Patented Dec. 4, 1945 2,390,295

UNITED STATES PATENT OFFICE

2,390,295

SOAP COMPOSITION

Lawrence H. Flett, Hamburg, N. Y., assignor to Allied Chemical & Dye Corporation, a corporation of New York

No Drawing. Application July 19, 1941, Serial No. 403,235

12 Claims. (Cl. 252—121)

This invention relates to soap compositions. It relates more particularly to soap compositions adapted for general detergent use in hard water as well as in salt water (for example, sea-water) and in acid aqueous solutions.

The water-soluble soaps are well known detergents and surface-active agents and find use for many purposes in industry, particularly the textile industry, and for domestic and toilet purposes. The term "water-soluble soap" is used herein in the broad sense including curd soaps, rosin curd soaps, soft soaps, sulfonated oil soaps and the like, which in general are salts of higher fatty acids (containing from 10 to 20 carbon atoms) with alkali metals, ammonia or suitable organic amines (for example methylamine, triethanolamine, etc.). The water-soluble soaps have a number of advantageous properties which render them desirable for use in certain connections. Thus, ordinary soaps of good quality are efficient washing agents for most materials in soft water; they have lubricating and softening properties which improve the handling of yarns and the feel of textile materials that have been washed with their aid; and they have a slippery feel and lathering properties which are popularly associated with washing agents for toilet purposes.

In regions where only hard water is available, or for uses in sea-water or in acid aqueous solutions, the disadvantages of such soaps outweigh their advantages. Thus, if soap alone is used for washing in hard water, at least a portion of the soap is converted into a calcium soap which precipitates in the form of sticky curds. These curds not only have no cleansing properties but they constitute impurities that must be dispersed by a part of the unconverted soap thereby reducing the amount of soap available for cleansing; so that, for effective washing in hard water, a relatively large quantity of soap is required and the economic advantage of soap as a washing agent is largely reduced. Further, a scum is formed which adheres to the tubs, sinks and washing machines as well as to the goods, chinaware, glassware, etc.

If the usual alkaline water softeners are used with soap, they require heating of the water and an additional item of cost is introduced without materially increasing the cleansing efficiency of the resulting solution; since, while these water softeners act to disperse grease, they are not good washing agents for removing solid dirt. Also, a cleansing solution containing such water softeners is strongly alkaline and therefore has an undesirable effect upon the hands of the user and upon delicate fabrics. Another disadvantage noticed in connection with the use of alkaline water softeners is the fact that their softening action does not extend to the rinsing operation. When a textile material that has been washed in a hard water solution of a soap and an alkaline water softener is rinsed with hard water, the calcium salts in the water react with the soap in the material to form insoluble soaps that are difficult to remove.

It has heretofore been proposed to overcome the disadvantages of water-soluble soaps by mixing with them wetting agents which are resistant to hard water and acids; that is, wetting agents whose free acids and calcium and magnesium salts are soluble under the conditions of use. Thus, according to U. S. P. 1,730,037 to Gunther and Nusslein, aromatic sulfonic acids possessing a high wetting power, and particularly isopropylated and butylated naphthalene sulfonic acid salts, are added to soaps and baths containing them for the purpose of increasing their stability to hard water and acid solutions. Such sulfonic acid compounds have the disadvantages, however, that they do not adequately disperse the soap precipitates, especially in connection with rinsing in hard water; and they increase considerably the cost of the soap compositions. Since the said aromatic sulfonic acids contribute little, if any, to the washing action of the soap, the same amount of soap is required as is used in the absence of the wetting agent. Owing to the fact that the cleansing properties of solutions of the resulting compositions are not sufficiently superior to those of soap alone to justify the added cost of the wetting agents, such compositions, if used at all, are used only in special applications.

An object of the present invention is to provide relatively inexpensive soap compositions which are effective washing agents when used in hard water, sea-water and acid solutions. A further object of the invention is to provide soap compositions which have the desirable softening properties of soap and which may be used in hard water, sea-water and acid aqueous solutions without displaying the objectionable properties of soaps, which compositions possess a detergent action substantially greater than that resulting from the soap component of the composition.

Other objects of the invention in part will be obvious and in part will appear hereinafter.

It has been discovered in accordance with the present invention that an efficient soap compo-

sition is obtained, which is materially superior to an ordinary soap for cleansing in hard water, sea-water and acid aqueous solutions, by incorporating with a water-soluble soap, and especially a water-soluble salt of a higher fatty acid (containing 10 to 20 carbon atoms), a limited amount of a particular type of mixture of alkyl aromatic sulfonates identified more fully below. As a feature of the present invention it has been discovered that the said mixtures of alkyl aromatic sulfonates have the advantageous properties of preventing "lime soap" curds and related insoluble fatty acids and salts from depositing from aqueous suspensions thereof, while being themselves effective detergents and washing agents in hard water, sea-water and acid aqueous solutions. Thus, I have made the surprising discovery that when a limited amount of a said mixture of alkyl aromatic sulfonates is added to an ordinary water-soluble soap and the resulting soap composition is employed for example for washing wool in hard water, instead of sticky curds being formed a fine suspension of material of a crystal-like nature is formed which material is prevented from depositing on the goods by the mixture of alkyl aromatic sulfonates.

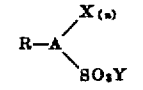
As another feature of the present invention it has been found that the advantages flowing from the combination of a soap with a said mixture of alkyl aromatic sulfonates can be obtained with the use of a relatively small amount of the mixture. This makes possible the preparation of compositions composed of a major proportion of an ordinary soap which are nevertheless adapted for efficient use under conditions where soap alone cannot be used. For example, it has been discovered that the addition of as little as 5 parts by weight of a mixture of alkyl aromatic sulfonates of the type hereinafter described to 100 parts by weight of an ordinary soap produces an admixture which has the advantages of soap without having the disadvantages of soap, especially when used in hard water, sea-water and acid aqueous solutions.

Since the soap compositions of the present invention have the advantageous property of preventing soap deposits in goods washed with soap, when goods washed with the soap compositions of the present invention are rinsed with hard water, the presence of the mixtures of alkyl aromatic sulfonates in the goods along with the soap prevents the formation of soap deposits from the rinse water.

The advantages of the improved soap compositions are further shown by the washing results obtained with them. China and glassware cleaned with the compositions of the present invention have a clear, sparkling appearance. Textile goods are whiter and have a smooth, soft feel. When used as a toilet soap, the compositions of the present invention possess improved lathering power in hard water without loss of the soapy feel and other characteristics associated with soap.

The mixtures of aromatic sulfonates employed in accordance with the present invention are mixtures of substituted derivatives of aromatic sulfonates which contain not more than two benzene nuclei in the aromatic radical and of which a substituent in the aromatic radical or nucleus contains between 12 and 16 carbon atoms (both inclusive) and is derived from a poly-component, non-aromatic hydrocarbon mixture of the type of a petroleum distillate, and preferably of mineral origin, of which at least 80 per cent boils (distills) between 210° and 275° C. and over a maximum range of 55°. (Ranges herein stated include the limits. The term "a poly-component non-aromatic hydrocarbon mixture" as employed herein, means a hydrocarbon mixture, such as petroleum or a petroleum distillate or otherwise refined petroleum fraction, or other mixture of similar composition, containing straight and/or branched chain alkanes and which may also contain cycloalkanes and aryl hydrocarbons but does not contain more than 20 per cent of aryl hydrocarbons. For convenience, the mixtures of substituted derivatives of aromatic sulfonates are referred to as "mixtures of alkyl aromatic sulfonates," the term "alkyl" being used in its broad sense to include straight or branched, open-chain aliphatic hydrocarbon radicals, as well as radicals derived from cycloaliphatic and aromatic-aliphatic hydrocarbons which may be present in the polycomponent hydrocarbon mixture.)

They are mixtures of water-soluble products represented by the general formula



wherein A represents an aromatic nucleus containing not more than two benzene nuclei which may be condensed or not (for example, a benzene nucleus, a naphthalene nucleus, a diphenyl nucleus, or a diphenyl oxide nucleus);

R represents an "alkyl" group which is directly attached to a carbon atom of the nucleus represented by A and which is derived from the hydrocarbon mixture and corresponds with a component thereof, the "alkyl" groups represented by R in the mixtures containing for the most part 12 to 16 carbon atoms with the average molecular carbon content falling within that range;

X represents a replaceable hydrogen of the aromatic nucleus represented by A or a substituent; such as, an alkyl group containing 1 to 8 carbon atoms, a hydroxyl group, an alkoxy or aralkoxy group containing 1 to 8 carbon atoms, or halogen;

n represents the numbers 1, 2 or 3; and

SO_3Y represents a sulfonate group which is attached to a carbon atom of the aromatic nucleus represented by A and in which Y is hydrogen or its stoichiometric equivalent of a salt-forming metal or radical; such as sodium, potassium, ammonium, alkyl ammonium, hydroxy alkyl ammonium and the like.

Thus the mixtures of alkyl aromatic sulfonates employed in accordance with the present invention may be derived from benzene, toluene, xylene, phenol, cresol, anisole, phenetole, chlorbenzene, diphenyl, hydroxydiphenyl, diphenyl oxide, naphthalene, alpha-naphthol, beta-naphthol, etc. Those derived from aromatic compounds of the benzene series, and especially benzene and phenol, are preferred. Ordinarily the sodium salts are preferred by reason of their lower cost.

Preferably, they are mixtures of monoalkyl derivatives of aromatic monosulfonates of the benzene series of which the alkyl groups are derived from a petroleum hydrocarbon mixture of which at least 80 per cent boils over a maximum range of 55° C. and between 210° and 275° C., and obtained by a process comprising chlorinating the petroleum hydrocarbon mixture to form

mixed alkyl chlorides, condensing resulting mixed alkyl chlorides with an aromatic hydrocarbon of the benzene series or a derivative thereof (particularly benzene or a phenol) to produce a mixture of alkyl derivatives of said aromatic hydrocarbon or derivative, and sulfonating a mixture of said alkyl derivatives.

The amounts of the mixtures of alkyl aromatic sulfonates and soap employed in accordance with the present invention may vary within limits. Thus, for some purposes, for example, for washing in water of limited hardness (e. g., less than 5° hard, American scale), as little as 5 parts of a said mixture of alkyl aromatic sulfonates per hundred parts by weight of soap may be employed while obtaining a decided improvement in the detergent properties of the soap. The proportions of soap are on a dry basis. The average ordinary soap contains about 15 per cent of water. With water of greater hardness (e. g., 10° or harder, American scale), the proportion of the mixture of alkyl aromatic sulfonates is preferably at least 10 parts per hundred parts by weight of soap. For general use, compositions are preferred containing from 25 to 54 parts by weight of a said mixture of alkyl aromatic sulfonates per hundred parts by weight of soap. In order to retain the essential characteristics of soap, the amount of the mixture of alkyl aromatic sulfonates should ordinarily not exceed 100 parts by weight per hundred parts by weight of soap. The most advantageous proportions of mixtures of alkyl aromatic sulfonates to soap depend somewhat upon the conditions of use and, to a lesser degree, upon the nature of the soap (e. g., a lesser amount is required with a soap derived from a fatty acid of lower molecular weight, such as a coconut oil soap, than is required with a soap derived from a fatty acid of higher molecular weight, such as a tallow soap).

It is noted that the mixtures of alkyl aromatic sulfonates as produced commercially may contain substantial amounts of inorganic salts. Such salt-containing sulfonates may be employed in accordance with the present invention. The above proportions are on the basis of salt-free mixtures of alkyl aromatic sulfonates. They refer to the organic constituents of mixtures of alkyl aromatic sulfonates containing inorganic salts in admixture therewith; so that in the case of soap compositions prepared with salt-containing mixtures, correspondingly greater amounts of the latter are employed. One of the advantages of the invention arises from the property of the said mixtures of alkyl aromatic sulfonates of imparting to the compositions the ability to hold salts and alkaline builders in amounts greater than would otherwise be suitable. Thus, not withstanding the presence of large amounts of sodium sulfate in mixtures of alkyl aromatic sulfonates useful in accordance with the present invention, soap compositions made therewith can be formed into bars without crumbling, as would be the case in the absence of the mixtures of alkyl aromatic sulfonates.

The mixtures of alkyl aromatic sulfonates may be prepared in various ways, a number of which are disclosed in my copending applications Serial Nos. 691,082, filed September 26, 1933, now U. S. Patent 2,249,757; 93,521, filed July 30, 1936, now U. S. Patent 2,283,199; and 257,720, filed February 21, 1939, now U. S. Patent 2,267,725, of which applications the present application is a continuation-in-part, and in my United States Patents 2,196,985 (of which applications Serial Nos. 93,521 and 257,720 are continuations-in-part); 2,223,364; 2,223,408; and 2,247,365. In preparing the mixtures of alkyl aromatic sulfonates for use in the present invention, in accordance with one preferred method of procedure, an aliphatic hydrocarbon distillate of the character described above is chlorinated or otherwise halogenated, for example, in accordance with known processes for the production of chlorinated or other halogenated derivatives of aliphatic hydrocarbons, whereby mixtures comprising chlorinated or other halogenated aliphatic hydrocarbons are produced; an aromatic hydrocarbon, or derivative, adapted to provide the desired aryl radical of the product is then converted to a mixture of alkyl aromatic compounds in which the alkyl groups correspond with hydrocarbons of the aliphatic hydrocarbon mixture from which it is produced, by a process including reaction of the aromatic compound with the mixed chlorinated or other halogenated aliphatic hydrocarbons, or with a selected portion thereof; the resulting mixture of alkyl aromatic compounds, or a selected portion thereof is then sulfonated with or without previous conversion to further derivatives thereof; and the resulting mixture of sulfonic acids is converted into a mixture of their corresponding salts. If inorganic salts are simultaneously formed, they may be left in the mixture of said sulfonic acid salts, or they may be separated therefrom, as the use of the product may determine.

The hydrocarbon mixtures employed as starting materials for the said mixtures of alkyl aromatic sulfonates are the non-aromatic hydrocarbon mixtures, and especially mineral oil distillates, of which at least 80 per cent boils (distills) over a maximum range of 55° C. (and preferably over a maximum range of 30° C.) and between 210° and 275° C. For the production of mixed alkyl aromatic sulfonates derived from aromatic compounds of the benzene series free from a solubilizing group other than the sulfo group, a hydrocarbon mixture of the above type is preferably employed of which at least 80 per cent boils between 210° and 265° C. Distillates of this type are believed to correspond with hydrocarbons containing mainly 12 to 16 carbon atoms per molecule.

The boiling point range of the hydrocarbon mixtures employed may vary with respect to the boiling point limits thereof; provided at least 80 per cent thereof, and preferably at least a middle 80 per cent thereof, has the boiling characteristics above referred to. Thus, hydrocarbon material of which the first 10 per cent boils considerably below the preferred lower limit and/or the last 10 per cent boils considerably above the preferred upper limit may be employed in accordance with the present invention, if it has the characteristics herein referred to.

The preferred hydrocarbon mixtures employed in accordance with the present invention are exemplified by fractions of Pennsylvania and Michigan (Mount Pleasant) petroleum distillates in the ranges mentioned above, and especially those whose boiling point limits are 210° and 290° C. These distillates consist essentially of open chain aliphatic (paraffinic) hydrocarbons a large portion of which are probably relatively long carbon chains rather than more condensed molecules. Such distillates will be referred to as "of the Pennsylvania type," whether derived

from natural sources or derived by processing or by purification of less favorable distillates from other sources.

Thus, the mixtures of alkyl aromatic sulfonates may be prepared as described in the following specific examples in which the parts are by weight and temperatures are in degrees centigrade, although the invention is not limited to the use of mixtures of alkyl aromatic sulfonates prepared in accordance therewith. For convenience, where a kerosene fraction of petroleum is used in the processes disclosed in the examples, as the source of the alkyl radicals in the products resulting therefrom, the composite alkyl radicals of the products are termed "keryl"; thus the product obtained by chlorinating this fraction is termed "keryl" chloride and the product obtained by condensing the "keryl" chloride with benzene, for example, is termed "keryl" benzene. It will be understood that the specific character of the "keryl" chlorides and "keryl" benzenes or other "keryl" aryl products will be dependent upon the particular kerosene used and the manner in which the process is carried out.

Example A.—Pennsylvania kerosene boiling from 185° to 275°, and of which 80 per cent boiled between 210° and 265°, was chlorinated between 60° and 70° in the presence of 0.38 part iodine per 1000 parts kerosene, until the specific gravity of the latter had increased from 0.788 at 24° to 0.914 at 24°, corresponding to a weight increase due to absorbed chlorine of about 21 per cent. 10 parts of the resulting chlorinated hydrocarbon mixture, 20 parts of benzene and 0.5 part of anhydrous aluminum chloride were mixed at 35°; the mixture was agitated for about 1½ hours at 45°, then allowed to stratify; the upper layer of oil was removed from the tarry lower layer and distilled; and the fraction boiling between 150° at 75 mm. and 250° at 14 mm. of mercury absolute pressure was collected as "keryl" benzene. The collected fraction was refined with 100 per cent sulfuric acid by agitating it with 18.4 per cent of its weight of acid at 25° to 30° for 45 minutes, allowing the mass to settle 30 minutes and discarding the lower acid layer. The refined oil was mixed with 1.32 times its weight of 100 per cent sulfuric acid at 30° to 35°; the mixture was warmed to 55° to 60°, agitated at that temperature for 1 hour, allowed to stratify for about 1 hour, and the middle stratum was separated from an upper layer of oil and from a lower layer of spent acid. The middle stratum was diluted with 10 parts of ice for every 100 parts of "keryl" benzene fraction sulfonated. After allowing the resulting mixture to stratify for about three-quarters of an hour, the bottom layer of dilute spent acid was drawn off and discarded. The organic sulfonate layer was drowned in approximately four times its weight of ice water, neutralized with 50 per cent aqueous caustic soda and drum dried. The dried product contained about 90 per cent of sodium "keryl" benzene sulfonate and about 10 per cent of inorganic salts (mostly sodium sulfate).

Example B.—Pennsylvania kerosene having a boiling range of 185° to 275°, a specific gravity of 0.788 at 24°, and of which 80 per cent distilled between 210° and 265° was converted to a "keryl" benzene sulfonate detergent by the process of Example 5 of U. S. P. 2,247,365. Prior to the final drying operation sodium sulfate was added in such an amount that the resulting product was a mixture of alkyl benzene sulfonates containing approximately 37 per cent sodium "keryl" benzene sulfonate and approximately 63 per cent of sodium sulfate.

Example C.—500 lbs. of Pennsylvania kerosene boiling from 200° to 280°, and of which 80 per cent boiled between 210° and 265°, were charged into a lead-lined kettle fitted with an agitator, thermometer well and other accessories. 6 lbs. of phosphorus trichloride were added and chlorine gas run into the agitated mixture at a rate of approximately 40 lbs. per hour. The temperature was kept below 50° throughout the chlorination, which was continued until the chlorination mixture weighed 580 lbs. and had a specific gravity of 0.915. The chlorination period lasted about 5 hours.

550 lbs. of the kerosene chlorinated as described above, 344 lbs. of phenol, and 55 lbs. of zinc chloride were agitated together and heated gradually to 135° over a period of two hours. After agitating at about 135° for 5 hours to complete the reaction, the reaction mixture was allowed to cool to 80° and was then washed with water until free of mineral acid.

The crude washed reaction mixture was placed in a still with 5 lbs. of caustic soda, and distilled under reduced pressure. After water, phenol and unreacted kerosene had distilled off, the "keryl" phenol fraction was collected from 120° to 230° at 5 mm. of mercury absolute pressure. Most of this fraction was collected from 160° to 230° at 5 mm. of mercury absolute pressure.

130 lbs. of the "keryl" phenol fraction were charged to a lead-lined sulfonation kettle. 130 lbs. of 100 per cent sulfuric acid were run in with agitation during about ½ hour, the temperature being held at 25° to 30°. Agitation was continued for ½ to 1 hour or until a test portion of the sulfonation mass diluted with water and neutralized gave a clear solution at 1 per cent concentration.

The sulfonation mass was diluted with approximately 1000 lbs. of cold water and neutralized with a 45 per cent aqueous caustic soda solution. One half of one per cent of secondary sodium phosphate based on the estimated weight of dry "keryl" phenol sulfonate was added to the diluted sulfonation mass prior to neutralization. The resulting solution was drum dried. The dried product contained about 45 per cent of sodium "keryl" phenol sulfonate and about 55 per cent of inorganic salts (mostly sodium sulfate).

Example D.—A kerosene boiling from about 195° to about 300° of which 80 per cent boiled from about 225° to 275°, having a specific gravity of 0.799 at 24°, containing about 5.6 per cent of unsaturated hydrocarbons, and having a probable average carbon content of about 13.4 carbon atoms was chlorinated, condensed with phenol, and the crude "keryl" phenol was fractionally distilled, as disclosed in Example 3 of U. S. P. 2,196,985. The resulting alkyl phenol mixture was converted to a "keryl" phenol sulfonate detergent by the process of Examples 24 of U. S. P. 2,196,985. The product contained approximately 45 per cent of a mixture of sodium alkyl phenol sulfonates and approximately 55 per cent of inorganic salts (mostly sodium sulfate).

Example E.—A mixture of alkyl cresols was prepared by condensing crude cresylic acid with the aid of zinc chloride as condensing agent with a mixture of alkyl chlorides obtained by reacting a saturated petroleum distillate having a boiling range from 220° to 240°, and containing an alkyl hydrocarbon chain having about 13

to 14 carbon atoms, with chlorine until its weight has increased approximately 18.5%. 100 parts by weight of this alkylated cresol mixture were agitated rapidly while 128 parts of 100% sulfuric acid were added with temperature of the sulfonation mixture controlled to remain around 30° through the addition. The sulfonation mass was then warmed to 75° and held there until a sample was completely soluble in water and did not precipitate calcium salts (about 30 minutes). The sulfonation mass was then diluted, neutralized with caustic soda, filtered and evaporated to dryness. The resulting product is a mixture of alkyl cresol sulfonates, of which the principal components are monoalkyl cresol sulfonates containing about 13 to 14 carbon atoms in an alkyl group some of which have a branched carbon chain.

Example F.—A mixture of alkylated chlor phenols, prepared in accordance with the process of Example E by substituting o-chlorophenol for the cresylic acid employed therein, was sulfonated and isolated in exactly the same manner as described in Example E. The resulting product is a mixture of alkylated o-chlorophenol sulfonates consisting mainly of monoalkyl derivatives of o-chlorophenol having about 13 to 14 carbon atoms in an alkyl group some of which have a branched carbon chain.

The soap compositions of the present invention may be prepared by any suitable method which results in an admixture of a soap and a mixture of the alkyl aromatic sulfonates, in the proportions above specified, in dry, suspended or dissolved form. For example, the ingredients may be intermingled in solid form, or by mixing the alkyl aromatic sulfonate mixture with molten soap, or by intermixing the mixtures of alkyl aromatic sulfonates with soaps in solutions or suspensions. The compositions may be prepared by means of mixing machinery ordinarily used in making milled soaps; and they may be prepared by dissolving the individual components in water to form baths which may be used for cleaning or otherwise treating materials, for example, textiles. A preferred method of preparing the compositions in solid form is to spray dry or drum dry a concentrated aqueous solution or slurry of the components of the composition.

The compositions of the present invention may be produced in various physical forms. Thus, they may be compacted into solid cakes or bars similar to cakes and bars of toilet soap; and they may be prepared in the form of chips, fine or coarse powders, or granules by the usual methods employed for soaps. When the compositions are to be used as shampoos, shaving creams or dentifrices, they may be prepared and marketed as pastes or as solutions, which pastes and/or solutions may contain thickeners.

The compositions of the present invention can be used generally as surface-active agents, e. g., in textile processing, and for general detergent purposes, particularly in hard water, sea-water and related salt waters, and acid aqueous solutions. Thus, they are valuable for cleaning, laundering, scouring, scrubbing, wetting, emulsifying, textile processing (such as, bowking, bleaching, dyeing, fulling, and felting), for breaking water-in-oil emulsions, etc. When marketed, they may advantageously contain other components which make the resulting compositions suitable for particular uses. Thus, they may contain one or more of the following, depending upon the intended use of the composition: protective colloids (e. g., starch, sulfite waste liquor, proteins, cellulose ethers), solvents (e. g., naphtha), alkaline agents (e. g., water glass, soda ash, borax, trisodium phosphate), inorganic salts (e. g., Na_2SO_4, NaCl), abrasives (e. g., crushed sand, pumice), colloidal mineral matter (e. g., bentonite, kaolin), disinfectants (e. g., cresols, mercury compounds), perfumes and flavors of all sorts, coloring materials, etc. For example, flavors may be included in a tooth paste composition, abrasives may be included in a scouring powder.

The invention will be further illustrated in accordance with the following specific examples in which the parts are by weight. It will be realized by those skilled in the art that the invention is not limited hereto except as indicated in the appended patent claims.

Example 1.—A soap composition in bar form was prepared by milling, plodding and pressing a mixture of the following ingredients, using standard soap-making equipment (granite roll mill, plodder and press):

80 parts of the sodium "keryl" benzene sulfonate product of Example A,

160 parts of toilet soap stock containing 15 per cent of water and made from a mixture of 80 per cent tallow and 20 per cent coconut oil base,

2.4 parts of perfume oil (1 per cent),

0.3 part of titanium oxide pigment.

The batch was worked up into bar form without difficulty and without the further addition of water. The resulting bars lathered and washed excellently in sea-water and other waters of extreme hardness.

Additional compositions of the same type were prepared in which the ratio of soap to sodium "keryl" benzene sulfonate was varied. When more than 66 parts by weight of the sodium "keryl" benzene sulfonate product (the product of Example A) were employed, per hundred parts by weight of the soap stock, the compositions were difficult to handle in the usual soap-working equipment because of stickiness. When the amount of the sodium "keryl" benzene sulfonate product was less than 25 parts per hundred parts by weight of the soap stock, the efficiency of the washing action in sea-water or very hard water was decreased below that desired.

Example 2.—Detergent solutions containing 0.2 per cent to 2.5 per cent of the following washing agents were prepared:

1. Marseilles soap,
2. Sodium "keryl" phenol sulfonate product of Example C, and
3. A mixture of 30 per cent Marseilles soap and 70 per cent of the sodium "keryl" phenol sulfonate product.

The mixture was found to have a washing action superior to either the soap or the sodium "keryl" phenol sulfonate product when employed in washing tests carried out with wool soiled with lamp black.

Example 3.—A mixture of 1 part of a good grade of soap (e. g., Marseilles) and 2 parts of the sodium "keryl" phenol sulfonate product of Example D are added to hard water in the proportion of 2 grams of the mixture per liter of water. (The hard water may contain the equivalent of, for example, as much as 0.505 gram calcium oxide in the form of a salt in solution—so-called 42° hardness.) The presence of the "keryl"

phenol sulfonate inhibits the production of any insoluble soap (insoluble alkaline earth metal salts of soap) in the form of curds of visible (or tacky) deposits, and improves the detergency of the solution.

Example 4.—To a bowking solution containing 10 grams of caustic soda and 2.5 grams of soap, per liter of solution, 4 grams of the sodium "keryl" phenol sulfonate product of Example D are added. The bowking process (e. g., kier-boiling) is accomplished as usual. With the "keryl" phenol sulfonates present, the bowking treatment is complete in approximately 75 per cent of the time otherwise required, and more complete emulsification of waxes and their removal from the treated fabric are effected. The deposition of soap curds (alkaline earth salts of soaps) on the material is prevented, furthermore, by the dispersive action of the "keryl" phenol sulfonate.

Example 5.—2 ounces of palm soap are dissolved in one gallon of water. One ounce of the sodium "keryl" phenol sulfonate product of Example D is added, and the mix is stirred until complete solution is obtained. This solution is added as required to the liquid in the fulling mill in which the fabric is being subjected to the fulling operation. The effect of the addition of the solution containing the "keryl" phenol sulfonate is very marked in reducing the time required for rinsing after the fulling operation, and in preventing any soap deposits in and on the fiber.

Example 6.—50 parts of the product of Example B and 400 parts of silicate of soda solution (Philadelphia Quartz Company "N" brand consisting of 9.1 per cent Na_2O, 28.5 per cent SiO_2, and 65.4 per cent water) are heated together and stirred until a homogeneous mass is obtained. The hot mass is then added slowly with constant stirring to 500 parts of molten kettle soap (containing about 35 per cent of water and 65 per cent of soap, and made from 40 per cent tallow, 40 per cent white grease and 20 per cent coconut oil). A smooth, homogeneous mixture is obtained which can be readily formed into bars. The resulting soap composition is a highly filled silicated white laundry soap having excellent washing power.

When the product of Example B is not used in the preparation of this silicated laundry soap, the silicate tends to separate in the form of "pockets" of liquid; such separated solution prevents desirable homogeneity in the soap composition, and makes conversion of the composition into uniform, merchantable bar forms difficult and impracticable.

I claim:

1. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble soap and a mixture of alkyl derivatives of an aromatic sulfonate containing at most two benzene nuclei in the aromatic radical, of which the alkyl groups are derived from a polycomponent non-aromatic hydrocarbon mixture of which at least 80 per cent boils between 210° and 275° C. and over a maximum range of 55° C., said mixture of alkyl derivatives and said soap being present in the composition in ratios varying from 5 to 100 parts of the mixture of alkyl derivatives per 100 parts by weight of soap.

2. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble soap and a mixture of alkyl derivatives of a mononuclear aromatic sulfonate in which the alkyl groups are derived from a polycomponent non-aromatic hydrocarbon mixture of which at least 80 per cent boils between 210° and 275° C. and over a maximum range of 55° C., said mixture of alkyl derivatives and said soap being present in the composition in ratios varying from 5 to 100 parts of the mixture of alkyl derivatives per 100 parts by weight of soap.

3. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble soap and a mixture of monoalkyl derivatives of an aromatic sulfonate containing at most two benzene nuclei in the aromatic radical of which the alkyl groups are derived from a mixture of alkyl chlorides resulting from chlorination of a petroleum distillate of which at least 80 per cent boils between 210° and 275° C. and over a maximum range of 55° C., said mixture of alkyl derivatives and said soap being present in the composition in ratios varying from 5 to 100 parts of the mixture of alkyl derivatives per 100 parts by weight of soap.

4. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble salt of a higher fatty acid and a mixture of alkyl derivatives of a mononuclear aromatic sulfonate of which the alkyl groups are derived from a mixture of alkyl chlorides resulting from chlorination of a petroleum distillate of which at least 80 per cent boils between 210° and 275° C. and over a maximum range of 55° C., said mixture of alkyl derivatives and said water-soluble salt of a higher fatty acid being present in the composition in ratios varying from 5 to 54 parts of the mixture of alkyl derivatives per 100 parts by weight of higher fatty acid salt.

5. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble salt of a higher fatty acid and a mixture of alkyl derivatives of an alkali metal salt of benzene sulfonic acid of which the alkyl groups are derived from a petroleum distillate of which at least 80 per cent boils between 210° and 275° C. and over a maximum range of 55° C., said mixture of alkyl derivatives and said water-soluble salt of a higher fatty acid being present in the composition in ratios varying from 10 to 54 parts of the mixture of alkyl derivatives per 100 parts by weight of higher fatty acid salt.

6. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble soap and a mixture of alkyl derivatives of an alkali metal salt of benzene sulfonic acid of which the alkyl groups are derived from a mixture of alkyl chlorides resulting from chlorination of a petroleum distillate of which at least 80 per cent boils between 210° and 275° C. and over a maximum range of 55° C., said mixture of alkyl derivatives and said soap being present in the composition in ratios varying from 10 to 54 parts of the mixture of alkyl derivatives per 100 parts by weight of soap.

7. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble salt of a higher fatty acid and a mixture of monoalkyl derivatives of sodium benzene sulfonate of which the alkyl groups are derived from a mixture of alkyl chlorides resulting from chlorination of a Pennsylvania type petroleum distillate of which at least 80 per cent boils between 210° and 265° C., said

mixture of alkyl derivatives and said water-soluble salt of a higher fatty acid being present in the composition in ratios varying from 5 to 100 parts of the mixture of alkyl derivatives per 100 parts by weight of higher fatty acid salt.

8. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble soap and a mixture of monoalkyl derivatives of an alkali metal salt of a hydroxy-benzene sulfonic acid of which the alkyl groups are derived from a mixture of alkyl chlorides resulting from chlorination of a petroleum distillate of which at least 80 per cent boils between 210° and 275° C. and over a maximum range of 55° C., said mixture of alkyl derivatives and said soap being present in the composition in ratios varying from 10 to 54 parts of the mixture of alkyl derivatives per 100 parts by weight of soap.

9. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble salt of a higher fatty acid and a mixture of monoalkyl derivatives of sodium phenol sulfonate of which the alkyl groups are derived from a mixture of alkyl chlorides resulting from chlorination of a Pennsylvania type petroleum distillate of which at least 80 per cent boils between 210° and 275° C. and over a maximum range of 55° C., said mixture of alkyl derivatives and said water-soluble salt of a higher fatty acid being present in the composition in ratios varying from 5 to 100 parts of the mixture of alkyl derivatives per 100 parts by weight of higher fatty acid salt.

10. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble soap and a mixture of monoalkyl derivatives of sodium benzene sulfonate of which the alkyl groups are derived from a mixture of alkyl chlorides resulting from chlorination of a petroleum distillate of which at least 80 per cent boils between 210° and 275° C. and over a maximum range of 55° C., said mixture of alkyl derivatives and said soap being present in the composition in ratios varying from 25 to 54 parts of the mixture of alkyl derivatives per 100 parts by weight of soap.

11. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble salt of a higher fatty acid and a mixture of monoalkyl derivatives of sodium benzene sulfonate of which the alkyl groups are derived from a mixture of alkyl chlorides resulting from chlorination of a Pennsylvania type petroleum distillate of which at least 80 per cent boils between 210° and 265° C., said mixture of alkyl derivatives and said water-soluble salt of a higher fatty acid being present in the composition in ratios varying from 10 to 54 parts of the mixture of alkyl derivatives per 100 parts by weight of higher fatty acid salt.

12. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble soap and a mixture of monoalkyl derivatives of sodium phenol sulfonate of which the alkyl groups are derived from a mixture of alkyl chlorides resulting from chlorination of a petroleum distillate of which at least 80 per cent boils between 210° and 275° C. and over a maximum range of 55° C., said mixture of alkyl derivatives and said soap being present in the composition in ratios varying from 25 to 54 parts of the mixture of alkyl derivatives per 100 parts by weight of soap.

LAWRENCE H. FLETT.

CERTIFICATE OF CORRECTION.

Patent No. 2,390,295. December 4, 1945.

LAWRENCE H. FLETT.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 4, for "2,223,408" read --2,233,408--; page 5, first column, line 7, for "through" read --throughout--; and second column, line 18, for "hereto" read --thereto--; page 6, second column, line 2, claim 2, for "in" read --of--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 9th day of April, A. D. 1946.

Leslie Frazer

(Seal) First Assistant Commissioner of Patents.

mixture of alkyl derivatives and said water-soluble salt of a higher fatty acid being present in the composition in ratios varying from 5 to 100 parts of the mixture of alkyl derivatives per 100 parts by weight of higher fatty acid salt.

8. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble soap and a mixture of monoalkyl derivatives of an alkali metal salt of a hydroxy-benzene sulfonic acid of which the alkyl groups are derived from a mixture of alkyl chlorides resulting from chlorination of a petroleum distillate of which at least 80 per cent boils between 210° and 275° C. and over a maximum range of 55° C., said mixture of alkyl derivatives and said soap being present in the composition in ratios varying from 10 to 54 parts of the mixture of alkyl derivatives per 100 parts by weight of soap.

9. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble salt of a higher fatty acid and a mixture of monoalkyl derivatives of sodium phenol sulfonate of which the alkyl groups are derived from a mixture of alkyl chlorides resulting from chlorination of a Pennsylvania type petroleum distillate of which at least 80 per cent boils between 210° and 275° C. and over a maximum range of 55° C., said mixture of alkyl derivatives and said water-soluble salt of a higher fatty acid being present in the composition in ratios varying from 5 to 100 parts of the mixture of alkyl derivatives per 100 parts by weight of higher fatty acid salt.

10. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble soap and a mixture of monoalkyl derivatives of sodium benzene sulfonate of which the alkyl groups are derived from a mixture of alkyl chlorides resulting from chlorination of a petroleum distillate of which at least 80 per cent boils between 210° and 275° C. and over a maximum range of 55° C., said mixture of alkyl derivatives and said soap being present in the composition in ratios varying from 25 to 54 parts of the mixture of alkyl derivatives per 100 parts by weight of soap.

11. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble salt of a higher fatty acid and a mixture of monoalkyl derivatives of sodium benzene sulfonate of which the alkyl groups are derived from a mixture of alkyl chlorides resulting from chlorination of a Pennsylvania type petroleum distillate of which at least 80 per cent boils between 210° and 265° C., said mixture of alkyl derivatives and said water-soluble salt of a higher fatty acid being present in the composition in ratios varying from 10 to 54 parts of the mixture of alkyl derivatives per 100 parts by weight of higher fatty acid salt.

12. A soap composition adapted for use in hard water, sea-water, and acid aqueous solutions, comprising a water-soluble soap and a mixture of monoalkyl derivatives of sodium phenol sulfonate of which the alkyl groups are derived from a mixture of alkyl chlorides resulting from chlorination of a petroleum distillate of which at least 80 per cent boils between 210° and 275° C. and over a maximum range of 55° C., said mixture of alkyl derivatives and said soap being present in the composition in ratios varying from 25 to 54 parts of the mixture of alkyl derivatives per 100 parts by weight of soap.

LAWRENCE H. FLETT.

CERTIFICATE OF CORRECTION.

Patent No. 2,390,295. December 4, 1945.

LAWRENCE H. FLETT.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 4, for "2,223,408" read --2,233,408--; page 5, first column, line 7, for "through" read --throughout--; and second column, line 18, for "hereto" read --thereto--; page 6, second column, line 2, claim 2, for "in" read --of--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 9th day of April, A. D. 1946.

Leslie Frazer

(Seal) First Assistant Commissioner of Patents.