

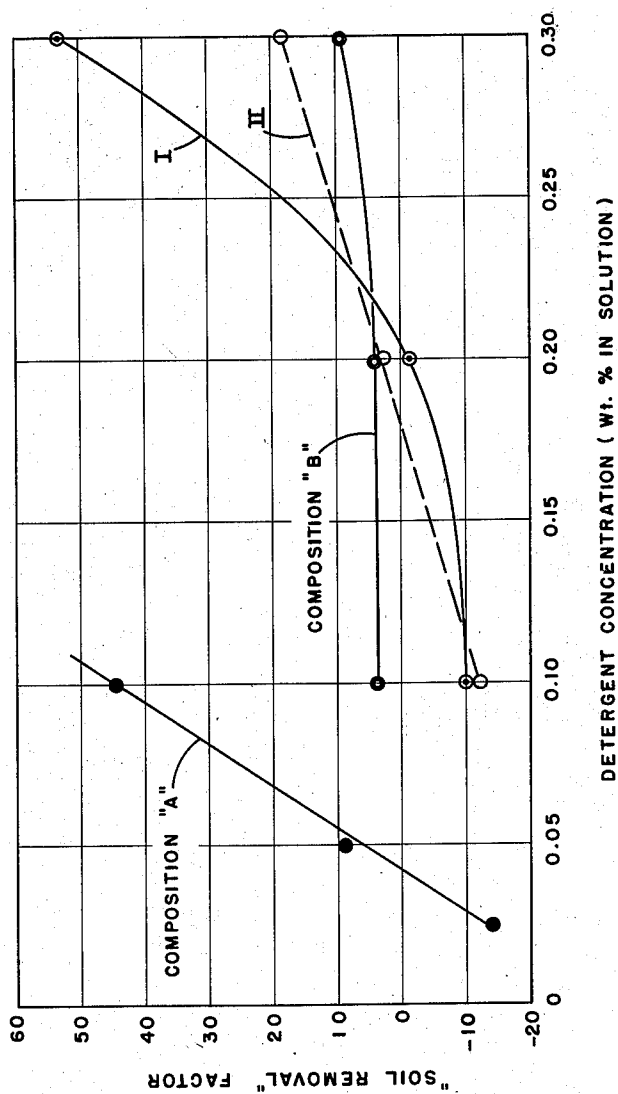
April 7, 1953

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2,634,240

ALKYL ARYL SULFONATE DETERGENT COMPOSITION

Filed July 9, 1949



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UNITED STATES PATENT OFFICE

2,634,240

ALKYL ARYL SULFONATE DETERGENT
COMPOSITION

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Application July 9, 1949, Serial No. 103,854

10 Claims. (Cl. 252—161)

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The present invention is directed to a new composition having detergency properties.

Prior to the present invention, it has been known to employ as detergents alkylated derivatives of aryl sulfonic acids as alkali metal salts thereof. Thus, in U. S. 2,161,174, Kyrides teaches the employment of compositions comprising the alkylated derivatives of benzene sulfonic acids as their alkali metal salts. Kyrides prepares his compounds by chlorinating kerosene fractions to obtain alkyl chlorides which are condensed, by means of a Friedel-Crafts catalyst, with an aromatic hydrocarbon, such as benzene, toluene, naphthalene or the like, which is then sulfonated to form the sulfonic acid, following which the sodium salt is formed. The compounds mentioned by Kyrides are quite active as detergents and have achieved considerable utility in industry.

The preparation of similar alkali metal alkyl aryl sulfonate detergents by a similar chemical reaction is taught by Flett in U. S. 2,387,572. Flett chooses to identify these compounds, which contain alkyl side chains derived from kerosene, as "keryl aryl sulfonates." This terminology is adopted for use herein, for convenience in differentiating between the long chain alkyl aryl sulfonates of known detergent quality and the xylene sulfonates employed in our invention. It is understood that the term "keryl aryl sulfonates," as used herein, comprises not only compounds whose alkyl chain is derived from kerosene itself, but also those compounds of like chemical structure and formula whose alkyl chain is obtained from other known sources, such as olefin polymers and the like. The alkyl chain in these compounds may contain from nine to sixteen carbon atoms, that being the range normally met with in kerosene.

It is also known, and has been described, i. e. in the above mentioned patent to Flett, that excellent detergent compositions may be prepared by admixing 40 to 65 weight per cent of a water soluble salt, such as an alkali sulfate, with 60 to 35 weight per cent of a keryl aryl sulfonate.

It is well known that keryl aryl sulfonates, in order to be useful as detergents, must be prepared from selected feed stocks in carefully controlled reactions; thus the minimum cost at which these compounds may be prepared is fixed by the conditions required in their preparation. On the other hand, alkali metal xylene sulfonates are frequently met with as by-products, or contained in waste products, in ordinary petroleum refinery practice. For example, they may be contained

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in the spent caustic which has been used in the neutralization of acid treated aromatic petroleum distillate fractions, usually those which have previously been subjected to a hydrocarbon conversion operation, such as reforming. In many cases the xylene sulfonates are not recovered, but instead are discarded with the spent caustic.

It is also well known that the alkali metal xylene sulfonates, although they are good wetting agents, are useless as detergents.

It is the main object of the present invention to provide an improved composition having detergency characteristics which comprises a substantial portion of xylene sulfonates.

Another object of the present invention is to provide a detergent composition comprising a lower amount of active detergent compound than heretofore required, together with a substantial amount of xylene sulfonates and a substantial amount of a water soluble inorganic salt.

Another object of our invention is to provide a composition comprising both xylene sulfonates and keryl aryl sulfonates in such a manner that the synergistic effect exerted by these compounds upon one another will permit the use of substantially lower concentrations of keryl aryl sulfonate than would be required to provide a desired detergency in the absence of xylene sulfonates.

The objects of the present invention may be achieved by forming a composition comprising a major amount of a mixture of alkali metal salts of xylene sulfonic acids and a water soluble salt having an inorganic cation, such as illustrated by the water soluble sulfates, sulfites, thiosulfates, chlorides, dihydrogen phosphates, borates, and acetates, and a minor amount of alkali metal salts of keryl aryl sulfonic acids. Thus the present invention may be described briefly as involving a composition comprising a mixture of a sodium salt of xylene sulfonic acid and a water soluble inorganic salt as illustrated above in a major amount of a sodium salt of a keryl aryl sulfonic acid, the amount of the salt of the keryl aryl sulfonic acid being less than the amount of the salt of xylene sulfonic acid in the composition.

The sodium salts of the xylene sulfonic acids may be prepared in the conventional manner by sulfonating xylenes with concentrated sulfuric acid, contacting the sulfonated xylenes with an aqueous solution of sodium hydroxide, and finally evaporating to dryness. If a selected excess of sulfuric acid is employed, the solid residue which is obtained consists of a mixture of sodium xylene sulfonates and sodium sulfate, which is desirable

for use in the compositions of our invention. On the other hand, sodium xylene sulfonates may be recovered from spent caustic which has been previously employed in neutralizing sulfuric-acid treated, xylene-containing hydrocarbon fractions, such as hydroformed naphthenic gasoline- or kerosene-range distillates or the like, by neutralizing the remaining free alkali with a small amount of an inorganic acid, such as sulfuric acid, and evaporating the product to dryness. The residue will contain sodium xylene sulfonates and sodium sulfate, usually in the approximate weight ratio of 60:40. Since meta xylene is sulfonated more readily than the other isomers, sulfonated meta xylene is the predominant constituent of the resulting product. The mixture of sodium xylene sulfonates and sodium sulfate prepared as described above is useful as a wetting agent but has little utility as a detergent since it exhibits none of the characteristics of a detergent.

The alkali metal salt of a keryl aryl sulfonic acid employed in our invention may be prepared as described in the aforesaid patent, U. S. 2,161,174 to Kyrides, or may be obtained separately or admixed with alkali metal sulfate as described by Flett in U. S. 2,387,572, or by other methods known to the art.

The alkali metal salt of the xylene sulfonic acid employed in our invention is preferably a sodium salt, but the potassium and lithium salts may be used in lieu of the sodium salt although the latter is preferred. The xylene which is sulfonated and neutralized with the alkali metal hydroxide may be ortho-, meta-, or para-xylene, or a mixture thereof. Meta-xylene may be sulfonated with an excess of concentrated sulfuric acid of at least 98 weight per cent concentration and the sulfonated xylene contacted with an aqueous solution of sodium hydroxide, which may be of 20° Bé. gravity, to form a mixture of form a mixture of sodium meta-xylene sulfonate and sodium sulfate which may be heated to remove water by evaporation and the mixture then employed in the composition of the present invention.

This invention will be further illustrated by comparative tests carried out on a composition according to this invention and on a conventional detergent composition. The compositions were dissolved in water, in varying concentrations, and tested for detergency characteristics in a launderometer such as described in the article by Bacon and Smith, Industrial and Engineering Chemistry, vol. 40, No. 12, pages 2361-2370, December 1948. The launderometer was operated at 42 revolutions per minute, and 15 steel balls were employed in the tests. The test consisted, briefly, of washing soiled swatches of unsized, bleached white, cotton muslin of about 80 by 80 thread count. The muslin was soiled with a standard soiling solution comprising 216 grams of extra white petrolatum and 108 grams of lamp black in 18 liters of carbon tetrachloride. The soiled swatches were passed through the soiling solution in a soiling machine, dried in air, and aged for 5 days before use. The aged swatches were then placed in a bottle containing 200 cc. of a solution of varying concentrations of detergent in tap water of about 23 P. P. M. hardness. The launderometer was operated at 42 revolutions per minute for 25 minutes at 120° F., following which the machine was stopped and the volume of the suds in each jar, initially and after 5 minutes, was noted. The

washed swatches were removed from the jars, drained without squeezing or working, and then rinsed with tap water and dried. After drying, the "Hunter value," which is the fraction of light reflected from the laundered swatches, measured on a Hunter reflectometer, was determined in accordance with the method described by Hunter in Paint Varnish Production Manager, vol 21, page 207 and following, 1941. The "Hunter value" being indicative of the fraction of light reflected from a sample, a relatively high "Hunter value" is indicative of good detergent action by the solution tested. A "blank" was run by subjecting a sample immersed in water containing no added detergent composition to the procedure described above.

A "soil removal factor" was calculated for each test by subtracting the average "Hunter value" obtained from the "blank" runs from the "Hunter value" of the cloth washed in the test solution, and multiplying the difference obtained by a factor of 1,000. A high "soil removal factor" is indicative of good detergent action of the test solution. It is not unusual for the "soil removal factor" to be a negative value where a test solution has substantially no detergency.

In order to determine the detergent action of a composition prepared according to my invention, tests were made on the following three compositions:

Composition A was a commercial household detergent whose active ingredient is a keryl aryl sulfonate. This detergent consists of approximately 49 weight per cent of the keryl aryl sulfonate and approximately 60% of sodium sulfate.

Composition B consisted of 60 weight per cent sodium xylene sulfonates, preponderantly the sulfonate of meta-xylene, admixed with 40% of sodium sulfate.

Composition C was prepared by admixing 4 parts by weight of composition B with 1 part by weight of composition A. Thus, composition C consisted of 8% of sodium keryl aryl sulfonate, 48% of sodium xylene sulfonates and 44% of sodium sulfate.

The detergency value of these compositions was tested by the above described procedure, employing a launderometer and Hunter reflectometer. The results of these tests are presented in the table.

Table

Composition	Concentration, Wt. Per cent	Suds, Inches		Hunter Value	Soil Removal Factor
		Initial	5 Min.		
A-----	0.025	1/2	1/2	0.161	-14
A-----	0.05	2	3/4	0.184	+9
A-----	0.10	2	1 1/2	0.220	+45
B-----	0.10	None	-----	0.179	+4
B-----	0.20	None	-----	0.179	+4
B-----	0.30	None	-----	0.184	+9
C-----	0.10	None	-----	0.165	-10
C-----	0.20	1/4	1/4	0.174	-1
C-----	0.30	1/4	1/4	0.229	+54
Blank-----	-----	-----	-----	0.180	-----
Blank-----	-----	-----	-----	0.180	-----

For ease of interpretation, the results of these tests have been plotted graphically in the sole figure of the drawing which presents a plot of "soil removal factor" against the concentration of detergent in the solution tested. It is seen that in the case of composition A the "soil removal factor" increases in a linear relationship with detergent concentration over the range tested. It is also seen that composition B has

substantially no deterative action in the range tested.

The increase of "soil removal factor" with detergent concentration in the case of composition C has been plotted as curve I. Curve II presents the calculated values for the "soil removal factor" which would be expected of composition C if the deterative action of compositions A and B were merely additive. The method by which these values were calculated is best illustrated by means of an example. To calculate the expected "soil removal factor" corresponding to a given concentration of composition C in the test solution, the weight per cent of each component making up composition C is multiplied by the "soil removal factor" corresponding to that concentration, as read from the graphs.

Thus, for 0.30 weight per cent of composition C, the concentration of composition A (which makes up 20% of composition C) would be $0.20 \times 0.30 = 0.06\%$, and similarly the concentration of composition B = 0.24% . The "soil removal factor" for 0.06% of composition A, as read from the curve therefor, is +14 and that for 0.24% of composition B is +5. The total, or "calculated expected soil removal factor" of 0.30 weight per cent of composition C, therefore, is +19. Since the experimentally determined "soil removal factor" of an 0.30% solution of composition C is +54, it is obvious that the addition of the xylene sulfonate to a normally ineffective small concentration of keryl aryl sulfonate has exercised a synergistic effect sufficient to produce a solution of good detergency.

In additional tests, carried out under laundrometer conditions slightly different from those described above, compositions containing 10% and 20% respectively, of composition A, and 90% and 80%, respectively, of composition B, were compared for detergency characteristics. The composition containing 10% of composition A, and thus only 4% of keryl aryl sulfonate, was found to be only slightly inferior to the composition containing 20% of composition A.

Components preferably employed according to our invention are: keryl aryl sulfonates having a benzene or toluene nucleus and having 12 to 16 carbon atoms in the alkyl side chain which is only slightly branched or unbranched; xylene sulfonates comprising a major portion of the sulfonate of meta-xylene, which may be segregated from spent caustic previously contacted with hydrocarbon conversion products containing xylenes; and sodium sulfate as the inorganic ingredient.

The proportions of these ingredients preferably used will depend to some extent on the specific use contemplated for the product. In some applications the use of a relatively larger amount of the keryl aryl sulfonate may be justified, whereas in others the lowest possible amount of the keryl aryl sulfonate, namely as little as 4 to 8 per cent, may be desired to produce a very inexpensive detergent of good detergency. The amount of xylene sulfonates in the preferred composition is adjusted so that the total concentration of alkyl aryl sulfonates, including the xylene sulfonates, amounts to 40 to 60 weight per cent.

The compositions of the present invention ordinarily will comprise: from 4 to 35 weight per cent of an alkali metal alkyl aryl sulfonate having from 9 to 16 carbon atoms in the alkyl side chain; from 10 to 60 weight per cent of xylene sulfonates; and from 30 to 60 weight per cent of a water solu-

ble alkali metal salt such as the sodium, potassium, and lithium sulfates, sulfites, thiosulfates, chlorides, dihydrogen phosphates, borates, and acetates, but preferably an alkali metal sulfate.

In illustration of the compositions in accordance with the present invention, the ingredients may be present in the following distribution:

alkali metal keryl aryl sulfonate:
alkali metal xylene sulfonate:
alkali metal sulfate=
5:50:45 or 10:40:50 or 10:20:60.

The nature and objects of the present invention having been fully described and illustrated, what we wish to claim as new and useful and to secure by Letters Patent is:

1. A composition adapted for use as a detergent which consists of from 10 to 60 weight per cent of alkali metal salts of xylene sulfonic acids, from 4 to 35 weight per cent of alkali metal salts of alkyl aryl sulfonic acids having from 9 to 16 carbon atoms in the alkyl side chain, and from 30 to 60 weight per cent of a water soluble inorganic alkali metal salt.

2. A composition in accordance with claim 1 in which the alkali metal is sodium.

3. A composition in accordance with claim 1 in which the alkali metal is potassium.

4. A composition in accordance with claim 1 in which the alkali metal is lithium.

5. A composition in accordance with claim 1 in which the xylene is meta-xylene.

6. A composition in accordance with claim 1 in which the water soluble alkali metal salt is sodium sulfate.

7. A composition in accordance with claim 1 in which the alkyl aryl sulfonates are alkyl benzene sulfonates having from 12 to 16 carbon atoms in the alkyl side chain.

8. A composition in accordance with claim 1 in which the alkyl aryl sulfonates are alkyl toluene sulfonates having from 12 to 16 carbon atoms in the alkyl side chain.

9. A composition adapted for use as a detergent which consists of from 40 to 50 weight per cent of sodium salts of xylene sulfonic acids, from 8 to 12 weight per cent of sodium salts of alkyl aryl sulfonic acids having from 12 to 16 carbon atoms in the alkyl side chain, and from 38 to 52 weight per cent of sodium sulfate.

10. A composition adapted for use as a detergent which consists of 48 weight per cent of sodium salts of xylene sulfonic acids, the preponderant portion of which is derived from meta-xylene, 8 weight per cent of sodium salts of alkyl benzene sulfonic acid having from 12 to 16 carbon atoms in the alkyl side chain, and 44 weight per cent of sodium sulfate.

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