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DETERGENT COMPOSITION FOR USE IN
HARD WATER

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This invention relates to water softening agents and more particularly to water softening agents for use in association with alkali metal-fatty acid soap compounds.

One object of the invention is to provide a water softening agent which, in addition to being reactive as a deionization agent towards the usual water hardening compounds, is also reactive as an electrolyte-carrier and is compatible and miscible in all proportions with alkali metal-fatty acid soap compounds, in their hydrous or anhydrous state, thereby to form detergent compositions utilizable in hard, saline or hard-saline water.

Another object is to provide a deionization and electrolyte-carrying agent compatible with alkali metal-fatty acid soap compounds in the solid or liquid phases or in aqueous solution.

Still another object is to provide an alkali metal salt of an aliphatic amino-polycarboxylic acid possessing in aqueous solution deionization properties towards water hardening salts and electrolyte-carrying properties towards neutral salts such as strong electrolytes and which is miscible with alkali metal-fatty acid soap compounds in all proportions either in their dry or liquid phases or in aqueous solution.

Other objects will be apparent as the invention is more fully hereinafter disclosed.

In accordance with these objects I have discovered that the acid-alkali metal salts of the aliphatic amino-polycarboxylic acids are non-electrolytes towards the alkali metal-fatty acid soap compounds and are electrolyte-carriers towards strong electrolytes normally reactive to insolubilize or "salt-out" the said soap compounds in aqueous solution as well as being strong deionizing agents and that these said acid-alkali metal salts of the said amino acids are miscible in all proportions with alkali metal-fatty acid soap compounds in their hydrous or anhydrous forms.

Heretofore in the art, as exemplified by Munz Patent No. 2,240,957 issued May 6, 1941, the use of the aliphatic amino-polycarboxylic acids and the alkali metal salts of said acids as a deionization agent in hard waters in association with water soluble soap compounds has been disclosed. I have found, however, that whereas these acids and the alkali metal salts of these acids are excellent deionization agents for hard waters they are not utilizable in association with water soluble soap compounds of the alkali metal-fatty acid type for the reason that the amino acid reacts with the alkali metal-fatty acid soap compounds to insolubilize the same as free fatty acids while the alkali metal salts of these amino acids, in

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aqueous solution, hydrolyze and liberate free caustic alkali which is a strong electrolyte operating to "salt-out" the said alkali metal-fatty acid soap compounds from aqueous solution, when present in any great concentration therein.

I have found that the addition of enough of the free amino acid or of the alkali metal salt of said acid to even moderately hard water to deionize the said water is generally sufficient to cause extensive insolubilizing of the alkali metal-fatty acid soap compounds and that neither the amino acid nor the alkali metal salt of the acid is miscible with the alkali metal-fatty acid soap compounds in their solid or liquid anhydrous phases or in concentrated aqueous solution. This limits the utility of these amino compounds materially as such compounds may not be added to or incorporated in concentrated hydrous soap solutions or mixed with anhydrous soap compounds to form bar, flake, powder products or liquid soap compositions.

After extensive investigation I have discovered that in aqueous solution the amino acid, for example, ethylene diamine tetracarboxylic acid, and caustic alkali form a plurality of acid-alkali metal salts having more than two (2) but less than four (4) of carboxylic acid groups neutralized by the alkali, which acid-alkali metal salts are stable in aqueous solution. These acid-alkali metal salts are not recoverable from aqueous solutions as anhydrous compounds, and in aqueous solution are non-electrolytes towards alkali metal-fatty acid soap compounds and act as strong electrolyte-carriers towards neutral electrolytes, such as sodium chloride, and sodium sulfate, which normally react to insolubilize or "salt out" alkali metal-fatty acid soap compounds. In addition these acid-alkali metal salts of the amino acid are highly reactive towards basic oxides, hydroxides and carbonates to deionize the same and are completely miscible in all proportions with alkali metal-fatty acid soap compounds (hydrous or anhydrous) to form detergent compositions therewith that are utilizable with all types of hard, saline and hard-saline water.

As one specific embodiment of the present invention, but not as a limitation thereof, the invention will be described as it has been adapted with respect to the acid-alkali metal salts of ethylene diamine tetracarboxylic acid, one of the plurality of amino polycarboxylic acids disclosed in the above identified Munz patent, it being understood, however, that any of the aliphatic amino-polycarboxylic acids known in the art and disclosed in said Munz patent as an equivalent

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for ethylene diamine tetracarboxylic acid, which have more than two (2) carboxylic acid groups therein, may be substituted for ethylene diamine tetracarboxylic acid without departure from the present invention.

Ethylene diamine tetracarboxylic acid may be prepared in a number of different ways. It is best prepared by the method disclosed and claimed in my co-pending application Serial No. 491,669 filed June 21, 1943, which is assigned to the same assignee as the present invention. By the practice of the invention of said copending application I first obtain an aqueous solution consisting principally of the tetra alkali metal (sodium) salt of ethylene diamine tetracarboxylic acid. The free amino acid is recovered from this solution by acidifying the solution with a strong mineral acid, such as HCl or H₂SO₄, to a pH approximating pH 1.6. At this pH the free amino acid is of low solubility in the highly concentrated sodium chloride or sulfate solution and precipitates out as a white crystalline powder. The free amino acid is insoluble in cold water and may be washed free of the mother liquor with cold pure water on a suction filter.

In accordance with the present invention, the aqueous solution of the acid alkali metal salt of the free acid is prepared in the following manner:

One molar weight of the free acid and three molar weights of a caustic alkali (NaOH or KOH) are added to one liter of pure water and the mixture is heated for an extended time interval until a clear solution is obtained. The pH of the clear solution is adjusted by additions of the free acid or of caustic alkali thereto, as may be required, to obtain a pH within the range 7 pH to 9.5 pH.

My experiments have indicated that the pH of the acid-trisodium salt of ethylene diamine tetracarboxylic acid approximates 7.4 in aqueous solutions of this concentration. The pH of the tetrasodium salt of this acid approximates 10.5 and the pH of the acid-disodium salt approximates 3.8. For the purposes of the present invention, namely, to provide a deionizing and electrolyte-carrying agent which is compatible with alkali metal-fatty acid soap compounds in their solid and liquid phases and miscible therewith in aqueous solutions, I have found that any of the acid-sodium salts which in molar strength solution have a pH within the range 7 to 9.5 are satisfactory but I prefer to closely approximate a pH of about 8.

In the production of detergent compositions consisting of a mixture of alkali metal-fatty acid soap compounds and the acid-alkali metal salt of the present invention, the amount of the deionizing and electrolyte-carrying acid-salt of the present invention that is added to the soap compounds varies with respect to the hardness and to the amount of electrolyte present in the water in which the detergent is to be used. As an illustration, in hard water of the type known generally as from moderately hard to hard, I have found that about 5% (based on the weight of the soap compounds) of the above acid-sodium salt of ethylene diamine tetracarboxylic acid, calculated from the estimated dry weight of the salt in the molar weight solution obtained above, is sufficient to soften the water so that the soap compounds are freely functionable therein as a detergent.

An aliquot portion of the molar weight aqueous solution of the acid-trisodium salt of ethyl-

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ene diamine tetracarboxylic acid containing the desired dry weight of the said salt may be added to a concentrated aqueous solution of the alkali metal-fatty acid soap compounds to form a soap solution utilizable in the laundry trade, for example, as a stock soap solution; or, alternatively may be added to soap stock, solid or liquid, and following thorough admixture therewith may be formed into bar, flake, powder or liquid soap products by any of the methods heretofore employed in the art.

Where soap solutions of bar, flake, powder or liquid soap products utilizable in very hard water, or in water containing large amounts of strong electrolytes, are desired, the amount of the acid-trisodium salt of ethylene diamine tetracarboxylic acid incorporated therein may be increased to as high as 25% without detrimentally effecting the detergent properties of the soap compounds in the water. In general, I have found 10% (by weight) of the acid-trisodium salt to be adequate in most very hard water and in water containing moderate amounts of strong electrolytes such as sodium chloride or sodium sulfate. In hard and saline water, such as sea water, I have found that 20 to 25% (by weight) of the acid-trisodium salt is preferable.

It is believed apparent, from the above disclosure that many modifications and departures may be made in the above disclosed invention without essential departure therefrom. In place of ethylene diamine tetracarboxylic acid, for example, any of the aliphatic amino polycarboxylic acids heretofore identified as deionization agents for hard water, may be substituted without departure from the present invention, particularly those having more than two carboxylic groups attached directly to amino nitrogens which, in aqueous solution, form acid-alkali metal salts having a pH within the range 7 to 9.5 as hereinabove disclosed with respect to the acid-alkali metal salts of ethylene diamine tetracarboxylic acid. All of these amino acids and the alkali metal salts of these acids react similarly to ethylene diamine tetracarboxylic acid insofar as forming acid-salts of the type herein described that are stable only in aqueous solution. None of the acid-alkali metal salts of these acids have heretofore been either recognized or utilized as deionization agents or have been produced with sufficient purity to permit the study and identification of their particular chemical properties, such as herein described.

As an alternative procedure to the practice hereinabove disclosed, the acid-trisodium metal salt of the present invention may be produced in the following manner:

To an aqueous solution of the tetrasodium salt of ethylene diamine tetracarboxylic acid, containing one molar weight of the salt per liter, heated to elevated temperatures up to the boiling point of the solution, ethylene diamine tetracarboxylic acid is added, until a pH within the range 7 to 9.5 is obtained. In this reaction one molar weight of the free amino acid normally is sufficient to lower the pH of the solution from a pH of about 10.5 to a pH of about 8, which is approximately the pH of the trisodium salt of ethylene diamine tetracarboxylic acid. The solution thus obtained is then diluted to obtain a molar weight solution of the acid-trisodium salt of ethylene diamine tetracarboxylic acid for convenience in handling and in calculating the aliquot portions thereof for use in mixing with soap compounds or soap solutions.

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Various other organic and inorganic acids may be employed in place of the ethylene diamine tetracarboxylic acid in the above alternative procedure without essential departure from the present invention, the strong electrolyte-carrying properties of the acid-trisodium salt being such as to render innocuous any neutral electrolyte salts formed by the use of such acids.

Various other modifications and departures will occur to those skilled in the art and all such are contemplated as may fall within the scope of the following claims.

What I claim is:

1. A detergent composition for use in hard waters, in water containing strong electrolytes, and in hard and saline waters, said composition consisting of a mixture of alkali metal-fatty acid soap compounds and 5% to 25% of the acid-tri-alkali metal salt of ethylene diamine tetracarboxylic acid.

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2. A detergent composition for use in very moderately hard to hard water, said composition consisting of a mixture of alkali metal-fatty acid soap compounds and about 5% of the acid-tri-alkali metal salt of ethylene diamine tetracarboxylic acid.

3. A detergent composition for use in very hard water and in water containing moderate amounts of strong electrolytes, said composition consisting of a mixture of alkali metal-fatty acid soap compounds and about 10% of the acid-tri-alkali metal salt of ethylene diamine tetracarboxylic acid.

4. A detergent composition for use in hard and saline water, said composition consisting of a mixture of alkali metal-fatty acid soap compounds and about 20 to 25% of the acid-tri-alkali metal salt of ethylene diamine tetracarboxylic acid.

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