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DETERGENT COMPOSITIONS OF SOAP AND A UREA-OLEFIN-SULFURIC ACID CONDENSATION PRODUCT

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ABSTRACT OF THE DISCLOSURE

Detergent compositions comprising soap and a water-soluble salt of an urea-olefin-sulfuric acid condensate. The olefin is either butadiene or a mixture of a major amount of butadiene and a minor amount of cyclopentadiene, unhindered tertiary mono-olefin, 2-alkyl-1,3-butadiene, or mixtures thereof. The detergent composition may also contain an inorganic detergent builder.

The present invention relates to novel detergent compositions and, more particularly, to detergent compositions comprising soap and synthetic detergent.

Water-soluble soaps are well known and have been used for many years in industry and for domestic washing and cleaning purposes. Soaps have a number of advantageous properties when used in soft water, among which are low cost, high detergency, lubricating and softening properties which improve the handling of yarns and the feel of textile materials, and good surface active properties, valuable in dyeing operation. To a certain extent soaps may serve as their own water-softening agent, but in the main the advantages of soap enumerated above are not available in hard water and are outweighed by certain disadvantages.

The use of soap alone in hard water results in the conversion of at least part of the soap into insoluble, usually, calcium and/or magnesium salts of the soap acids, commonly referred to as lime soaps. Such precipitated lime soaps tend to coagulate into sticky curds which deposit on containers such as washbowls, bath tubs, and laundry tubs and on fabrics, particularly in rinsing operations where dilution of the soap becomes great enough to destroy its foaming and dispersing power. In addition, fabrics containing the lime soap deposits will yellow upon ironing. A similar deposit of lime soap curds also occurs in the hair when soap is employed as a shampoo in hard water. These lime soap curds not only have no cleansing properties but, as impurities, must be dispersed by the remaining unconverted soap, thus reducing the amount of soap available for cleaning. A relatively larger amount of soap must thus be used for effective cleaning in hard water, the economic advantage of soap being thereby greatly lessened. Accordingly it is an object of the present invention to overcome the aforementioned problems and disadvantages.

Another object of the present invention is to provide relatively inexpensive soap compositions which are effective washing agents when used in hard water.

Another object of the invention is to provide soap compositions which have the desirable cleaning and softening properties of soaps and which may be used in hard water without displaying the objectionable curd-forming properties of soaps.

A further object of the invention is to increase the resistance of detergent-containing soap compositions to precipitation of lime soaps when used in hard water and to coagulation thereof to form curds which cling to and dull textiles, which form a dull film on the hair in shampooing, and which leave sticky deposits in laundry tubs, washbowls, etc.

A further object is to provide novel compositions comprising soap and synthetic detergent.

A still further object is to provide novel compositions comprising soap, synthetic detergent and inorganic builder.

The above and other objects will be apparent in the following description and in the appended claims.

Detergent compositions which fulfill the foregoing objects comprise soap and a synthetic detergent which is the water-soluble salt of an urea-olefin-sulfuric acid condensation product.

The condensation products of the present invention are condensates of urea, sulfuric acid, and olefin, wherein the olefin is either 1,3-butadiene or a mixture of a major amount of 1,3-butadiene and a minor amount of cyclopentadiene, unhindered tertiary mono-olefin, 2-alkyl-1,3-butadiene, or mixtures thereof, preferably at least 75 mole percent of the olefin being 1,3-butadiene.

The term "unhindered tertiary mono-olefin" as used herein denotes tertiary mono-olefins in which carbon atoms alpha, beta, and gamma to the tertiary olefinic carbon atom are free of side chain carbon. Typical examples of unhindered tertiary mono-olefins are isobutylene, 2-methyl-1-pentene, 2-methyl-2-butene, 2-methyl-1-butene, 2-methyl-2-pentene, 3-methyl-2-pentene, 2-methyl-1-hexene, 2-methyl-2-hexene, and the like. The preferred unhindered tertiary mono-olefin is isobutylene.

The 2-alkyl-1, 3-butadiene is one wherein the alkyl group is unbranched and contains from 1 to 3 carbon atoms, that is diolefins of the formula

$$CH_2=CR—CH=CH_2$$

where R is an unbranched alkyl group containing from 1 to 3 carbon atoms. Examples of such diolefins are 2-methyl-1, 3-butadiene (isoprene), 2-ethyl-1, 3-butadiene, and 2-propyl-1, 3-butadiene. The preferred 2-alkyl-1, 3-butadiene is isoprene.

Although the amount of urea, olefin, and sulfuric acid used to prepare the condensation products can vary widely, the preferred condensates are those which contain on an average, per urea residue, from about 2 to about 50 diolefin residues, from about 0.1 to about 1.5 sulfate groups, and from about 0.1 to about 10 carbon to carbon double bonds.

The condensation products are used in the form of their water-soluble salts. Of these, the alkali metal (e.g. sodium and potassium) and ammonium salts are preferred though other salts, such as amine and alkanol amine, can be used if desired.

The condensation products of the present invention and suitable methods for their preparation are fully described in copending application Ser. No. 419,201 filed Dec. 17, 1964, the disclosure of which is incorporated herein by reference. Briefly the condensation products are prepared by reacting butadiene, alone or in admixture with 2-alkyl butadiene, cyclopentadiene, or unhindered tertiary mono-olefin, with a solution or suspension of urea in concentrated sulfuric acid and neutralizing the resulting product.

These condensation products contribute both detergency and lime-soap dispersability to the compositions. In illustration of the lime-soap dispersing power of the condensates, it has been found that as little as 1 gram of the sodium salt of a condensation product of urea, butadiene, and sulfuric acid is sufficient to maintain about 7–10 grams of calcium oleate in finely-divided dispersion in 200 parts per million hard water at 25° C. The alkali metal salts of condensation products of urea, butadiene isobutylene, sulfuric acid have similarly been observed to be effective lime soap dispersants under similar conditions.

The soap used in the compositions of the present in-

vention may be any of the well-known soaps having surface active properties exemplified by the alkali metal salt of a higher fatty acid or mixture of fatty acids, such as sodium stearate, potassium palmitate, sodium laurate, sodium oleate, or an alkali metal salt of the mixed fatty acids obtained by saponifying natural fats and oils such as tallow, palm oil, coconut oil, and the like.

The amounts of soap and condensation product incorporated in the compositions of the present invention can vary widely and depends to a large extent on the particular conditions under which the compositions are to be used and on economic considerations. Excellent results have been obtained with compositions wherein the proportion of soap to condensation product ranges from about 3:1 to about 50:1.

In addition, detergent compositions in accordance with the invention may contain a minor proportion of any of the conventional inorganic detergent builders. The term "inorganic detergent builder" is well known in the art and refers to various inorganic compounds which promote detergent action. Builders which can be used in the detergent compositions of the present invention include alkali metal carbonates such as sodium carbonates, alkali metal bicarbonates, condensed phosphates such as potassium pyrophosphate and sodium polyphospate, silicates such as sodium silicate, and the like. Additives such as water softeners, wetting agents, ion sequestering agents, optical brighteners or chemical bleaching agents, antiredeposition agents, such as carboxymethyl cellulose and sodium carboxymethyl cellulose, foaming agents, and the like can also be used. The specific builders and additives and the amounts thereof employed in the detergent compositions of the present invention can vary widely and depends to a large extent on economic considerations and on the particular conditions under which the detergent compositions are utilized.

The following examples illustrate the manner in which the invention may be practiced, but it is to be understood that such details are given merely for exemplification purposes and are not to be construed as limiting the scope of the appended claims. Unless otherwise indicated, the proportions are expressed in parts by weight.

Example I

80 parts of sodium stearate and 20 parts of the sodium salt of a sulfated butadiene-urea condensate prepared from 3 moles of butadiene, 1 mole of urea, and 1.5 moles of sulfuric acid and having an acid number of 14, and iodine number of 132, a melting point of 105–114° C., 4.96% nitrogen, and 5.24% sulfur, both in the forms of dry solids, are placed in a high speed household type blender and blended until the finely particulated material is an even light yellow color. The blend is completely soluble in water and has excellent detersive properties.

Example II

80 parts of the sodium salt of mixed tallow acid and coconut oil fatty acid in the proportions of about 85 to 15 weight percent, as obtained by saponifying a corresponding mixture of tallow and coconut oil, and 20 parts of the potassium salt of a sulfated 9:1 butadiene-isoprene-urea condensate, prepared from 3.6 moles butadiene, 0.4 mole isoprene, 1 mole of urea, and 1.5 moles of sulfuric acid and having an acid number of 8.6, and iodine number of 171, 3.30% nitrogen, and 4.80% sulfur, are placed in a household high-speed blender as in Example I and blended to a finely particulated light yellow powder.

Example III

70 parts of granular sodium stearate, 10 parts of sodium carbonate, and 20 parts of the sodium salt of a sulfated 19:1 butadiene-isobutylene-urea condensate, prepared from 3.8 moles of butadiene, 0.2 mole of isobutylene, 1 mole of urea, and 1.5 moles of sulfuric acid and having an iodine number of 154 and 3.92% nitrogen, are blended in a household high-speed blender as in Example 1. The detergency of this blend is tested by the standard Terg-O-Tometer method on standard soiled cotton cloth in 200 parts per million (p.p.m.) hard water at 120° F. at a total detergent blend concentration of 0.25 weight percent. The increase in reflectance of the washed test cloth is 102% relative to that of standard test cloth washed in a standard detergent taken as 100% (15% Ultrawet K, a standard commercial sodium dodecylbenzenesulfonate, 35% sodium tripolyphosphate, 10% sodium metasilicate, 39% sodium carbonate, 1% carboxymethylcellulose sodium salt).

Example IV

Similarly to Example 3, 70 parts of standard sodium soap, 10 parts of sodium carbonate, and 20 parts of the sodium salt of a sulfated 9:1 butadiene-isobutylene-urea condensate prepared from 3.6 moles butadiene, 0.4 mole iosbutylene, 1 mole of urea, and 1.5 moles of sulfuric acid, are blended in a household high-speed blender to give a light yellow built soap-detergent powder.

Example V

70 parts of standard sodium soap granules, 25 parts of sodium tripolyphosphate, and 5 parts of sodium salts of sulfated 3.5:1 butadiene-cyclopentadiene-urea condensate, prepared from 3.1 moles butadiene, 0.9 mole cyclopentadiene, 1 mole urea, and 1.5 moles sulfuric acid, are blended in a household high-speed blender to give a light yellow finely powdered built soap-detergent blend.

Example VI

80 parts of sodium soap, 15 parts of sodium carbonate, and 5 parts of the sodium salt of sulfated butadiene-urea condensate, prepared from 3 moles of butadiene, 1 mole of urea, and 1.5 moles of sulfuric acid, are blended in a household high-speed blender to give a light yellow finely powdered built soap-detergent blend. The detergency of this blend is tested by the method of Example 3, the increase in reflectance of the washed test cloth being 102% relative to that of test cloth (reflectance increase taken as 100%) washed under the same conditions with the standard detergent of Example 3.

Example VII

70 parts of sodium soap, 20 parts sodium carbonate, and 10 parts of sodium salt of sulfated butadiene-urea condensate, prepared from 3 moles of butadiene, 1 mole of urea, and 1.5 moles of sulfuric acid, are blended in a household high-speed blender to give a finely-powdered built soap-detergent blend. In the detergency test performed in the manner of Example 3, the relative increase in reflectance of the standard test soiled cotton cloth washed with this blend is 103.4%.

Example VIII

67.5 parts of sodium soap, 4.5 parts of sodium sulfate, 25 parts of tetrasodium pyrophosphate, and 3 parts of sodium salt of sulfated butadiene-urea condensate, prepared from 3 moles of butadiene, 1 mole of urea, and 1.5 moles of sulfuric acid, are blended in a household high-speed blender to give a light yellow powder. In the detergency test as in Example 3, the relative increase in reflectance of standard test soiled cotton cloth washed with this soap-detergent blend is 106.8%.

The yellowing or graying of fabrics on repeated laundering with soap is known to be due, at least in part, to the accumulation of deposited lime soap residues in the fabric. Such yellowing or graying is largely prevented when detergent compositions of the invention are substituted for soap as the following comparative test shows.

Unsized, bleached scoured white cotton cloth was cut into 4-inch squares. The squares in groups of 4 were dried for 1 hour at 85° C. in a forced air oven to simulate conditions in a clothes dryer. The yellowness index (YI) of the groups of squares was determined by measuring

the reflectance first with the green, then the amber, then the blue filter in a reflectometer:

$$YI = \frac{\text{amber reflectance minus blue reflectance}}{\text{green reflectance}}$$

An increase in the YI indicates increasing yellowness and a decrease indicates increasing blueness. The groups of squares were then washed in 200 p.p.m. hard water with 0.25% soap or soap-polymer blend in the bath by the standard Terg-O-Tometer procedure. After each washing and 2 rinses, the cloths were dried at 85° C. for 1 hour then ironed with a household iron set at 250° C. Four passes of 1–2 seconds each were made on each side of the cloths. The YI was again determined. The wash-dry-iron cycle was repeated for a total of 10 cycles. Results of the tests are given below in Table I.

TABLE I

No. of Wash-Dry-Iron Cycles	Yellowness Index (YI)	
	Soap (Ivory Snow)	Product of Example VII
0	0.025	0.022
3	0.050	0.026
5	[1] 0.076	[2] 0.068
7	[3] 0.115	[1] 0.074
10	[4] 0.107	[1] 0.088

[1] Visually slightly yellow, nearly white.
[2] Visually faintly yellow, nearly white.
[3] Visually light yellow.
[4] Visually definite light yellow-gray.

Thus the compositions of the invention have been shown to possess unique properties. They are excellent lime soap dispersants, have high detergency, and have a tendency to cause a minimum amount of yellowing of fabrics in wash-dry-iron cycling when used under standard washing conditions.

The above examples and description are to be taken as only illustrative of the invention and a number of its preferred embodiments and it is to be understood that many further variations and modifications of the invention may be made by those skilled in the art without departing from the scope and spirit of the invention which are defined in the appended claims.

What is claimed is:

1. A detergent composition consisting essentially of soap and water-soluble salt of an urea-olefin-sulfuric acid condensation product wherein the proportion of soap to said water-soluble salt of an urea-olefin-sulfuric acid condensation product is from about 3:1 to about 50:1, said condensation product being prepared by (1) forming a suspension of urea and from 0.75 to 3.0 molar proportions of a sulfuric acid solution containing from 85 to 105 percent by weight of equivalent H_2SO_4 in an inert organic diluent; (2) introducing into the said suspension, with continuous agitation and at a temperature of from −10° C. to 70° C., from 0.8 to 10 molar proportions of an olefin selected from the group consisting of 1,3-butadiene and a mixture of a major proportion of 1,3-butadiene and a minor proportion of a member selected from the group consisting of cyclopentadiene, unhindered tertiary mono-olefins, 2 alkyl-1,3-butadiene wherein the alkyl group is unbranched and contains from 1 to 3 carbon atoms, and mixtures thereof; (3) and recovering the condensation product from the reaction mixture, all of said molar proportions being per molar proportion of urea.

2. The detergent composition of claim **1** wherein the soap is an alkali metal salt of higher fatty acid.

3. The detergent composition of claim **2** wherein the said water-soluble salt is an alkali metal salt or ammonium salt.

4. A detergent composition consisting essentially of a major proportion of the composition of claim **3** and a minor proportion of an inorganic detergent builder.

5. The detergent composition of claim **4** wherein the inorganic detergent builder is selected from the group consisting of alkali metal carbonates, alkali metal bicarbonates, alkali metal condensed phosphates, alkali metal silicates, and mixtures thereof.

6. The detergent composition of claim **5** wherein the urea-olefin-sulfuric acid condensation product is prepared by (1) forming a suspension of urea and from 0.75 to 3.0 molar proportions of a sulfuric acid solution containing from 85 to 105 percent by weight of equivalent H_2SO_4 in an inert organic diluent; (2) introducing into the said suspension, with continuous agitation and at a temperature of from −10° C. to 70° C., from 0.8 to 10 molar proportions of a mixture of a major proportion of 1,3-butadiene and a minor proportion of a member selected from the group consisting of a 2-alkyl-1,3-butadiene wherein the alkyl group is unbranched and contains from 1 to 3 carbon atoms, unhindered tertiary mono-olefin, and cyclopentadiene; (3) and recovering the condensation product from the reaction mixture, all of said molar proportions being per molar proportion of urea.

7. The detergent composition of claim **6** wherein the said mixture consists of a major proportion of 1,3-butadiene and a minor proportion of isobutylene.

8. The detergent composition of claim **7** wherein the alkali metal salt of fatty acid is selected from the group consisting of sodium stearate, potassium palmitate, sodium laurate, sodium oleate, alkali metal salt of tallow fatty acid, alkali metal salt of coconut oil fatty acid, and alkali metal salt of palm oil fatty acid and the said mixture is a mixture of 1,3-butadiene and isobutylene in the ratio of 19 to 1.

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