from first to last use of the container are realized, because the propellant level in the product is constant. The reserve layer will typically occupy 0.1 to 10% of the container volume. Close control over propellant levels can be secured by appropriate selection of amine. In Table III following there are tabulated the results of tests to determine the percent by weight soluble hydrocarbon propellant in solutions of coconut fatty acid (7.5%) soap with various amines at the neutral point.

TABLE III

Amine in 7.5% coconut fatty acid soap	Weight percent amine	pH	Soluble hydrocarbon
Monoethanolamine.....	2.20	9.45	3.06
Diethanolamine.....	3.75	8.90	2.72
Triethanolamine.....	5.36	8.43	4.95
Diisopropanolamine.....	4.75	8.70	3.78
Triisopropanolamine.....	6.80	8.17	4.60
Aminomethyl propanediol....	3.75	8.85	4.00
Aminomethyl propanediol....	4.25	8.98	4.32
Amino butanol.....	3.16	9.04	4.95
Aminomethyl propanol.....	3.16	9.30	3.86

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EXAMPLE 1

A clear homogeneous foamable soap solution was prepared by mixing together, in percent by weight

Triethanolamine	7.0
Coconut fatty acids	3.25
Oleic acid	4.0
Hexachlorophene	0.25
Water q.s.	96.5
Isobutane/propane (85/15)	3.5

under appropriate temperature and pressure conditions. On dispensing from a conventional aerosol package this clear solution burst into a highly useful foamed lather. The presence of hexachlorophene did not detract from the clarity of the solution.

EXAMPLE 2

A clear, homogeneous, foamable soap solution was prepared by mixing together, in percent by weight

Diethanolamine	3.3
Oleic acid	4.75
Coconut fatty acid	1.50
Diethanolamine coconut fatty acid amide (2 to 1)	2.00
Hexachlorophen	0.25
Halosalicylanilide	0.20
Water q.s.	96.00
Isobutane/propane (85/15)	4.00

under appropriate temperature and pressure conditions. On dispensing from a conventional aerosol package, this clear solution formed a highly useful soap foam. The presence of germicides and amide did not detract from the clarity of the solution.

EXAMPLE 3

A clear, homogeneous, foamable soap solution particularly useful as a shave cream was prepared by mixing together, in percent by weight

2-amino-2-methyl-1,3-propanediol	3.5
Stearic acid	6.0
Diethanolamine lauric acid amide	2.5
Propylene glycol	5.0
Ethylene diamine tetraacetic acid	0.1
Water q.s.	96.0
Isobutane/propane (85/15)	4.0

under appropriate temperature and pressure conditions. On dispensing from a conventional aerosol shave cream dispenser this clear solution formed a highly useful shaving lather.

EXAMPLE 4

Example 3 is duplicated using 7% dichlorodifluoromethane in place of the 4% hydrocarbon propellant. Results are equivalent.

EXAMPLE 5

Example 3 is duplicated but charging to the container 6% propellant an amount greater than that soluble in the soap solution to form a layer of liquefied propellant on top of the solution equal to about 1% of the container volume. The product was dispensed successively. The layer progressively vaporized to maintain head space pressure. Foam density was substantially constant from first to last discharge because no propellant was lost from the soap solution to the head space.

Prior to addition of the propellant to the above formulation solid stearic acid could be seen in the soap solution. Upon addition of the propellant, however, the solution clarified. This phenomenon demonstrates that in contrast with heretofore known aerosol soap packages in which three phases are present, namely an upper hydrocarbon rich phase, an intermediate soluble soap solution phase and a lower insoluble soap fraction (fatty acid) phase, the

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present invention provides a single liquid phase, free of insoluble soap fraction and under a gaseous hydrocarbon propellant. Thus although the fatty acid soap fraction is not soluble in the aqueous soap solution, on addition of propellant, which, in theory, lowers the solubility of the soap in aqueous solution, this fraction surprisingly is solubilized in the soap-propellant mixture, with resulting clarification of the entire formulation.

EXAMPLE 6

A clear homogeneous, foamable soap solution was prepared by mixing together, in percent by weight

Amino butanol	10
Coconut fatty acids	20
Water q.s.	96
Isobutane/propane (85/15)	4

under appropriate temperature and pressure conditions. This 30% soap solution was clear until release from a pressurized zone to foam into a satisfactory lather.

The term "soluble" or "solution" is used herein to refer to homogeneous, visually single phase, clear mixtures or the ability to form such. The term "water-soluble soap" refers to solubility in water in the mutual solution formulation described herein.

I claim:

1. An aerosol package containing a visually clear, homogeneous apparently single phase and foamable liquid soap composition for dispensing a soap foam without prior agitation which consists essentially by weight of

(1) from 60 to 90% water, and dissolved in the water,

(2) from 7.5 to 30% water soluble soap of an unsubstituted monocarboxylic fatty acid containing 12 to 18 carbon atoms inclusive and a water soluble primary, secondary or tertiary alkanol amine containing 2 to 9 carbon atoms with no more than 4 carbon atoms in a single chain, and dissolved in the aqueous soap solution,

(3) in an amount sufficient to foam the same on discharge thereof from said container a liquid normally gaseous propellant selected from saturated hydrocarbon propellants containing 1 to 4 carbon atoms and halogenated hydrocarbon propellants containing 1 to 2 carbon atoms and having chlorine or fluorine atom substituents or combinations thereof, said fatty acid, amine and propellant being present in amounts within the area ABCD of FIG. 1, provided that amount of said amine being present in said aqueous soap solution is in an amount at least equal to that required to neutralize said fatty acid when said amine is primary or secondary and in an amount greater than that required to neutralize said fatty acid when said amine is tertiary thereby to produce a visually clear composition.

2. An aerosol package according to claim 1 in which said propellant is a saturated hydrocarbon propellant.

3. An aerosol package according to claim 1 in which said propellant is completely substituted with chloro or fluoro groups or combinations of chloro and fluoro groups.

4. An aerosol package according to claim 1 in which said fatty acid is saturated.

5. An aerosol package according to claim 1 in which said fatty acid is ethylenically unsaturated.

6. An aerosol package according to claim 1 in which said amine contains not more than one hydroxyl group for each two carbon atoms.

7. An aerosol package according to claim 6 in which said amine contains at least one hydroxyl group for each four carbon atoms or fraction thereof.

8. An aerosol package according to claim 1, in which said amine is a tertiary amine.

9. An aerosol package according to claim 7 in which said amine is a tertiary amine.

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10. An aerosol package according to claim 1 in which said liquid phase propellant is present in said solution in an amount above about 1.5 weight percent for hydrocarbon propellants, and above about 3 weight percent for halogenated hydrocarbon propellants.

11. An aerosol package according to claim 1 in which said solution consists essentially of 80 to 90 weight percent water, said propellant is a hydrocarbon, said fatty acid contains 12 carbon atoms and said propellant, amine and fatty acid are present in amounts within the area ABEF of FIG. 1.

12. An aerosol package according to claim 1 in which said solution contains 60 to 80 weight percent water.

13. Aerosol package according to claim 1 including also a layer of liquefied propellant between the clear foamable soap composition and said gas phase propellant, said liquefied propellant layer being progressively vaporizable with successive discharge of the composition from the package to maintain gas pressure above said soap composition sufficient to maintain a constant amount of liquefied propellant in the said solution.

14. Aerosol package according to claim 13 in which said liquefied propellant layer occupies from 0.1 to 10 percent of the package volume.

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