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DETERGENT COMPOSITION AND METHOD
OF MAKING SAMELawrence H. Flett, Hamburg, N. Y., assignor to
Allied Chemical & Dye Corporation, a corpora-
tion of New YorkNo Drawing. Application July 21, 1941,
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12 Claims. (Cl. 252-161)

This invention relates to improvements in the manufacture of detergents, more particularly to improvements in the manufacture of alkyl aryl sulfonate detergents.

It has been found that water-soluble alkyl aryl sulfonates have surface-active properties which make them suitable for use as wetting agents. Such sulfonates may be prepared by alkylating an aromatic compound such as benzene, naphthalene, phenol and the like to form a nuclear alkyl aryl compound, sulfonating this compound and neutralizing the sulfonic acid with an alkaline material to yield the desired sulfonate. I have disclosed in my copending application Serial No. 93,521, filed July 30, 1936, issued May 19, 1942, as Patent No. 2,283,199, that a preferred method of manufacturing substances of this type involves halogenating a suitable petroleum distillate comprising for the most part a mixture of aliphatic hydrocarbons, condensing the halogenated distillate with an aromatic compound in the presence of a condensing agent such as aluminum chloride, and then sulfonating the alkyl aryl compound thus produced. I have found, however, that such alkyl aryl sulfonates, particularly alkyl aryl sulfonates the alkyl side chains of which are derived from petroleum distillates, have relatively little effective washing action when employed in soft water for washing woollens, and to my knowledge no commercially successful detergent of the alkyl aryl sulfonate type with sufficient washing action to remove dirt from soiled wool has been marketed prior to my invention.

An object of this invention is to provide alkyl aryl sulfonate compositions having excellent detergent action.

A more specific object of this invention is to provide alkyl aryl sulfonate compositions capable of washing wool in soft waters.

Another object of this invention is to provide a method for improving the detergency of alkyl aryl sulfonates, more particularly alkyl aryl sulfonates the alkyl side chains of which are derived from petroleum distillates.

I have made the surprising discovery that alkyl aryl sulfonate compositions having excellent detergent properties may be obtained by incorporating carefully controlled amounts of water-soluble alkali, alkaline earth or ammonium salts with one or more alkyl aryl sulfonates, the alkyl side chains of which have an average carbon content of at least 12 and not more than 16 carbon atoms, so as to form a composition containing between 40% and 65% of the salt. A preferred embodiment of my invention involves improving the detergency of mixtures of alkyl aryl sulfonates, the alkyl side chains of which are derived from petroleum distillates containing hydrocarbons having an average carbon content of at least 12 and not more than 16 carbon atoms per molecule, e. g. kerosene fractions, by the incorporation therein of water-soluble alkali, alkaline earth or ammonium salts in the amounts indicated; thus, in accordance with this preferred embodiment the alkyl side chain of the alkyl aryl sulfonate treated may, for example, be derived from petroleum distillates, the lower boiling points of which are not below 80° C. at atmospheric pressure and the upper boiling points of which are not more than 350° C. at 25 mm. of mercury absolute pressure, the bulk of the distillate boiling over a range of 180° to 300° C.; such distillates may be suitably derived from Pennsylvania or Mt. Pleasant, Michigan, petroleum. (For convenience, when the alkyl side chain of the sulfonate composition which is treated in accordance with my invention is derived from a kerosene, the side chain is referred to as a "keryl" side chain.) The improvement in the detergency of such alkyl aryl sulfonates effected by my invention is particularly surprising, since these substances when not admixed with a salt of the above-mentioned type do not effectively remove solid soil from woollens or other textiles in soft water; the products of my invention, on the other hand, have been found to be particularly effective detergents, especially for woollens, in soft water. Thus, it is evident my invention constitutes an important advance in the alkyl aryl sulfonate field.

The importance of correlating the length of the alkyl side chain of the alkyl aryl sulfonate with the amount of salt present in the sulfonate composition in order to achieve improved detergent action was not realized by the art prior to this invention. In general, the solubility in water of alkyl aryl sulfonates decreases as the number of carbon atoms in the alkyl side chain increases. It has been pointed out by United States Patent 1,836,588, issued to Gunther December 15, 1931, that the wetting and emulsifying action of alkyl aryl sulfonates having relatively short alkyl side chains, such as, for example, butylated naphthalene sulfonate, are improved by the addition thereto of substantial amounts of water-soluble salts, the inference from this patent being that the greater the proportion of salt, within practical limitations, the more effective is the product obtained. However, the addition of such salts does not generally improve the wetting or emulsifying action of alkyl aryl sulfonates containing 12 or more carbon atoms in the alkyl side chain, but in some cases actually impairs the wetting and emulsifying action of such products. It has also been found that when employing aqueous solutions of alkyl aryl sulfonates, the alkyl side chains of which are relatively long, e. g. 18 to 20 carbon atoms, the addition thereto of substantial amounts of a salt such as sodium sulfate causes the sulfonate to precipitate from the solution in an objectionable form and thus destroy any desirable surface action of the sulfonate. In view of these facts it was not to be expected that alkyl aryl sulfonates, the alkyl side chains of which have a carbon content falling within the limited range of 12 to 16 carbon atoms, admixed with a controlled amount of a salt of the above type, such as sodium sulfate or sodium chloride, would be capable of exerting excellent detergent action and would, in particular, be highly effective for washing woollens in soft water; and these qualities of my compositions are the more surprising when it is realized that such excellent detergent action is not shown by alkyl aryl sulfonates with more or less carbon atoms in the alkyl side chains than are present in the alkyl groups of the alkyl aryl sulfonates of my compositions, and that the added salt in my compositions does not enhance their wetting action and seriously injures their emulsifying action.

In carrying out my invention, the amount of the water-soluble alkali, alkaline earth or ammonium salt incorporated with the alkyl aryl sulfonate must be carefully controlled. The incorporation of substantially more than 65% of such water-soluble salts considerably impairs the effective detergency of the sulfonate; on the other hand, incorporation of less than 40% of such salts in compositions of this type does not develop the desired washing action. Only by carefully controlling the amount of water-soluble salts incorporated in the composition so that the final composition contains between 40% and 65% thereof may the maximum detergent action of the sulfonate be achieved.

I have found that the compositions of my invention are more friable and when in granular or flake form show a reduced tendency to agglomerate into larger particles or to absorb moisture from the air than the pure sulfonates; the compositions of my invention also have a lighter color than the pure sulfonates and are more easily manufactured because they can be dried more quickly than the pure sulfonates. Furthermore,

the incorporation of such water-soluble salts in the compositions of my invention considerably reduces the final cost of the product while increasing their utility as washing agents. These factors all contribute toward making my compositions of pre-eminent value in the detergent field.

The alkyl aryl sulfonates which may be treated in accordance with my invention may be any one or a mixture of alkyl aryl sulfonates, the alkyl side chains of which contain at least 12 and not more than 16 carbon atoms, preferably at least 12 and not more than 15 carbon atoms. Thus, the aromatic nucleus of the sulfonate may be derived from benzene, toluene, naphthalene, phenol, naphthols, phenetole and similar aromatic compounds but preferably is derived from benzene. The alkyl side chain may be either straight or branched, but my invention is particularly effective when the side chain is branched. These alkyl groups may be derived from any suitable alkylating agent containing the desired number of carbon atoms, including, for example, non-aromatic alcohols such as primary monohydric alcohols, secondary monohydric alcohols, tertiary alcohols of all types, etc., olefin hydrocarbons, e. g. polymerized lower olefins, or halogenated derivatives of substantially saturated aliphatic hydrocarbons, by methods of condensing such alkylating agents with aromatic compounds well known in the art. As hereinabove noted, the alkyl aryl sulfonates preferably treated in accordance with my invention may be prepared by halogenating petroleum distillates of the Pennsylvania or Mt. Pleasant, Michigan, type having a boiling range between about 180° and 300° C. and containing hydrocarbons having an average carbon content of at least 12 and not more than 16, and preferably at least 12 and not more than 15, carbon atoms per molecule, condensing the halogenated hydrocarbon mixture with an aromatic compound in the presence of aluminum chloride and sulfonating the alkyl aryl compound thus produced to yield the desired alkyl aryl sulfonate.

The salts incorporated in the alkyl aryl sulfonate composition in accordance with my invention may be one or a mixture of water-soluble alkali, alkaline earth or ammonium salts; such salts are generally characterized by having a poor surface tension depressant action. Thus, for example, sodium, potassium, lithium and ammonium sulfates, sulfites, thiosulfates, chlorides, phosphates, borates, and acetates may be advantageously employed in the practice of this invention. Alkali metal sulfates and chlorides are preferred, sodium sulfate and sodium chloride being particularly suitable for incorporation in detergent compositions of my invention.

The incorporation of a water-soluble salt with the alkyl aryl sulfonate to furnish the improved detergents of my invention may be accomplished by merely adding the salt to salt-free sulfonate or in a variety of other manners. One method of effecting this incorporation which may be employed when the presence of a sulfate in the final composition is not objectionable involves sulfonating the alkyl aryl compound from which the sulfonate is prepared with an excess of sulfuric acid over the amount required for the sulfonation, so that upon neutralization of the sulfonation mass thus formed a composition is obtained containing the sulfonate and a sulfate in amounts equivalent to between about 40% and about 65% of the final composition. However,

this method is obviously limited to the preparation of compositions in which the added salt is a sulfate and thus cannot be employed for the incorporation of, for example, carbonates or phosphates with the sulfonate.

Another preferred method of obtaining the compositions of my invention involves sulfonating the alkyl aryl compound to form the sulfonic acid, separating the sulfonic acid from the unsulfonated impurities and from the excess sulfonating agent, neutralizing the acid and then mixing therewith the desired amount of the water-soluble salt to be added; the solution thus formed may then be dried to yield the desired composition. Furthermore, salt-free alkyl aryl sulfonates may be prepared by sulfonating the alkyl aryl compound with an excess of sulfuric acid, neutralizing the sulfonation mass, removing the inorganic salt from the neutralized mass by solution in alcohol, in which the alkyl aryl sulfonate is soluble, and the desired water-soluble salt then added to the salt-free sulfonate. It is to be understood that the sulfonic acid may be neutralized with a mixture of bases, if desired, and that the added salt need not have the same cation as that of the sulfonate.

The following examples are illustrative of the composition of my invention. Amounts are given in parts by weight and temperatures in degrees centigrade.

EXAMPLE 1

Part 1.—10,620 parts of Pennsylvania kerosene having an average carbon content of 13 to 14 carbon atoms per molecule and a boiling range of from 185° to 275° were charged into a lead-lined kettle and warmed to about 60°, 4.4 parts of iodine were dissolved therein and chlorine gas passed through the kerosene, which was maintained at a temperature between 60° and 70°, at an average rate of about 300 parts per hour until the specific gravity of the chlorinated kerosene amounted to 0.918 at 24°.

Part 2.—To a mixture of 13,272 parts of benzene and 332 parts of anhydrous aluminum chloride, 6,636 parts of the chlorinated kerosene prepared as described in Part 1 were added with agitation over a period of about three hours; during the addition the temperature of the mass rose to about 35°. When all the chlorinated kerosene had been added the mixture was heated to 45° and maintained at this temperature for about 1½ hours; at the end of this time agitation was stopped, the mass permitted to stand and the lower tarry layer withdrawn. The upper layer was stripped of its low-boiling hydrocarbons by distilling the liquid at 150° first under atmospheric pressure, and finally under reduced pressure at about 3 or 4 inches of mercury absolute. The stripped material was then vacuum distilled until about 7% of the charge in the still had been removed as distillate; the residue was further distilled and the distillate therefrom collected until the boiling point of the residue was about 250° at 14 mm. mercury pressure. The distillate thus recovered consisted chiefly of the condensation product of the chlorinated kerosene and benzene and for convenience is called "keryl benzene."

Part 3.—The "keryl" benzene was washed with 100% sulfuric acid by mixing it with about 15% of its weight of acid and agitating for about one hour at 40°; the washed mass was then permitted

to stand to separate the acid which was withdrawn and discarded.

The acid-washed "keryl" benzene was then mixed with about 1.25 times its weight of 100% sulfuric acid at a temperature between 30° and 35°, the mixture warmed to 55° and agitated at that temperature for one hour. It was then permitted to stand for two hours, during which time three layers of material separated, the upper layer consisting chiefly of unsulfonated material, the middle layer of sulfonated "keryl" benzene, and the lower layer of spent sulfuric acid. The middle layer was separated from the other layers, drowned in ice water and neutralized with an aqueous solution of sodium hydroxide. The solution thus obtained contained dissolved therein a composition consisting chiefly of 63% sodium "keryl" benzene sulfonate and 37% sodium sulfate. 8,590 parts of sodium sulfate were then dissolved in this solution and the resulting solution dried on a drum drier. The resulting product contained about 61.3% sodium sulfate and had excellent washing properties.

EXAMPLE 2

Part 1.—A Pennsylvania petroleum distillate (kerosene), which distilled from about 200° to about 266°, and of which about 80% distilled over the range of about 220° to 260°, and which comprised substantially a mixture of hydrocarbons which were chiefly aliphatic and saturated and had an average carbon content of 12 to 15 carbon atoms per molecule, was chlorinated at about 50° by passing through it a stream of chlorine gas until the chlorinated mixture had increased in weight by about 20% because of organically-combined chlorine therein. The resulting mixture of unchlorinated and chlorinated hydrocarbons was aerated to remove practically all dissolved hydrogen chloride. The chlorinated hydrocarbons in the mixture contained a preponderant amount of monochlor hydrocarbons.

Part 2.—30 parts of anhydrous aluminum chloride were added slowly to an agitated mixture of 200 parts of benzol and 300 parts of the chlorinated mixture prepared as described in Part 1. The mixture was cooled externally until the vigorous evolution of hydrogen chloride gases from the mixture had abated. It was then heated and maintained at its refluxing temperature for about one hour, or until the evolution of hydrogen chloride had ceased. The reaction mass was then cooled and drowned with a mixture of about 400 parts of crushed ice, 200 parts of water and 50 parts of commercial muriatic acid, the mixture permitted to stratify, and the organic oily layer separated, washed with a small amount of water, and distilled. The portion which distilled from about 160° to about 210° at 4 mm. of mercury pressure was collected; it consisted of a mixture of alkylated benzenes in which the alkyl groups contained predominantly from about 12 to about 15 carbon atoms.

Part 3.—100 parts of the distilled oil obtained according to Part 2 of this example were mixed with 130 parts of 20% oleum at a temperature of approximately 10°. The mixture was permitted to warm to 25° to 30° and was stirred at this temperature for 1½ to 3 hours, or until one part of a test portion, after neutralizing with sodium hydroxide, was soluble in 20 parts of water. The mixture was then poured into approximately 600 parts of an ice-water mixture, and the resulting

solution made neutral to Brilliant Yellow and Congo red papers with sodium hydroxide. The neutralized solution was evaporated to dryness on a rotary drum drier. The product obtained was in the form of light-buff to white flakes. It comprised chiefly a mixture of alkyl benzene sulfonates and alkali metal sulfate and contained about 50% of the sulfate; its aqueous solutions had excellent washing properties.

EXAMPLE 3

Part 1.—150 parts of a crude chlorinated kerosene prepared as described in Example 2, Part 1, 90 parts of naphthalene, and 25 parts of anhydrous zinc chloride were thoroughly mixed and heated to about 135° in a reactor fitted with a reflux condenser. The mixture was kept at about 135° for about 45 minutes or until the evolution of hydrogen chloride had practically ceased. The reaction mixture was then cooled, mixed with water, permitted to settle and the upper (organic) layer withdrawn and washed with water until reasonably free from water-soluble products. The washed organic liquid mass was distilled in vacuo, and the fraction which distilled between 145° and 250° at a pressure of 8 to 12 mm. of mercury was collected.

Part 2.—100 parts of the distilled oil obtained according to Part 1 of this example were treated, with good stirring, at 10° with 120 parts of 7% oleum. The mixture, while being stirred, was then permitted to warm up to 25° to 30° and maintained at that temperature for 1½ to 2 hour, or until a neutralized test portion was soluble in twenty times its weight of water. The sulfonation mixture was then drowned in three times its weight of an ice-water mixture and the resulting solution neutralized with caustic soda and evaporated to dryness, as in Example 2, Part 3. The product was in the form of light-buff to white flakes. It comprised chiefly a mixture of sulfonates of alkyl naphthalenes and about 50% sodium sulfate. Its aqueous solutions had good washing properties.

EXAMPLE 4

Part 1.—A kerosene fraction of Pennsylvania petroleum boiling from 185° to 280° was fractionated and a fraction collected between 91° at 13 mm. pressure and 109° at 12 mm. pressure. The collected fraction boiled from 200° to 235° at atmospheric pressure and 90% of it boiled between 212.5° and 231°; it had an average carbon content of 12 to 13 carbon atoms per molecule. Chlorine was then passed into 340 parts of this fraction at a temperature below 60°, in the presence of light, until there was an increase in weight of 88 parts.

Part 2.—150 parts of the chlorinated mixture produced in Part 1 of this example were added, with agitation and as rapidly as possible, to a mixture of 80 parts of benzene and 4 parts of anhydrous aluminum chloride at ordinary temperatures. The mixture was agitated for one hour and then permitted to separate. The resulting condensation product was decanted from the aluminum chloride sludge, washed with water, and the washed material stripped of unreacted materials by distilling. The portion boiling up to 118° at 10 mm. pressure and containing residual benzene was separated from the remainder which comprised a mixture of alkyl benzene and residual kerosene.

Part 3.—75 parts of the alkyl benzene product

of Part 2 of this example were sulfonated with 1¼ times their weight of 26% oleum. The oleum was added thereto at 10° to 15°, and the mixture then agitated at room temperature for about two hours. The sulfonation mixture was diluted with four times its weight of an ice-water mixture and neutralized with sodium hydroxide to a pH of 7.0 to 8.0. The neutral solution was evaporated to dryness on an atmospheric double drum drier, yielding an alkyl benzene sulfonate containing about 55% sodium sulfate.

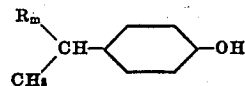
EXAMPLE 5

Part 1.—173 parts of chlorinated kerosene, prepared by chlorinating a Pennsylvania kerosene fraction boiling between 220° and 240° and having an average carbon content of 12 to 14 carbon atoms per molecule until the weight of the kerosene had increased by about 20% due to organically combined chlorine, were mixed with 175 parts of phenol and 150 parts of zinc chloride and the mixture refluxed with agitation at a temperature of about 135° until the evolution of hydrogen chloride gas had ceased. The mass was then further heated under reflux at a temperature of about 175° for about 16 hours. At the end of this time the mass was permitted to cool, was diluted with water, and the insoluble oil washed with water until free of water-insoluble impurities. The washed oil was then vacuum distilled and the fraction boiling between 185° and 210° at 8 mm. pressure was collected separately.

Part 2.—56 parts of 100% sulfuric acid were slowly added to 50 parts of the "keryl" phenol thus obtained, care being taken to maintain the temperature below 30° during addition of the acid. When all the acid had been added, the mass was warmed to 75° and held at that temperature for about twenty minutes until a test sample was completely soluble in neutral, acid and alkaline water and/or did not precipitate calcium salts from a calcium chloride solution containing the equivalent of 0.224 gram of calcium oxide per liter. The mass was then diluted with water and neutralized with sodium hydroxide; the neutral solution of the sulfonate was filtered and drum dried. The final "keryl" phenol sulfonate product contained about 55% sodium sulfate and its solutions had excellent washing properties.

EXAMPLE 6

100 parts of commercial cetyl alcohol, (containing 30% to 40% of normal cetyl alcohol, 30% to 40% of higher alcohols than cetyl, e. g. stearyl alcohol, etc., about 10% of normal lauryl alcohol and about 20% of normal myristyl alcohol), 100 parts of phenol, and 100 parts of anhydrous zinc chloride were heated at 160° to 180°, under a reflux condenser, with agitation for sixteen hours. The condensation product was washed with water until practically free from water-soluble products. The resulting oil was fractionally distilled in vacuo. The fraction of the distillate which was collected between 195° and 240° at 15 mm. pressure of mercury was a faint yellow to water-white oil consisting chiefly of a mixture of alkyl phenols having the probable general formula:



in which R_m is a straight-chain hydrocarbon radical having the formula:



the compound in which R_m is $C_{14}H_{29}$ being a predominating compound, with a small amount of normal alkyl phenols and probably some ortho isomers present.

100 parts of the resulting purified alkyl phenol mixture, 40 parts of acetic anhydride and 106 parts of sulfuric acid monohydrate were mixed together and warmed gently to 70° to 75° until the product was completely soluble in water and a neutral 0.2% solution did not precipitate calcium salts from a calcium chloride or other soluble calcium salt solution containing the equivalent of 0.224 gram calcium oxide per liter. The mass was diluted with water to a final volume of 450 to 600 parts and neutralized with alkali, as, for example, caustic soda or caustic potash or their equivalents. The neutral solution was clarified, if desired, by filtration, and evaporated to dryness. The product was a brown to white solid, soluble in water to give brown to water-white solutions. It comprised a mixture of inorganic salts (e. g. sodium salts) with sulfonates of the said alkyl phenols (e. g. in the form of the sodium salts), of which mixture the inorganic salts constituted in the neighborhood of 60%. The alkyl phenol sulfonates present were soluble in alcohol, benzene and other organic solvents.

EXAMPLE 7

533 parts of Pennsylvania kerosene, boiling over the range 208° to 280° at atmospheric pressure with 80% distilling within the range 233° to 267° and having an average carbon content of 13 to 15 carbon atoms per molecule, were charged into a lead-lined vessel. 0.25 part of iodine was dissolved in the kerosene with agitation, and a stream of chlorine was run therethrough at a rate of 40 to 50 parts of chlorine per hour. The temperature was held at 45° to 55° during chlorination, which was continued until the specific gravity of the chlorinated kerosene was 0.920 at 24°. 327 parts of this chlorinated kerosene and 164 parts of phenol were then charged into a cast-iron jacketed kettle and 33 parts of anhydrous zinc chloride added thereto with agitation during the course of ten minutes, the temperature being held below 50°. The batch was gradually heated to 160° over a period of two to three hours and held at 160° for five hours with continued agitation. Heating was then discontinued, the agitation stopped, and the batch permitted to settle for at least four hours. The oil layer (crude "keryl" phenol) was then drawn off from the zinc chloride settlings which were discarded.

The crude "keryl" phenol was then charged to a suitable kettle and stripped under reduced pressure. The stripping was stopped when the vapor temperature in degrees centigrade was equal to 100 plus the absolute pressure in millimeters of mercury. It is desirable to add a small amount of caustic soda to the crude "keryl" phenol before stripping, as this aids in controlling corrosion difficulties.

239 parts of stripped "keryl" phenol were charged into an iron kettle. 73 parts of a 50% caustic soda solution were added to the "keryl" phenol with agitation and the temperature of the mixture adjusted to 75° to 85°. 68 parts of diethyl sulfate were then gradually added to the mass over a period of one hour with continued

agitation, the temperature being held at 80° to 90°. The mass was then gradually heated to 135° over a period of about three hours, a slight vacuum (1-3 inches of mercury) being maintained. The vacuum was then released and the batch cooled to 110°. 239 parts of water were added and about 5 parts of 50° Bé. sulfuric acid were run in until a strong acid reaction was obtained. After agitating at 80° to 90° for fifteen minutes, the agitation was stopped and the mass permitted to stand for about one hour. The lower aqueous layer was drawn off and discarded.

The water-insoluble oil (crude "keryl" phenetole) was treated with a small amount of caustic and dried by heating to 110° to 120° under slightly reduced pressure (3-5 inches of mercury vacuum).

The crude dried "keryl" phenetole was then charged into a still, together with 1% of its weight of flake caustic soda, and distilled under reduced pressure. Samples of the distillate were collected and tested for solubility in an equal volume of 100% sulfuric acid. When the vapor temperature in degrees centigrade was equal to 115 plus the absolute pressure in millimeters of mercury, a test sample of the distillate was soluble in 100% sulfuric acid to the extent of 10%. The distillate collected up to this point was discarded. Distillation was continued and the distillate collected until the vapor temperature equaled 250° plus the absolute pressure in millimeters of mercury.

107 parts of the "keryl" phenetole fraction thus collected were charged into an enamelled kettle and 188 parts of 100% sulfuric acid were slowly and evenly added over a period of one to two hours with agitation, the temperature being kept at 15° to 20°. The batch was then warmed to 25° to 30° and agitation continued for three hours, at which time a neutralized test sample was completely soluble in distilled water.

The sulfonation mass thus obtained was run into an agitated mixture of 167 parts of water, 800 parts of cracked ice and 1 part of disodium phosphate, and the diluted mass neutralized with about 300 parts of caustic soda (50% solution), care being taken to keep the temperature below 30°. The neutralized solution was dried on a double drum drier, yielding a product consisting mainly of "keryl" phenetole sulfonate and about 60% sodium sulfate.

In order to illustrate the improved detergent action of the composition of my invention, the following series of detergent compositions were prepared and tested as indicated in the subsequent examples.

EXAMPLE 8

Large batches of sodium "keryl" benzene sulfonate, sodium "keryl" phenol sulfonate, sodium cetyl phenol sulfonate and sodium "keryl" phenetole sulfonate were prepared by processes similar to those illustrated in Examples 1, 5, 6 and 7 respectively. These products were then each extracted with ethyl alcohol, whereby the sulfonate was separated from the sulfate and a salt-free detergent material was obtained; the ethyl alcohol solutions were drum dried. Measured portions of these salt-free detergent materials were then mixed with different proportions of anhydrous sodium sulfate dissolved in distilled water, and the resulting aqueous solutions were drum dried. The products thus obtained constituted a series of compositions containing varying

amounts of sodium sulfate admixed with an alkyl aryl sulfonate.

Comparative washings with 0.2% aqueous solutions of these compositions were then made in a Launderometer as follows:

A sample of cloth was uniformly soiled with lampblack, tallow and mineral oil. It was then cut into pieces of approximately equal size (4" x 4") which were washed in a Launderometer in 200 cc. of solution for thirty minutes at 50°. The degree of washing was determined by taking readings of reflected light (brightness) with a Zeiss-Pulfrich photometer; the readings represent increased brightness which is measured by the differences between the readings obtained with the photometer on the soiled unwashed cloth and on the soiled cloth after washing. The results obtained by these tests are indicated in the following tables:

TABLE IV

Effect of sodium sulfate on the washing power of solutions of sodium "keryl" phenetole sulfonate

Detergent composition		Wool washing		Wool washing	
Per cent sol. organic salt	Per cent sol. inorganic salt	Soft water	10° hard water	Soft water	10° hard water
		Absolute brightness increase		Absolute brightness increase divided by "keryl" aryl sulfonate concentrations in tenths of per cent	
100	None	23	31	12	16
55	45	40	28	36	25
45	55	39	25	43	28
35	65	38	18	54	26

TABLE I

Effect of sodium sulfate on the washing power of solutions of sodium "keryl" benzene sulfonate

Detergent composition		Cotton washing		Wool washing		Cotton washing		Wool washing	
Per cent sol. organic salt	Per cent sol. inorganic salt	Soft water	10° hard water	Soft water	10° hard water	Soft water	10° hard water	Soft water	10° hard water
		Absolute brightness increase				Absolute brightness increase divided by "keryl" aryl sulfonate concentrations in tenths of percent			
100	None	7.0	9.0	8.5	12.0	3.5	4.5	4.3	6.0
80	40	19.5	26.0	39.0	28.0	16.2	21.7	32.5	23.3
55	45	19.0	24.0	36.5	33.0	17.3	21.8	33.2	30.0
50	50	20.5	24.0	39.0	31.5	20.5	24.0	39.0	31.5
45	55	22.0	23.5	27.5	37.0	22.5	26.2	30.6	41.1
40	60	20.0	21.5	26.0	42.5	25.0	28.9	32.5	53.1
35	65	19.0	22.0	29.0	33.0	27.1	31.5	41.4	47.2

TABLE II

Effect of sodium sulfate on the washing power of solutions of sodium "keryl" phenol sulfonate

Detergent composition		Wool washing		Wool washing	
Per cent sol. organic salt	Per cent sol. inorganic salt	Soft water	10° hard water	Soft water	10° hard water
		Absolute brightness increase		Absolute brightness increase divided by "keryl" aryl sulfonate concentrations in tenths of per cent	
100	None	24	19	12	10
55	45	33	29	30	26
45	55	29	18	32	20

TABLE III

Effect of sodium sulfate on the washing power of solutions of sodium cetyl phenol sulfonate

Detergent composition		Wool washing		Wool washing	
Per cent sol. organic salt	Per cent sol. inorganic salt	Soft water	10° hard water	Soft water	10° hard water
		Absolute brightness increase		Absolute brightness increase divided by "keryl" aryl sulfonate concentrations in tenths of per cent	
100	None	10	44	5	22
55	45	17	44	15	40
45	55	18	43	20	48
35	65	17	43	24	61

EXAMPLE 9

Sodium "keryl" benzene sulfonate and sodium cetyl phenol sulfonate were prepared by processes similar to those given in Examples 1 and 6 above, respectively. These sulfonates were freed of inorganic salts by extraction with alcohol and the alcohol solutions of the sulfonates drum dried. Solutions of these sulfonates containing varying amounts of sodium sulfate were then made up and the wetting power of these solutions determined by preparing 500 cc. of the test solution, placing the solution in a 600-cc. beaker maintained at 50°, cupping a #10 canvas or wool felt disc, 1" in diameter, in a long-stem inverted funnel, forcing the disc below the liquid level to a depth of 5 to 6 cm. and determining the time

It will be noted from the above tables that the presence of the sodium sulfate markedly increased the washing power of the sulfonate. While in some cases the absolute brightness increase observed in connection with the use of compositions containing sodium sulfate was not much greater or even slightly less than the absolute increase when employing pure sulfonate alone, it must be remembered that in such cases the solutions contained a much lower concentration of the sulfonate than when the pure sulfonate was employed and, hence, in the absence of the sodium sulfate would have shown a much poorer detergent action per unit of pure sulfonate. In order to illustrate the fact that the addition of sodium sulfate to alkyl aryl sulfonates, the alkyl side chains of which contain from 12 to 16 carbon atoms, does not improve the wetting properties of such sulfonates, the following example was carried out:

required for the disc to fall out of the funnel. The results of these tests are given in the following tables:

of application Serial No. 737,777, filed July 31, 1934, issued as United States Patent 2,196,985 of April 16, 1940.

TABLE V

Effect of added salt on wetting power of "keryl" benzene sulfonate

Composition tested		Wetting time with cotton canvas discs		Wetting time with wool felt discs	
Percent alkyl aryl sulfonate	Percent Na_2SO_4	Composition tested at .1% conc.	Composition tested at conc. taken so as to keep conc. of "keryl" benzene sulfonate at .1%	Composition tested at .5% conc.	Composition tested at conc. taken so as to keep conc. of "keryl" benzene sulfonate at .5%
100.0	-----	11 sec.-----	11 sec.-----	4½ sec.-----	4½ sec.
85.4	14.6	15½ sec.-----	14½ sec.-----	6 sec.-----	4½ sec.
50.0	50.0	26 sec.-----	14½ sec.-----	6½ sec.-----	4½ sec.
35.0	65.0	35 sec.-----	9 sec.-----	5 min.-----	3½ sec.
20.0	80.0	49 sec.-----	11 sec.-----	5 min.-----	3½ sec.

TABLE VI

Effect of added salt on wetting power of cetyl phenol sulfonate

Composition tested		Wetting time with cotton canvas discs		Wetting time with wool felt discs	
Percent alkyl aryl sulfonate	Percent Na_2SO_4	Composition tested at .1% conc.	Composition tested at conc. taken so as to keep conc. of cetyl phenol sulfonate at .1%	Composition tested at .5% conc.	Composition tested at conc. taken so as to keep conc. of cetyl phenol sulfonate at .5%
100	-----	30 sec.-----	30 sec.-----	10 sec.-----	10 sec.
80	20	39 sec.-----	28 sec.-----	13 sec.-----	11 sec.
55	45	48 sec.-----	28 sec.-----	19 sec.-----	9 sec.
35	65	71 sec.-----	24 sec.-----	23 sec.-----	9 sec.
20	80	121 sec.-----	26 sec.-----	5 min.-----	8 sec.

It will be noted that when the concentrations of the solutions tested were adjusted so that the sulfonate concentration was constant throughout the tests, the wetting-out time remained substantially the same, indicating the added sodium sulfate did not improve the wetting properties of the sulfonates.

While the action of the water-soluble salts upon the detergent power of the alkyl aryl sulfonates tested in accordance with my invention is not clear, I believe that compositions in which such salts have been incorporated with the alkyl aryl sulfonates in the amounts indicated tend to form solutions of a more colloidal nature upon being dissolved in water than is the case when the salt-free sulfonates are dissolved in water, due to a salting-out action exerted on the solution of the sulfonates by the salts; such colloidal solutions, I believe, are more effective detergents than the true solutions of the sulfonates in water. Incorporation of salts in the amounts indicated apparently serves to adjust the colloidal nature of the solution so that maximum detergency is achieved. It is to be understood, however, that this invention is in no way limited by any particular theory which may be applicable thereto.

This application is a continuation-in-part of my following copending applications: Serial No. 691,082, filed September 26, 1933, issued July 22, 1941, as Patent No. 2,249,757; Serial No. 42,164, filed September 25, 1935, issued February 3, 1942, as Patent No. 2,271,635; Serial No. 93,521, filed July 30, 1936, issued May 19, 1942, as Patent No. 2,283,199; which is in turn a continuation-in-part

Since certain changes may be made in the above compositions of matter and different embodiments of the invention could be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. An improved detergent composition comprising alkyl aryl sulfonates, the alkyl groups of which are derived from an aliphatic hydrocarbon mixture, the lower boiling point of which is not below 80° C. at atmospheric pressure and the upper boiling point of which is not above 350° C. at 25 mm. pressure, and a water soluble salt having an inorganic cation selected from the group consisting of water soluble sulfates, sulfites, thiosulfates, chlorides, dihydrogen phosphates, borates and acetates, the amount of said water-soluble salt having an inorganic cation being such that the sulfonate-salt mixture contains between about 40% and about 65% by weight thereof.

2. An improved detergent composition comprising alkyl aryl sulfonates, the alkyl side chains of which are derived from a kerosene fraction at least 80% of which boils within the range 180° to 300° C., and a water soluble salt having an inorganic cation selected from the group consisting of water soluble sulfates, sulfites, thiosulfates, chlorides, dihydrogen phosphates, borates and acetates, the amount of said water-soluble salt having an inorganic cation being such that the

sulfonate-salt mixture contains between about 40% and about 65% by weight thereof.

3. An improved detergent composition comprising alkyl aryl sulfonates, the alkyl side chains of which are derived from a kerosene fraction at least 80% of which boils within the range of 180° to 300° C., and sodium sulfate in an amount such that the sulfonate-sodium sulfate mixture contains between about 40% and about 65% by weight thereof.

4. An improved detergent composition comprising alkyl benzene sulfonates, the alkyl side chains of which are derived from a kerosene fraction at least 80% of which boils within the range 180° to 300° C., and a water soluble salt having an inorganic cation selected from the group consisting of water soluble sulfates, sulfites, thiosulfates, chlorides, dihydrogen phosphates, borates and acetates, the amount of said water-soluble salt having an inorganic cation being such that the sulfonate-salt mixture contains between about 40% and about 65% by weight thereof.

5. An improved detergent composition comprising alkyl benzene sulfonates, the alkyl side chains of which are derived from a kerosene fraction containing hydrocarbons having an average carbon content of at least 12 and not more than 16 carbon atoms per molecule, at least 80% of which boils within the range 180° to 300° C., and between 40% and about 65% by weight sodium sulfate.

6. A method for obtaining improved alkyl benzene sulfonate detergent compositions, which comprises incorporating with alkyl benzene sulfonates, the alkyl side chains of which are derived from a kerosene fraction containing hydrocarbons having an average carbon content of at least 12 and not more than 16 carbon atoms per molecule, at least 80% of which boils within the range of 180° to 300° C., sodium sulfate in an amount such that the mixture formed contains between about 40% and about 65% by weight of the sulfate, said incorporation being effected by sulfonating the alkyl benzene with such an excess of sulfonating agent that upon neutralization of the sulfonation mass said mixture of sulfonate and sulfate is formed.

7. A method for obtaining improved alkyl benzene sulfonate detergent compositions, which comprises incorporating with alkyl benzene sulfonates, the alkyl side chains of which are derived from a kerosene fraction containing hydrocarbons having an average carbon content of at least 12 and not more than 16 carbon atoms per molecule, at least 80% of which boils within the range 180° to 300° C., sodium sulfate in an amount such that the mixture formed contains between

about 40% and about 65% by weight thereof, said incorporation being effected by sulfonating the alkyl benzene compound, removing unsulfonated materials and excess sulfonating agent from the mass, neutralizing the sulfonic acid and adding the sodium sulfate to the sulfonate.

8. A method for obtaining improved alkyl benzene sulfonate detergent compositions, which comprises incorporating with alkyl benzene sulfonates, the alkyl side chains of which are derived from a kerosene fraction containing hydrocarbons having an average carbon content of at least 12 and not more than 16 carbon atoms per molecule, at least 80% of which boils within the range of 180° to 300° C., sodium sulfate in an amount such that the mixture formed contains between about 40% and about 65% by weight thereof, said incorporation being effected by sulfonating the alkyl benzene compound, neutralizing the sulfonation mass, separating the sulfonate from the mass and adding the sodium sulfate to said sulfonate.

9. An improved detergent composition comprising alkyl aryl sulfonates, the alkyl side chains of which are derived from a kerosene fraction at least 80% of which boils within the range of 180° to 300° C., and sodium chloride in an amount such that the sulfonate-sodium chloride mixture contains between about 40% and about 65% by weight thereof.

10. An improved detergent composition comprising alkyl aryl sulfonates, the alkyl side chains of which are derived from a kerosene fraction at least 80% of which boils within the range of 180° to 300° C., and sodium acetate in an amount such that the sulfonate-sodium acetate mixture contains between about 40% and about 65% by weight thereof.

11. An improved detergent composition comprising alkyl benzene sulfonates, the alkyl side chains of which are derived from a kerosene fraction containing hydrocarbons having an average carbon content of at least 12 and not more than 16 carbon atoms per molecule, at least 80% of which boils within the range 180° to 300° C., and between 40% and about 65% by weight sodium chloride.

12. An improved detergent composition comprising alkyl benzene sulfonates, the alkyl side chains of which are derived from a kerosene fraction containing hydrocarbons having an average carbon content of at least 12 and not more than 16 carbon atoms per molecule, at least 80% of which boils within the range 180° to 300° C., and between 40% and about 65% by weight sodium acetate.

LAWRENCE H. FLETT.