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## DETERGENT FOR HARD WATER

Robert D. Aylesworth, Glendale, Ohio, assignor to Emery Industries, Inc., Cincinnati, Ohio, a corporation of Ohio

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This invention relates to soap compositions for use in hard water.

Soaps, as a general term, are the sodium, potassium, and sometimes the ammonium salts of fatty acids. The fatty acids employed in soap making are generally those obtained by splitting the glyceryl esters which constitute the animal, vegetable, and marine fats and oils. The adverse effects of hard water on soaps are well-known and include the scum formed in the wash bowl, the tendency to turn textiles a greyish color when repeatedly washed in hard water, and the so-called "bath tub ring."

These undesirable effects result from the reaction of the water soluble or colloiddally water soluble sodium or potassium soaps with the calcium and magnesium salts present in hard water to form the insoluble and often sticky calcium and magnesium soaps. These insoluble soaps may become dispersed when soap is used in excess of the amount required to react with the hardness of the water. However, they again flocculate during rinsing operations due to the introduction of additional hardness by the rinse water and the reduction of soap concentration.

The inability of soaps to withstand hard water has encouraged the development of synthetic detergents. These are usually sulfonated materials which have been formulated to be resistant to precipitation by hard water. They have found wide acceptance for many types of detergent applications but have not been readily adapted for the production of detergents in bar form, such as toilet soaps.

The compounds causing hardness in water can also either be precipitated by the use of inorganic water softening agents or inactivated by organic sequestering agents. Such methods are inconvenient to apply. In the case of the inorganic softeners, the water must be treated prior to the introduction of the soap. The sequestering agents, which are relatively expensive, must be used in quantities sufficient to react with the hardness and their use is usually impractical and uneconomical.

It is the purpose of this invention to provide fatty acid soap compositions which may be used in hard water without encountering the disadvantages of ordinary fatty acid soaps. Although the compositions of my invention may be used in any type of soap, that is, granular, flake or built soaps, it is particularly the purpose of this invention to provide compositions which are adaptable to the production of bar soaps which are hard-water resistant.

I have discovered and determined that quaternary ammonium compounds, when employed with the normal fatty acid soaps, prevent the formation of the objectionable sticky soap scum which normally accompanies the use of conventional fatty acid soaps in hard water.

This result is highly unexpected in that it has been generally assumed that the quaternary compounds, which are cationic, are inherently incompatible in water solution with fatty acid soaps, which are anionic compounds. Thus in Thomssen, E. G., and McCutcheon, J. W., "Soaps and Detergents" (1949) on page 408 the following statement

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is found: "(quaternary ammonium compounds) are not compatible with soap nor with anion synthetic detergents. A consideration of the ions involved will show why this is true. The large portion of the quaternary compound being positively charged will combine with the large negatively charged portion of the anion active material giving an insoluble precipitate."

Also Schwartz, A. M., and Perry, J. W., "Surface Active Agents," 1949, page 151 states "In general the cationic and anionic surface active agents will mutually precipitate when brought together in aqueous solution. This is due to the formation of the high molecular weight, poorly ionizable salt of the hydrophobic anion and the hydrophobic cation."

These statements are typical of those found throughout the literature. However, contrary to these reports, I have found that soaps and quaternary compounds are compatible and will give clear, sparkling solutions in distilled water, provided that the amount of quaternary employed is limited. Generally, the quaternary should not be more than 25% by weight of the amount of soap present or 20% of the soap quaternary mixture.

For example, a 4% solution in distilled water of the quaternary compound, para di isobutyl phenoxy ethoxy ethyl di methyl benzyl ammonium chloride, which is sold under the trade name "Hyamine 1622" and a 4% solution of the potassium soap of coconut oil are both practically water white clear solutions. When 80 parts of the quaternary solution and 20 parts of the soap solution are mixed, a cloudy liquid results which separates into two layers on standing. Likewise when 50 parts of each solution are mixed, the mixture becomes milky in appearance but when 80 parts of the soap solution and 20 parts of the quaternary solution are mixed, the combined solutions remain clear and free-flowing.

A similar phenomenon is observed at higher concentrations except that the higher ratios of quaternary form pastes rather than cloudy liquids while the low ratios of quaternary to soap continue to yield clear solutions. Thus, I have determined that compatible systems of soap and quaternary can be obtained by controlling the ratio of quaternary to soap. I have further determined that these compatible systems may be used in hard water without producing the gummy soap scum which results when soap alone is used.

I have also found that all surface active quaternaries within certain molecular weight limits possess this property, some to a greater degree than others, but all have a beneficial effect, whereas it would be expected that quaternaries would aggravate the problem, that is, they would tend to increase precipitation rather than to prevent it.

If ordinary soap is added slowly to hard water, it will be observed that the first small addition of soap results in the formation of a cloudy precipitate, as more soap is added the precipitate becomes heavier and with only slight agitation the precipitate will generally agglomerate and form a curd which floats on the surface and then attaches itself to the container at the water line. During this time no suds are produced. As the addition of soap is continued, precipitation will continue until sufficient soap has been added to react with all of the hardness. On further addition of soap, suds will be formed and with violent agitation at least a part of the sticky agglomerate can be dispersed.

When appropriate combinations of soap and quaternary are added to hard water, a precipitate forms, but it is very finely dispersed and produces a silky appearance, or a slight cloudiness. As additional amounts of the mixture are added, the solution may become more opaque, but even with strong agitation no agglomeration occurs and

there is no film adhering to the walls of the container. During the operation a slight suds is produced; the suds is neither heavy nor permanent but the solution is sudsy, not inert and covered with a floating scum. Further additions of the quaternary soap mixture result in the formation of a heavy permanent suds.

A great many quaternaries have been tested for effectiveness in preventing scum formation. Those which are too low in molecular weight are not effective, presumably because they are too water soluble to possess good surface active properties. Those which are too high in molecular weight or are difficultly water soluble are less effective probably because of their lack of sufficient water solubility. The quaternaries which are effective are the water-soluble quaternaries ranging in molecular weight from 175 to 600. Quaternaries within this molecular weight range which have been tested and found effective include a wide variety of cationic groups combined with an equally wide range of anions. The quaternaries derived through tertiary amine derivatives from long-chain amines, such as lauryl, cetyl, and stearyl amine quaternized with alkyl or aryl halides, phosphates, or sulfates, are effective. For example, lauryl di methyl benzyl ammonium chloride, cetyl tri-methyl ammonium bromide, cetyl di methyl benzyl ammonium chloride, cetyl di methyl ethyl ammonium bromide, lauryl dimethyl 3,4 di chloro benzyl ammonium chloride, octa decyl di methyl benzyl ammonium chloride, lauryl tri methyl ammonium chloride, stearyl tri ethyl ammonium di ethyl phosphate, stearyl tri ethyl ammonium ethyl sulfate, lauryl di methyl ethyl ammonium ethyl sulfate, stearyl di methyl ethyl ammonium di ethyl phosphate, and lauryl di-ethyl methyl ammonium di ethyl phosphate.

The nitrogen can also be part of a ring as in N cetyl N ethyl morpholinium sulfate, or other polar groups may be in the molecule, as para di isobutyl phenoxy ethoxy ethyl di methyl benzyl ammonium chloride.

Quaternaries which have good effectiveness and also have excellent color stability may be obtained by reacting fatty acids with substituted diamines and quaternizing the resulting product with a variety of quaternizing agents. Examples of this type of quaternary which have been investigated include (3-stearamido propyl) di methyl ethyl ammonium ethyl sulfate, (3-lauramido propyl) di methyl ethyl ammonium ethyl sulfate and similar compounds derived from oleic acid and pelargonic acid. In place of di ethyl sulfate, tri ethyl phosphate and benzyl chloride have been employed as quaternizing agents.

A fourth class of compounds are those derived from di amines in which ring closure has been effected to produce an imidazoline ring. Typical products which have been tested include [1-ethyl 2-heptadecenyl 3(B amino ethyl)] imidazolinium di ethyl phosphate, [1-ethyl 2-heptadecyl 3-(B amino ethyl)] imidazolinium ethyl sulfate, [1-ethyl 2-octyl 3(B hydroxy ethyl)] imidazolinium di ethyl phosphate. Similar compounds have been made with various combinations of stearic, oleic and pelargonic acid and sulfate or phosphate quaternizing agents and di ethylene tri amine or amino ethyl ethanol amine as typical 1-2 diamines.

All products of this type were effective in preventing the formation of soap curd in hard water but in many cases, color and stability of color were rather poor.

Still another class of compounds tested were the mono esters of tri ethanol amines which had been quaternized with di ethyl sulfate, methyl p. toluene sulfonate tri ethyl phosphate or benzyl chloride. These products, if within the molecular weight range, were also effective dispersing agents.

The quaternaries tested have included a wide variation in the cationic portion of the molecule with the valencies of the penta valent nitrogen being satisfied by aliphatic groups or combinations of aliphatic and aromatic or other closed ring structures. The anionic groups may include chlorine, bromine, sulfate and phosphate radicals. An

almost infinite variety of combinations is possible and since all combinations exhibit similar behavior, it would appear that the physical or colloidal properties of the compounds rather than their chemical structure is controlling.

It is, of course, necessary to consider other properties such as color, odor, stability of color, physical form, i. e., whether solid or liquid, and cost in selecting a suitable quaternary for use with soap. The characteristics desired in the finished soap should also be considered, that is, whether the soap is to be produced as a concentrated liquid soap such as a shampoo or as a bar of toilet soap. A liquid quaternary or one which gives a thin water solution would be more suitable for the former application, while a solid quaternary would be more suitable in the latter case.

The quaternaries may be used with soaps produced from all types of soap-making ingredients including the soaps of fatty acids ranging in chain length from C8 to C22 carbon atoms, saturated and unsaturated, as derived from naturally occurring fats and oils or produced synthetically. The soaps of rosin and tall oil may be used, and fillers, builders, foam stabilizers and the additives normally employed in commercial soaps may be present. For example, I have found that the action of the quaternary is not diminished by the presence of alkaline materials such as soda ash or silicates, nor by sulfonated compounds such as those constituting the synthetic detergents.

The amount of quaternary which is compatible with soap varies to some extent, depending upon the molecular weight and solubility of both the quaternary and the soap. The maximum of quaternary to soap ranges from 10% with the high molecular weight soaps up to 25% with low molecular weight soaps. The low molecular weight quaternaries generally are more compatible than the higher molecular weight compounds. From 10% to 20% of quaternary to total soap-quaternary mixture on an anhydrous basis is required to provide resistance to scumming in hard water. Here again the soaps of higher molecular weight acids, such as those derived from tallow, generally require somewhat more quaternary to provide adequate resistance than do the soaps of the lower molecular weight acids, such as those obtained from coconut oil.

Soap compositions containing quaternary compounds produce more suds than similar compositions in the absence of quaternary when the soaps are used in quantities less than is required to react with the hardness of the water. However, when quantities in excess of that required to react with the hardness of the water are used, the lathering and sudsing characteristics may be somewhat less than similar compositions without the quaternary would produce. If it is desired to maintain lathering and sudsing characteristics, it may be desirable to alter the soap composition by incorporating a somewhat higher proportion of coconut soaps which increase the lathering characteristics.

Although the results of my invention are readily observed, the mechanism involved has not been fully explained. It is believed, however, that the quaternary compounds function as dispersing agents for the calcium and magnesium soaps. Since they themselves are not precipitated by hard water, they function under hard water conditions, and being surface active, contribute to the sudsing and detergent action of the soap. This explanation, which is offered for the benefit of those skilled in the art, is intended only as an initial hypothesis.

My invention is more fully illustrated by the following examples:

#### EXAMPLE 1.—COMPATABILITY OF SOAPS AND QUATERNARIES

4% distilled water solutions were prepared of—

- A. Potash soap of coconut oil
- B. Quaternary 1. lauryl di methyl benzyl ammonium chloride

### C. Quaternary 2. para di isobutyl phenoxy ethoxy ethyl di methyl benzyl ammonium chloride.

All solutions were clear. When 20 cc. of either quaternary B or quaternary C were added to 80 cc. of the soap solution, clear fluid liquids resulted. However, when equal quantities were mixed, cloudy solutions resulted and when 20 cc. of soap and 80 cc. of quaternary were used, cloudy solutions which separated into two layers, resulted.

When 15% solutions were used, the 50% concentrations of quaternary in soap resulted in the formation of pastes while 10% of quaternary and 90% of soap solution yielded clear fluid liquids.

The results show that quaternaries are compatible with soaps at the lower quaternary-to-soap ratios.

#### EXAMPLE 2

(a) 1500 ml. of warm tap water (295 p. p. m. hardness, as  $\text{CaCO}_3$ ) was placed in a 2-liter beaker. The hands were wetted in this water and 5 ml. of a 15% potash soap of coconut oil were applied to the hands in such manner as to enable formation of a good lather by normal procedure. Drippings were caught in the water in the beaker. After formation of good lather, the suds were thoroughly rinsed from the hands by submerging in the water in the beaker. The resulting solution was characterized by lack of suds and by the presence of a heavy surface scum, which tended to creep up on the sides of the beaker to form a typical tacky, water-repellent, "bath tub ring" deposit.

(b) The same procedure was followed, using 5 ml. of 15% solution of a blend of 20% quaternary ammonium salt [3 stearamido propyl di methyl ethyl ammonium ethyl sulfate] and 80% potash soap of coconut oil (instead of the 5 ml. of straight coconut oil soap as in Example 2(a)) for lather formulation.

The resulting solution was characterized by the presence of suds and by the absence of curd and scum such as had formed in absence of quaternary ammonium salt. The sides of the beaker remained clean, and there was no tendency for an adherent deposit to form.

#### EXAMPLE 3

Solutions were prepared at 0.125% concentration in water of 100 p. p. m. hardness, of blends of 20% various quaternary ammonium salts with 80% potash soap of coconut oil.

The degree of turbidity of the solutions was determined (after standing) using a Hellige Turbidimeter (10 ml. sample of solution). The tests were made on solutions which had not been subjected to shaking action, since shaking results in flocculation when soap alone is used and abnormally high readings are obtained.

The turbidity readings obtained are shown in Table I:

Table I.—Turbidity readings

[0.125% concentration, 20% QA salt—80% soap, 100 p. p. m. hardness]

#### QUATERNARY

| Material                        | Molecular Weight | Anion                | Turbidity Reading |
|---------------------------------|------------------|----------------------|-------------------|
| Distilled water (Blank)-----    |                  |                      | 4                 |
| Soap only-----                  |                  |                      | 31                |
| 80% soap, 20% Quaternary 1----- | 263              | Chloride-----        | 15                |
| 80% soap, 20% Quaternary 2----- | 339              | do-----              | 14                |
| 80% soap, 20% Quaternary 3----- | 376              | do-----              | 16                |
| 80% soap, 20% Quaternary 4----- | 404              | Bromide-----         | 16                |
| 80% soap, 20% Quaternary 5----- | 466              | Sulfate-----         | 17                |
| 80% soap, 20% Quaternary 6----- | 534              | Ethyl Phosphate----- | 21                |

#### Quaternary:

1. Lauryl tri methyl ammonium chloride.
2. Lauryl di emthyl benzyl ammonium chloride.
3. Para di isobutyl phenoxy ethoxy ethyl di methyl benzyl ammonium chloride.
4. Oleyl di methyl ethyl ammonium bromide.
5. N-cetyl N-ethyl morpholinium sulfate.
6. Amino ethyl ethanol stearamide alkylated with triethyl phosphate.

The low turbidity of the solutions containing quaternary ammonium salts shows that quaternary ammonium salts of widely varying composition and molecular weight are effective in suppressing precipitation of "hard water soap" from solution. Such effect is further shown by the fact that little change occurs with the solutions containing quaternary ammonium salt if they are shaken, whereas separation of flocculent material and formation of curd occurs when solution of the soap solution containing no quaternary ammonium salt, is shaken.

#### EXAMPLE 4.—VARIATION IN TYPE OF SOAP

.0625% solution of the potassium soap of coconut oil, a 50/50 blend of the potassium soap of coconut oil and potassium soap of tallow, and straight potassium soap of tallow were prepared in water of 100 p. p. m. hardness. Similar concentrations were prepared of mixtures of 80% of the same soaps and 20% of a quaternary consisting of lauryl di methyl benzyl ammonium chloride, which is known as Roccal, a trade name. The solutions were examined, showing:

|                      | Coconut Soap      | 50% Coconut Soap, 50% Tallow Soap | Tallow Soap      |
|----------------------|-------------------|-----------------------------------|------------------|
| 100% soap-----       | Curd and scum.    | Curd and slight scum.             | Curd and scum.   |
| 80% soap—20% Roccal. | Curd but no scum. | Slight curd but no scum.          | No curd or scum. |

NOTE.—Scum is the tacky, water-repellent precipitate which tends to adhere to glass, etc. surfaces ("bath tub ring"). The curd noted above is a flocculent material, readily redispersed and having no tendency to adhere to glass surface.

#### EXAMPLE 5

Toilet bar soaps were prepared as follows:

(a) From 100% coconut fatty acid soap.—728.2 parts of coconut oil fatty acid (Emery E-622) were heated to about 60° C. and charged into a stainless steel reactor which was equipped with a suitable baffle and stirrer. A solution of 135.3 parts of caustic soda in 236.5 parts of water, at 60° C. was added slowly but steadily to the heated fatty acid, regulating the rate of stirring to maintain good mixing. The formation of soda soap was accompanied by an increase in temperature to about 100° C. Mixing was continued after the caustic solution had been added and the temperature was held at 90° to 100° C. (If desired, perfume is added at this stage.) When the hot soap paste had acquired a uniform nature, it was transferred to suitable soap frame. When cooled, the soap slab was cut into bars, having the composition of approximately 71.3% soda soap, 2% FFA and 26.7% water.

(b) From 90% coconut fatty acid soap and 10% quaternary ammonium salt.—Soap was prepared in similar manner to contain about 10% quaternary ammonium compound on the weight of the solids. A mixture of 658.7 parts of coconut fatty acids (Emery E-622) and 80.7 parts of a quaternary ammonium compound was heated to about 65° C. and charged into the reactor. The quaternary ammonium compound may be either dissolved or dispersed in the fatty acids. A solution of 121.9 parts of caustic soda in 238.7 parts of water at about 65° C. was added slowly to the heated fatty acid-quaternary ammonium salt blend while stirring. The procedure was continued as with (a). The resulting soap bars had a composition of approximately 64% soda soap, 2% FFA, 7.3% quaternary ammonium salt and 26.7% water.

Samples of each type of soap, i. e. with and without quaternary ammonium salt incorporated, but identified only as A and B, were used by 21 individuals for routine tub bathing in city water having a hardness of approximately 200 parts per million as calcium carbonate.

The comparative rating of the soaps which considered primarily the presence or absence of observable precipitated soaps and/or of adherent deposits on the wash bowl

or tub but in addition the general overall performance, resulted in the following rating:

|                             | Excel-<br>lent | Good | Fair | Poor | Very<br>Poor |
|-----------------------------|----------------|------|------|------|--------------|
| Soap A (No quaternary)----  | 1              | 3    | 3    | 11   | 3            |
| Soap B (With quaternary)--- | 10             | 11   | 0    | 0    | 0            |

The quaternary ammonium compound used in this particular case was (3-stearamido propyl) dimethyl ethyl ammonium ethosulfate. Many other water soluble surface active quaternary ammonium compounds have been found effective when used in similar manner.

The benefits of the quaternary addition were evident to non-technical people under conditions of actual use.

Having described my invention, I claim:

1. A bar of soap consisting essentially of a homogeneous mixture of 80-90% by weight of the sodium salts of fatty acids of from 8-22 carbon atoms chain length and from 20-10% by weight of a water soluble quaternary

ammonium compound having a molecular weight of between 175 and 600, said soap composition being resistant to precipitation by hard water.

2. The method of preventing the precipitation of fatty acid soaps in hard water which comprises homogeneously combining 10-20% quaternary ammonium compound having a molecular weight of between 175 and 600 with fatty acid soap constituted by the sodium salts of fatty acids of from 8-22 carbon atoms chain length, the said proportion of quaternary ammonium compound being based upon the weight of the total homogeneous soap composition.

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