

[54] **LIQUID DETERGENT COMPOSITIONS**

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[58] Field of Search.....**252/307, 312, 545, 158, 153, 252/155, 160**

[56] **References Cited**

**UNITED STATES PATENTS**

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[57] **ABSTRACT**

A liquid detergent composition is provided having an aqueous layer and a layer of a liquid water-immiscible oily material, which composition when shaken, forms a temporary oil-in-water emulsion. The aqueous layer contains a foam-producing water-soluble organic detergent, a non-emulsifying foam stabilizer, and water.

**7 Claims, No Drawings**

**LIQUID DETERGENT COMPOSITIONS****BACKGROUND OF THE INVENTION****1. Field of the Invention**

The present invention relates to liquid detergent compositions. In one aspect the invention relates to a multi-phase liquid detergent composition having an aqueous phase and a liquid, water-immiscible, oil material phase, which composition when shaken forms a temporary oil-in-water emulsion.

**2. Brief Description of the Prior Art**

In the liquid detergent field, such as shampoos, the present trend is to produce a multi-phase product which, when shaken, forms a temporary emulsion. In such formulations, the lower phase is an aqueous phase which contains the necessary cleaning ingredients, and the upper phase is an oil material which conditions the hair. Further, similar compositions are employed as bubble bath/bath oil compositions, the basic distinction between the shampoo formulations and the bubble bath/bath oil compositions being in the proportion of oil in the upper phase.

The multi-layer physical state of the composition referred to above is essential so that the compositions will produce foam in a product designed to have good skin and hair cleansing properties, and yet, in the case of the bubble bath/bath oil compositions leave an oily film upon the skin of the bather and, in the case of the shampoo formulation, leave a suitable amount of oil on the hair so that the hair will be manageable for grooming. A problem encountered in manufacturing such a product has been that the conventional active-foam booster ingredients normally used in shampoos and the like emulsify the oil so that a clean phase split does not occur between the aqueous phase and the oily material phase. In an effort to overcome these problems, de-emulsifiers have been used to prevent emulsification of the aqueous phase and oily material phase. However, such de-emulsifiers are not always effective and often inhibit the desirable properties of the product. For example, many of the de-emulsifiers employed in prior art liquid detergent compositions having a multi-phase product have inhibited the effectiveness of the foam booster incorporated in the composition resulting in a product not possessing desired foam properties. Thus, new formulations are constantly being sought wherein a liquid detergent formulation can be employed to produce a two-phase product, and yet at the same time, remove the need for the incorporation of ingredients such as de-emulsifiers which inhibit the effectiveness of the resulting products.

**OBJECTS OF THE INVENTION**

An object of the present invention is to provide an improved liquid detergent composition. Another object of the present invention is to provide an improved multi-phase liquid detergent composition which possesses effective cleaning properties as well as conditioning properties without suffering from the deficiencies of the prior art multi-phase liquid detergent compositions. Another object of the present invention is to provide a novel multi-phase liquid detergent composition which possesses a clean phase split between the aqueous and oily material phase without inhibiting the desired cleaning and conditioning properties of the liquid detergent composition. These and other objects,

advantages and features of the present invention will become apparent to those skilled in the art from a reading of the following detailed description.

**SUMMARY OF THE INVENTION**

According to the present invention there is provided a liquid detergent composition having an aqueous phase and a liquid, water-immiscible oily material phase, which composition, when shaken, forms a temporary oil-in-water emulsion. The aqueous phase consists of a foam-producing water-soluble organic detergent, a non-emulsifying foam stabilizer, and water.

Further, according to the invention, there is provided a liquid detergent composition having an aqueous phase and a liquid, water-immiscible oily material phase wherein the non-emulsifying foam stabilizer incorporated into the aqueous phase in a water-soluble salt of an acrylic acid polymer.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The liquid detergent compositions of the present invention include compositions which provide detergency and simultaneously provide for the deposition of a certain amount of oily material on the subject being cleaned. As previously stated, typical examples of such liquid detergent compositions are bubble bath/bath oil compositions and shampoo compositions. The duality of properties possessed by such a multi-phase liquid detergent composition is due to the fact that the compositions contain an oily phase and an aqueous phase which form temporary oil-in-water emulsions when shaken. The aqueous phase contains a foam-producing water-soluble liquid detergent, a non-emulsifying foam stabilizer and water. The oily phase, as the name implies, furnishes oily material which serves as a hair conditioning aid, in the case of shampoo formulations, and as a skin softener, in the case of the bubble bath/bath oil composition.

Although the liquid detergent compositions of the invention exist in the form of separate phases or layers that are shaken prior to use whereupon they form oil-in-water emulsions which are only temporary. However, this emulsion state enables the user to measure out the required amount of the composite compositions each time the liquid detergent compositions are used. The actual time required for the detergent composition to return to the layered or multi-phase state will be dependent on the actual formulation, but generally such phase splitting will occur within about 12 hours.

In order that the multi-phase liquid detergent compositions have the desired properties described above, it is essential that they contain four ingredients, namely, a water-immiscible oily material, a foam-producing water-soluble organic detergent, a non-emulsifying foam stabilizer, and water. As is evident, the foam-producing water-soluble organic detergent, the non-emulsifying foam stabilizer and the water constituents form the aqueous phase and the water-immiscible oily material forms the oily phase. The amounts of the various ingredients can vary widely and will be dependent upon the nature of the particular ingredients present, as well as upon the nature or use of the composition.

The multi-phase liquid detergent compositions preferably contain at least 5 percent by weight of one

or more water-immiscible oily materials. Although in certain cases amounts up to 50 percent may be used, the amount of oily material usually will not be more than 50 percent. In the composite shampoo/hair conditioning compositions the amount of oily material is desirably from 5 to 20 percent by weight, while in the composite bubble bath/bath oil compositions the amount of oily material will usually be at least about 20 percent by weight. The oily material serves as a skin softener or emollient and as a hair conditioner or hair grooming aid.

Typical suitable oily materials which can be employed to form the oily phase of the compositions of the present invention include light to heavy mineral or hydrocarbon oils, such as the light mineral oils having a Saybolt viscosity of 65-75 cps. 38° C and a specific gravity of 0.835 to 0.845 at 15.5° C animal and vegetable oils, such as linseed oil, castor oil, olive oil, cotton seed oil, safflower oil, almond oil, peanut oil, coconut oil, coconut oil fractions, cornoil, sesame oil, and brominated vegetable oils; synthetic oils which are fatty acid alkyl esters containing a total of from 16 to 22 carbon atoms, such as isopropyl myristate, isopropyl palmitate and isopropyl stearate; and lanolin compounds, such as the well-known lanolin esters and lanolin alcohols. Desirable results are obtained wherein the oily material is mineral or hydrocarbon oil, because of the sharpness of the interface which occurs between the oil phase and the aqueous phase. In addition, the oily phase should be liquid at room temperature, and preferably also at 0° C.

As previously mentioned, the aqueous phase of the multi-phase liquid detergent composition contains a foam-producing water-soluble organic detergent, a non-emulsifying foam stabilizer, and water. The amount of foam-producing water-soluble organic detergent employed can vary widely depending upon the particular formulation desired and its use. Generally, however, the foam-producing water-soluble organic detergent will be present in an amount within the range of from about 5 to 40 percent by weight, based on the total weight of the aqueous phase.

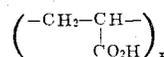
In the composite bubble bath/bath oil compositions the amount of the foaming organic detergent is preferably from 5 to 25 percent by weight, while in the composite shampoo/hair conditioning compositions the amount of the foaming organic detergent is preferably from 10 to 30 percent by weight.

The foam-producing organic detergent compositions which can be employed comprises one or more water-soluble non-cationic surface-active agents, i.e. an anionic, or amphoteric surfactant, or a mixture thereof, which produces acceptable foam. Preferred anionic detergents are sulfonated and sulfated anionic detergents and in particular the sodium, magnesium, ammonium, mono, di- and triethanolamine salts of sulfated fatty alcohols as well as these salts of the sulfonated alkylaryl compounds, all of which have a total of from 12 to 21 carbon atoms. Typical anionic detergents include sodium lauryl sulfate, sodium oleyl succinate, ammonium lauryl sulfosuccinate, sodium lauryl ether sulfate, ammonium lauryl sulfate, monoethanolamine lauryl sulfate, triethanolamine lauryl sulfate, sodium dodecylbenzene sulfonate, triethanolamine dodecylbenzene sulfonate and sodium N-lauroyl sarcosinate. Other

anionic detergents include triethanolamine alurate-myristate and triethanolamine oleate.

Amphoteric or ampholytic detergents include N-lauryl-N'-carboxymethyl-N'-(2-hydroxyethyl)ethylenediamine, coco-beta-alanine, and the Miranol compounds described in U.S. Pat. Nos. 2,528,378 and 2,781,354.

The second essential ingredient of the composition which is present in the aqueous layer is the non-emulsifying foam stabilizer. The amount of the non-emulsifying foam stabilizer can vary widely but is generally present in an amount of from about 2 to about 10 percent by weight based upon the total weight of the aqueous phase of the composition. Desirable results have been obtained wherein the non-emulsifying foam stabilizer is present in the amount of about 3 to 5 weight percent. The non-emulsifying foam stabilizers which can be employed in the composition of the present invention are the water-soluble salts of acrylic acid polymers. This acrylic acid polymers can be represented by the structural formula



wherein x is an integer from about 550 to about 2,250. The polymers are neutralized to form a salt and the cation constituent of the salt is selected from the group consisting of sodium, magnesium, ammonium, mono-, di-, and triethanolamine. Especially desirable results have been obtained wherein the salt is the sodium salt or the triethanolamine salt and the molecular weight of the resulting acrylate is from about 50,000 to about 150,000 with the lower molecular weight polymer being the most desired.

The third essential ingredient in the aqueous phase is water and the amount will vary depending upon the amount of the foam producing organic detergent and non-emulsifying foam stabilizer employed. In addition, the amount of water in the total composition will vary depending upon the amount of oily material present in the total composition.

While the compositions of the invention contained the above-mentioned ingredients, other compatible adjuvants can also be included therein. Thus the composition may, for example, contain one or more of the following: a perfume or essential oil, an oil-soluble or water-soluble dye, a germicide, a protein hydrolysate, and the like.

The compositions of the invention can be prepared merely by blending together the various ingredients. Usually the ingredients required to form the aqueous phase component of the composition will be blended together separately, and then admixed with the ingredients employed to produce the oily phase of the composition.

In order to more fully describe the invention the following examples are presented. However, it is to be understood that the examples are for illustrative purposes only and any enumeration or details contained therein are not to be interpreted as a limitation on the invention except as indicated in the appended claims. All parts and percentages of constituents referred to in the following examples are by weight unless otherwise indicated.

## EXAMPLE

A series of experiments were conducted on the novel multi-phase liquid detergent composition to determine its foam producing properties, the stability of the foam generated, and the compositions ability to form a clean phase split between the oily material phase and the aqueous phase. In each experiment triethanolamine lauryl sulfate was used as the foam-producing water-soluble organic detergent constituent, sodium polyacrylate, having a molecular weight ranging from 50,000 to about 150,000, was employed as the non-emulsifying foam stabilizer and the oily material constituent was light mineral oil or a blend of about one-third olive oil and two-thirds light mineral oil. The materials were then admixed to form a liquid detergent formulation having an 87 percent aqueous phase and a 13 percent oily material phase. The aqueous phase of the liquid detergent contained about 21 percent triethanolamine-lauryl sulfate. The amount of sodium polyacrylate was varied, as shown in the following table to determine concentration variables for same. Tests were then run by the standard shampoo test which measures the foam generation ability by the milliliters of foam and the stability of the foam as the time required for 75 milliliters of the liquid to draw from the foam. Therefore, the higher values of the foam generated and the longer the time required for the drainage are desirable and indicate a product having the desired foam and foam stability properties.

The standard shampoo test referred to above and utilized to test the novel liquid detergent formulation is as set forth hereinbelow. The amount of the ingredients was varied as shown in Table I.

## TEST PROCEDURE

1. Weight 10.0 and 25.0 grams of test shampoo into separate 150 ml Griffin low form glass beakers.

2. Mix synthetic sebum which has been allowed to return to room temperature with a metal spatula. The sebum is a synthetic soil to simulate actual conditions.

3. Distribute 3.0 grams of sebum around the sides of the 150 ml beaker taking care not to allow it to come into contact with the shampoo nor to come up so high in the beaker to be above the water level when it is introduced.

4. Premeasure 90, 85, 80 and 75 ml of water of the desired hardness (50 and/or 250 ppm) in four separate 100 ml cylinders.

5. Add the hard water to the following manner to result in the following concentrations of shampoo:

Conc.	Hard Water (Ml)	Shampoo (Grams in Beaker)
10%	90	10.0
25%	75	25.0

6. After adding the required amount of hard water, add a magnetic stirring bar and place sample on the Thermolyne Stir Plate. Set glass thermometer into sample. Stir at full speed with heater on thereby allowing the temperature to reach 100° F in 4 to 5 minutes.

7. While the sample is warming, rinse out a 500 ml glass cylinder and prewarm with 100° F tap water. Cylinder should contain the capped plastic tube filled with water.

8. Drain the 500 ml glass cylinder when sample temperature reaches 98° F.

9. Pour sample into 500 ml cylinder when temperature reaches 100 degrees F being careful not to allow the magnetic stirring bar to drop into the cylinder.

10. Attach the 500 milliliter cylinder to the rotator assembly to keep the cylinder in the perpendicular plane when rotating.

11. Rotate the cylinder a total of 20 complete circles (40 half circles) to generate foam. The rate at which the cylinder is rotated is critical. Consistent results are obtained if the rotations are completed within 35-45 seconds. It is also important to rotate at a constant speed. If difficulties are encountered, a Metronome should be used.

12. Start the stopwatch immediately upon completion of the rotations.

13. Remove the stopper and read the total foam volume (including liquid). Record this as the volume of foam generated.

14. Remove the 500 ml graduated cylinder from the rotator assembly gently and set it on the table top.

15. Stop the stopwatch when the liquid level reaches the 100 ml mark. (Actually, 75 ml have drained since the plastic cylinder displaces 25 ml of liquid). Record the time interval from the completion of the rotations to the point at which 100 ml of apparent liquid has drained as the drainage time.

16. The test results are recorded as ml of foam/drainage time in seconds.

Results of the test on the novel liquid detergent composition of the present invention are tabulated in Table I. The data clearly illustrate the utility of the novel detergent composition as a two-phase shampoo wherein sodium polyacrylate is employed as a non-emulsifying foam stabilizer. Further, the data illustrate the effectiveness of the sodium polyacrylate in giving a clean phase split between the oily material phase and the aqueous phase.

TABLE I.—POLYACRYLATE CONCENTRATION

Formulation:  
21% triethanolamine lauryl sulfate; Polyacrylate as shown in table—87%  
Q.s. water  
Oil (type shown)—13%

Test conditions:  
250 p.p.m. Hardness  
3 grams Sebum  
10 and 25% shampoo

Run No.	Polyacrylate			Foam/drainage time, ml./sec.				Phase split	
	Molecu- lar wt.	Cation	Percent	$\frac{1}{2}$ olive oil, $\frac{2}{3}$ lt. mineral oil		Lt. mineral oil			
				10%	25%	10%	25%		
(1).....	60-1B	-----	0	-----	150/<5	-----	-----	3-layer, middle layer ref. to as cuff.	
(2).....	65-1A	50,000	Na	2.0	-----	-----	175/11	275/91	Oil phase not homogeneous.
(3).....	65-B	-----	-----	-----	200/20	280/73	-----	-----	Good.
(4).....	65-2A	50,000	Na	3.0	-----	-----	250/35	320/138	Do.
(5).....	65-B	-----	-----	-----	290/58	360/165	-----	-----	Do.
(6).....	14-1A	50,000	Na	3.5	-----	-----	275/45	330/153	Do.
(7).....	14-B	-----	-----	-----	300/65	375/192	-----	-----	Do.

TABLE I—POLYACRYLATE CONCENTRATION—Continued

Formulation:  
 21% triethanolamine lauryl sulfate; Polyacrylate as shown in table—57%  
 Q.s. water  
 Oil (type shown)—13%  
 Test conditions:  
 250 p.p.m. Hardness  
 3 grams Sebum  
 10 and 25% shampoo

Run No.	Polyacrylate			Foam/drainage time, ml./sec.				Phase split	
	Molecu- lar wt.	Cation	Percent	1/3 olive oil, 2/3 lt. mineral oil		Lt. mineral oil			
				10%	25%	10%	25%		
(8).....	65-3A	50,000	Na	4.0			250/60	340/167	Do.
(9).....	65-B				300/75	375/225			Do.
(10).....	65-4A	50,000	Na	5.0			225/96	325/254	V. large top layer.
(11).....	65-B				275/56	335/269			Good.
(12).....	65-5A	150,000	Na	1.7			225/32	230/82	Oil phase not homogeneous.
(13).....	65-B				220/28	275/106			Do.
(14).....	65-6A	150,000	Na	2.5			240/51	260/200	Good.
(15).....	65-B				275/66	260/186			Do.
(16).....	65-7A	150,000	Na	3.4			275/87	330/213	Do.
(17).....	65-B				265/77	225/202			Do.
(18).....	65-8A	150,000	Na	4.2			250/92	260/267	Oil phase not homogeneous.
(19).....	65-B				260/89	225/214			Do.
(20).....	65-9A	150,000	Na	5.4			235/150	235/450	V. large nonhomogeneous top layer.
(21).....	65-B				220/71	230/437			Do.
(22).....	186-1B	50,000	TEA*	3.0	190/15	225/27			Good.
(23).....	186-2B	50,000	TEA*	4.0	225/14	250/46			Do.
(24).....	186-3B	50,000	TEA*	5.0	235/25	250/56			Do.

\*Triethanolamine.

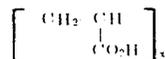
In addition to the above, experiments were conducted in which other types of water-soluble polymers were employed as the non-emulsifying foam stabilizer. These other types of water-soluble polymers were guar gum and ethylene maleic anhydride polymers. The formulation containing the guar gum was a thick gummy mixture showed no signs of splitting into two phases. The formulations containing the ethylene maleic anhydride copolymers produced three phase products at concentrations of both 2 and 5 weight percent.

Therefore, the above data clearly indicate that a multi-phase liquid detergent composition in which the aqueous phase contains a foam-producing, water-soluble organic detergent and a water-soluble salt of a polyacrylate possesses the desired foam and foam stability properties, as well as the desired phase splitting properties.

Having thus described the invention, I claim:

1. A liquid detergent composition having an aqueous phase and a liquid water-immiscible oily material phase which composition, when shaken, forms a temporary oil-in-water emulsion, said aqueous phase consisting essentially of a foam producing water-soluble, non-cationic organic detergent, a water-soluble neutralized salt of a polyacrylate having a molecular weight in the range of from about 50,000 to about 150,000 and water.

2. The composition of claim 1 wherein the poly portion of said water-soluble neutralized salt of a polyacrylate is represented by the formula



wherein x is an integer of from about 550 to about 2,250 and the cation constituent of said neutralized salt is selected from the group consisting of sodium, magnesium, ammonium, and mono-, di-, and triethanolamine.

3. The composition of claim 2 wherein said cation constituent is selected from sodium and triethanolamine.

4. The composition of claim 2 wherein said composition contains from about 5 to about 50 percent by weight of said water-immiscible oily material and from about 95 to 50 percent by weight said aqueous phase, said aqueous phase containing from about 5 to about 40 percent by weight of said foam-producing water-soluble organic detergent and from about 2 to about 10 percent by weight said water-soluble neutralized salt of said polyacrylate.

5. The composition of claim 4 wherein said water-immiscible oily material is present in an amount of at least 20 percent, said oily material being selected from the group consisting of mineral oils, and blends of mineral oils and vegetable oils, and said aqueous phase contains from about 5 to 25 percent of said foam-producing, water-soluble detergent and from about 3 to 5 percent of said water-soluble neutralized salt of said polyacrylate.

6. The composition in claim 4 wherein said water-immiscible oily material is present in an amount of about 5 to 20 percent, said oily material being selected from the group consisting of mineral oils, and blends of mineral oils and vegetable oils, and said aqueous phase contains from about 10 to 30 percent of said foam-producing, water-soluble detergent and from about 3 to 5 percent by weight of said water-soluble neutralized salts of said polyacrylate.

7. The composition of claim 6 wherein said oily material is present in an amount of about 13 percent, said aqueous phase is present in an amount of about 87 percent and the detergent constituent is triethanolamine lauryl sulfate and is present in an amount of about 2.1 percent.

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