

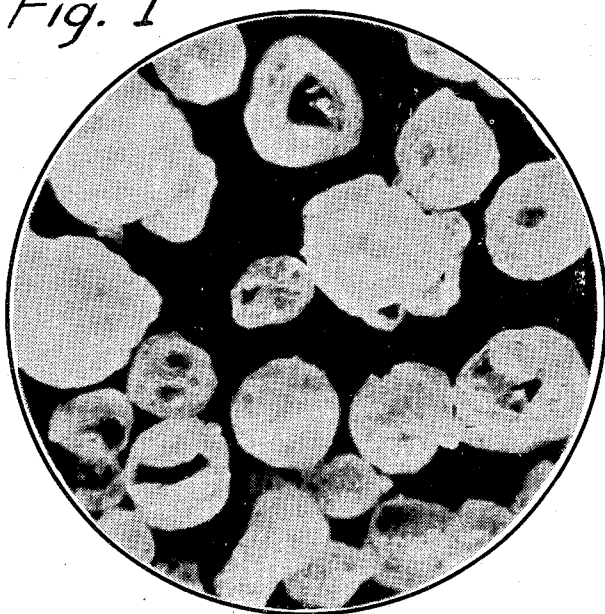
Dec. 12, 1944.

P. T. ZIZINIA ET AL
DETERGENT COMPOSITION

2,364,767

Filed Aug. 1, 1940

Fig. 1



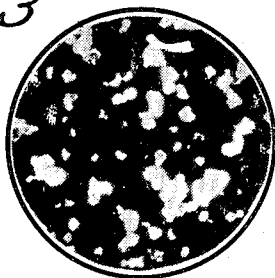
Magnification - 100X

Fig. 2



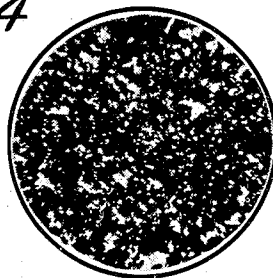
*Magnification
20X*

Fig. 3



Magnification - 125X

Fig. 4



Magnification - 20X

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2,364,767

DETERGENT COMPOSITION

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Application August 1, 1940, Serial No. 349,114

9 Claims. (Cl. 252—161)

This invention relates to alkyl aryl sulfonates in which the aryl radical is mononuclear and the alkyl radical contains from 12 to 23 carbon atoms, particularly to a new bulk form of such alkyl aryl sulfonates in which the mass of the material is made up of separate small globular particles.

Alkyl aryl sulfonates have been found useful for a large variety of purposes wherein cleansing, dispersing, wetting, surface-tension lowering, and similar action is required; for example, they have been incorporated in soaps, dyes, oils, waxes, plasticizers, insecticides, lubricants, and have found wide application as household cleansers. Particularly mononuclear aryl sulfonates which contain relatively large alkyl groups as nuclear substituents have been found advantageous for these uses. For example, compositions have recently been developed consisting of mixtures of benzene sulfonates or phenol sulfonates which contain as nuclear substituents radicals corresponding to the hydrocarbons present in petroleum distillates. Such mixtures are here included within the term "alkyl aryl sulfonates," the term "alkyl" being used in its broad sense to include cycloalkyl radicals as well as straight or branched open chain radicals. Depending upon the purpose for which they are to be used, these mixed alkyl aryl sulfonates may be derived from various petroleum fractions, such as fractions within the upper gasoline range, the kerosene range and higher ranges.

Alkyl aryl sulfonates in which the aryl group is mononuclear and the alkyl group contains from 12 to 23 carbon atoms have found particularly wide utility both for industrial and household uses. These compounds have been prepared by condensing a mononuclear aromatic compound such as benzene or a substituted benzene with an alkylating agent such as an aliphatic (including cycloaliphatic) alcohol or chlorhydrocarbon containing from 12 to 23 carbon atoms. For example, benzene or phenol may be condensed with a chlorinated kerosene to form such an alkylated aromatic compound. The alkylated aromatic compound is then sulfonated and the sulfonation reaction mixture neutralized to form an alkyl aryl sulfonate solution, which may be evaporated to obtain the dry salt. Ordinary drying means such as vacuum pan driers may be employed but for convenience in handling, these products have usually been prepared in various comminuted solid forms; for example, a flake or chip form of these products made by a drum drying process has been prepared.

The flake form of these alkyl aryl sulfonates

has a number of undesirable properties. The individual particles vary from opaque flakes of variable thickness, uneven surface and irregular shape to fine, dust-like powder formed by the breaking of these fragile flakes. Particles so shaped and sized tend to pack into a dense mass, so that the bulk density of the comminuted mass approaches the actual density of the solid. Moreover, as the material is handled, these irregularly-shaped flakes interfere with the smooth flow of the solid material and break to form a larger proportion of the dust-like powder in the material. Further, the flake material tends to take up moisture from the air at a high rate. The moisture taken up promotes caking of the solid, a condition which is aggravated by the presence of a large proportion of finely divided powder, whereby cakes are formed, and the intended purpose of placing the material in flake form, namely, to improve the handling and use of the material, is defeated in many cases.

When alkyl aryl sulfonates in flake or chip form are added to water, the particles of material are not readily separated and distributed, probably due in part to the tendency of the material to pack and cake rather than flow freely; accordingly, the material agglomerates and forms lumps in the water. Again, a purpose of comminution, namely, to make the material more readily soluble in water, is defeated. Even with stirring, the time required for solution of the material is unusually long for some purposes and a part of the product often settles into a coagulated mass at the bottom of the vessel when the material is used for washing or similar purposes.

In an effort to obtain an improved particle form of these alkyl aryl sulfonates, it was attempted to use conventional spray drying methods to evaporate the water from solutions of the sulfonates and deposit the solid in the form of relatively small particles. Well known spray drying equipment was employed for this purpose involving the spraying of a solution of the alkyl aryl sulfonate into a whirling stream of hot air or hot gases of combustion. The material thus obtained, however, was powdery, and under high magnification, this product was seen to consist of fine particles highly irregular in shape. This form of product is shown in Figures 3 and 4 of the drawing. Even with slight handling, the product in this form produces a persistent dust in the air which is irritating, and because of its dust-like character, the product is in general annoying and difficult to handle. In this form, also, the dry solid tends to pack upon handling, does

not flow as readily as is desirable for some purposes, takes up moisture avidly in a humid atmosphere, and cakes readily. When this finely divided material is added to water, like the flake material it lumps and agglomerates and for some purposes requires an unreasonably long time for solution.

It is an object of this invention to provide a new bulk solid form of a mixed alkyl aryl sulfonate and inorganic sulfate composition, in which alkyl aryl sulfonate the aryl group is mononuclear and the alkyl group contains from 12 to 23 carbon atoms, the compositions in bulk being light weight, substantially uniform in size and shape of particles, free-flowing, non-caking, readily soluble and characterized by the fact that it may be handled, stored and used without giving rise to the difficulties encountered by forms of alkyl aryl sulfonates heretofore known.

It is a particular object of this invention to prepare in a new solid form having the above-described characteristics compositions consisting of mixtures of sodium sulfate and benzene or phenol sulfonates which contain as nuclear substituents radicals corresponding to the hydrocarbons present in petroleum distillates.

The product of our invention is a new solid form of a mixed composition comprising a neutral water-soluble salt of an alkyl aryl sulfonic acid, and from about 40% to 65% by weight of a water-soluble alkali metal or alkaline earth metal sulfate, in which alkyl aryl sulfonic acid salt the aryl radical is mononuclear and the alkyl radical contains from 12 to 23 carbon atoms; the bulk product is made up of discrete megascopic particles, substantially all of the same order of magnitude (i. e., containing substantially no "fines"), the individual particles being translucent, hollow beads, having smooth, rounded contours and approximately globular or spheroid in shape. The product in mass form differs surprisingly in a number of its physical properties from forms of alkyl aryl sulfonates heretofore known. In addition to the remarkable uniformity of particle size and shape mentioned above, our product is characterized by its unusually low bulk density, low hygroscopicity, and extremely rapid water solubility.

The accompanying drawing, which constitutes a part of this application, is illustrative of our new product and shows how it differs from other forms of alkyl aryl sulfonates. On the drawing:

Figure 1 is a reproduction of a photomicrograph of individual particles in our new product, photographed with a magnification of 100 diameters,

Figure 2 is also a reproduction of a photomicrograph of individual particles of our new product, photographed with a magnification of 20 diameters,

Figure 3 is a reproduction of a photomicrograph at a magnification of 125 diameters, for comparison with Figure 1, of individual particles of a spray dried product chemically the same as our product but not embodying our invention, and

Figure 4 is a reproduction of a photomicrograph of a product similar to that shown in Figure 3, at a magnification of 20 diameters for comparison with Figure 2.

As above indicated, the substances produced in the new solid form of our invention are alkyl aryl sulfonates in which the aryl group is mononuclear and the alkyl group contains from 12 to 23 carbon atoms, the term "alkyl" being used in its broad sense to include cycloalkyl radicals as well as

straight or branched open chain alkyl radicals. In preparing the alkyl aryl sulfonate product of our invention, there may be employed a carbocyclic or heterocyclic aromatic compound. It may be free from substituents or it may contain one or more atoms or groups attached to the carbon or other atoms of the nucleus, the following substituents being cited as examples: one or more hydroxyl radicals, one or more alkyl groups, one or more sulfonic acid radicals, or one or more of the atoms or radicals Cl, Br, I, F, NO₂, NH₂, COOH, CONH₂, NHR₁, NR₁R₂, COOR₁, COR₁, CONHR₁, OR₁, SR₁, SO₃R₁, and R₁ (in which R₁ and R₂ represent any alkyl aryl, heteroaryl, alkaryl, aralkyl, cycloalkyl or heterocyclic radical, which groups or radicals may be further substituted or not, and if more than one is present it may be the same or different). As examples of these compounds there may be mentioned benzene, a benzene homolog such as toluene or xylene, phenol, a phenol homolog such as cresol or xylenol, methoxyphenol, phenetol, salicylic acid, pyrogallol or a similar compound. Those products are of particular importance in which the aromatic compound employed is benzene or phenol free from further substituents.

Alkyl substituents may be introduced into the aromatic compound by means of alkylating agents such as non-aromatic alcohols (for example, primary, secondary or tertiary aliphatic alcohols of the straight chain or branched chain types, naphthenic or cycloaliphatic alcohols, etc.), olefinic hydrocarbons containing a straight or branched chain and containing one or more double bonds which may be variously located in the hydrocarbons, halogen derivatives of the hydrocarbons (for example, chlorides or bromides of the saturated and unsaturated hydrocarbons of the aliphatic class), and derivatives of all of these compounds, all containing from 12 to 23 carbon atoms in the alkyl chain.

It is advantageous to use as the source of the alkyl radical for introduction into the aromatic nucleus naturally occurring or synthetically prepared non-aromatic hydrocarbon mixtures. For example, the various fractions of petroleum distillates, hydrogenated coal distillates, polymerized olefins, etc., represent available and inexpensive sources of alkylating agents for the preparation of higher alkyl aromatic sulfonates. The preferred alkylating agent in the production of our new product is the mixture of chlorhydrocarbons resulting from the chlorination of a selected petroleum distillate, preferably of the kerosene boiling range. Such a mixture of chlorhydrocarbons may be prepared, for example, by chlorinating with gaseous chlorine a kerosene fraction of the petroleum until about one and one-fourth times the amount of chlorine theoretically necessary to yield the monochlor substitution products of the hydrocarbon mixture has been absorbed. The resulting chlorination product consists of a mixture of monochlor hydrocarbons, together with some highly chlorinated hydrocarbons and unchlorinated hydrocarbons.

An alkylating agent, as described above, may be reacted with an aromatic compound to introduce an alkyl radical into the aromatic nucleus by means of a condensing agent such as anhydrous zinc chloride, anhydrous aluminum chloride, anhydrous antimony chloride, anhydrous ferric chloride, zinc, sulfuric acid (66° Bé., 100% H₂SO₄, or oleum). The particular condensing agent and conditions employed vary with the al-

alkylating agent employed. For example, in using zinc chloride as a condensing agent, much less of it is generally required in condensing an alkyl chloride with an aromatic compound than when an alcohol is condensed with the aromatic compound. In general, a long chain alcohol (for example, lauryl or cetyl alcohol) requires about an equal weight of zinc chloride for best results, whereas a chlorinated long chain hydrocarbon requires only about 5% to 10% of its weight of zinc chloride.

Preferably, the proportion of alkylating agent employed with respect to the aromatic compound is such that no more than two alkyl radicals are contained in the resulting alkyl aromatic compound, and preferably only one.

The time during which the condensation reaction of the aromatic compound with the alkylating agent may be carried out also may be varied and will depend upon the nature of the alkylating agent. In general, the condensation between an alcohol and an aromatic compound is practically complete within about three to five hours at refluxing temperature, but the quality of the product appears to be improved by continuing the heating. The condensation of an alkyl chloride with an aromatic compound is satisfactorily complete in about one hour at refluxing temperature or in about three to six hours at 135° C. With zinc chloride as the condensing agent, the period of heating may be extended to sixteen hours or more without seriously harming the quality or decreasing the yield of the alkyl aromatic compound. The alkyl aromatic compound resulting from the condensation is preferably purified as, for example, by distillation, and the purified compound is preferably employed for sulfonation to produce the product of our invention.

In sulfonating the alkyl aromatic compound, an inert solvent and sulfonation assistant may or may not be used. As sulfonating agents, there may be employed sulfuric acids of various strengths (e. g., 66° Bé. sulfuric acid, sulfuric acid monohydrate, oleum) chlorosulfonic acid, and the like. As solvents and diluents, there may be employed halogenated hydrocarbons of the aliphatic series, as, for example, carbon tetrachloride, dichloroethane, tetrachlorethane, or dichlorobenzene. When an inert solvent or diluent is used, it may be separated mechanically or by evaporation from the alkaline aqueous solution of the sulfuric acid salt of the alkyl aromatic compounds, which results upon diluting the sulfonation mass with water and neutralizing. As sulfonation assistants, there may be employed the lower organic acids or their anhydrides, as, for example, acetic acid, acetic anhydride or the like. The temperatures at which the sulfonation is carried out may vary within wide limits, for example temperatures as low as about 0° C. and as high as about 140° C. may be employed. In general, the more vigorous the sulfonating agent, the lower the preferred temperature. Ordinarily the completion of the sulfonation is carried out at a temperature of about 50° to about 80° C. The ratio of sulfonating agent employed to alkyl aromatic compound also may be varied. An amount of sulfuric acid or other sulfonating agent ranging from one-half part to about five parts by weight of sulfonating agent per part of the aromatic compound may be employed.

The sulfonation of the alkyl aromatic compound may be carried out to an extent such that more or less than one sulfonic acid group (based

on the alkyl aromatic compound) is present in the final product. While, as above indicated, one or two alkyl groups may be introduced into the aromatic nucleus, and while more or less than one sulfonic acid group may be introduced on the average into the aromatic nucleus, those compounds which contain an average of only one nuclear alkyl group having 12 to 23 carbon atoms in each aromatic nucleus (but which may contain additional lower alkyl groups) and which are sulfonated to an extent substantially corresponding to the monosulfonic acid compound, are of substantial importance.

The sulfonic acids produced as above described are converted to salts by reacting the sulfonated product, either in the crude form resulting from the sulfonation, or in a purified form, with a metal oxide or hydroxide, ammonia or an organic base, or a suitable salt of one of these in an amount adapted to form a neutral product. Among the bases, oxides and salts which may be combined with the sulfonated products to produce salts are, for example, sodium, potassium and ammonium hydroxide, sodium, potassium and ammonium carbonates and bicarbonates, ammonia, magnesium oxide, organic amines such as ethylamine and triethanolamine. This neutralization of the sulfonation reaction mixture thus converts the sulfonic acids to sulfonic acid salts and the unused sulfuric acid to a sulfate of the neutralizing material. In addition to the sulfonic acid salts, therefore, the neutralized mixture contains a sulfate such as sodium sulfate, potassium sulfate, ammonium sulfate or magnesium sulfate. The expression "water-soluble alkali or alkaline earth metal sulfate" is used herein to include the above-named inorganic sulfates and their obvious equivalents.

The preferred procedure for the conversion of the sulfonation product to salts involves a dilution of the sulfonation reaction mixture with water or ice, followed by neutralization as above described. The neutralization mix may be treated to remove impurities, if desired. The inorganic salt (e. g. sodium sulfate) formed by the neutralization may be substantially removed, leaving a solution consisting substantially entirely of the alkyl aryl sulfonate. For the preferred product for use as a household cleanser, however, additional sodium sulfate is added to the solution so as to increase the inorganic salt content of the final product to about 55% to 65%, preferably to about 60% by weight.

We have found that our new form of alkyl aryl sulfonates may be prepared by a process of spray drying a solution of alkyl aryl sulfonates containing about 30% to 35% solute, including the inorganic salts which may be present. To obtain such solution, it may be necessary to concentrate or dilute the solution obtained from the above described neutralization step, or from subsequent treatment. The product of the neutralization may also be evaporated to form a solid product, e. g., by drum drying, and this product may be redissolved to form a solution of the desired concentration which may then be spray dried.

A solution of the above concentration is sprayed into the top of a drying tower which is from about 20 to 50 feet high, and hot drying gases, e. g., hot air, are passed into the top of the tower concurrently with the sprayed liquid. The air and sprayed liquid pass vertically downwards. The temperature of the liquid fed to the sprays should be from about 100° F. up to the boiling point of the solution. The pressure of the liquid sprayed

depends upon the size of the spray orifice. For a 2 mm. orifice, the pressure may be as low as 50 pounds per square inch; 50 to 150 pounds per square inch was found suitable for a $1\frac{1}{4}$ mm. orifice. The liquid may be sprayed into the tower at the rate of 20 to 60 pounds per minute.

The amount of air supplied may vary from 250 to 750 pounds per minute, the amount depending upon the temperature of the air and the amount of water it is desired to evaporate. The higher the temperature of the air, the smaller the amount used. As the air enters the tower it is passed between spaced vertical vanes designed to reduce to a minimum any whirling motion of the air. The air flows downwardly in straight vertical paths to the lower part of the tower, where it may be withdrawn from peripheral outlets. The temperature of the air introduced into the drying chamber may vary from 400° to 800° F. for a tower having at least 20 feet drying height. The temperature of the air leaving the drying tower may vary from 175° to 225° F.

As the sprayed particles of liquid pass downwardly with the air current, water is evaporated and the product is obtained in the solid particle form shown in Figures 1 and 2. The product settles into a hopper positioned underneath the tower, from which it may be withdrawn for storage or shipment.

The product thus obtained is a mass of essentially spherical or globular particles; i. e., particles having a generally rounded contour, as shown on Figures 1 and 2 of the drawing, and in this respect differs from the irregularly-shaped, rough, sharp-cornered particles which make up other solid particle forms of alkyl aryl sulfonates produced prior to our invention. For example, Figures 3 and 4 show a spray dried alkyl aryl sulfonate product not embodying our invention, in which the particles are of an irregular, jagged shape, rather than the smoothly rounded ball-like form of our product shown in Figures 1 and 2.

The globular particles of our product, as is seen on Figures 1 and 2, are hollow bead-like bodies having thin translucent walls. The internal voids and thin translucent walls are clearly in evidence in certain of the particles in which blow-holes have formed during drying, as seen in Figures 1 and 2. Each individual particle in our product is thus a thin-walled shell. Although the walls are thin, the spherical conformation gives the shell a strength which resists crushing, and the comparatively smooth, rounded surface causes the particles to roll and slide readily over one another. This is in contrast to the fragile irregularly-shaped opaque chips of variable thickness and uneven surface made by drum drying alkyl aryl sulfonates, and to the jagged, dust-like particles, as shown in Figures 3 and 4. The uniform, extremely thin-walled structure of the particles in our product also contributes to the unusually low bulk density and rapid water solubility of our product.

The particles which make up our product are megascopic in size, i. e., visible to the naked eye or with a lens of very slight magnifying power. In our product, substantially all the particles pass through a 20-mesh screen (opening .833 mm.) and at least 85%, preferably 90%, of the mass consists of particles which are retained on a 60-mesh screen (opening .246 mm.). The amount of material passing a 100-mesh screen (opening .147 mm.) does not generally exceed 10%, and preferably does not exceed 5%, although a product of which 15% passes through a 100-mesh

screen may in some instances be satisfactory. The amount of material (fines) passing a 200-mesh screen (opening .074 mm.) does not exceed $1\frac{1}{2}\%$ and preferably is less than 1%.

Further, the particles in our product are remarkably uniform in size. For example, a screen analysis of a typical sample of our product shows that over 90% of the material is made up of particles so uniformly sized that the diameter of the largest particle in this 90% is only about three times as great as the smallest particle; further, about 99% of the material is so uniformly sized that the diameter of the largest individual particle is only about ten times as great as the smallest particle in this 99%. That is, about 99% of the particles are of the same order of magnitude. This remarkable uniformity of particle size and the essentially spherical shape of the particles cause them to lie in a uniform, regular arrangement, with definite and fairly uniform interstices between the particles, the interstices being substantially free from fines and dust. Because of this arrangement, as well as the smooth, rounded conformation of the individual particles, the bulk material flows freely, even out of small openings, the material in mass quickly assumes a smooth surface of repose when disturbed, and the material has no appreciable tendency to pack into a dense mass when handled.

The product of our invention has a bulk density ranging from .07 to .15, preferably from .09 to .11; which is less than one-fifth of the density of the flake form of product. The bulk density of our product, moreover, does not increase substantially when the product is tamped as it is poured into containers. For example, a sample of our product, having a bulk density of .09 without tamping, increased in bulk density only to a value of .11 when the material was tamped. The remarkably low bulk density of our product, together with the freedom from a tendency to pack into a dense mass, makes it particularly easy to handle the material, to measure out desired quantities and to flow the material into water to form solutions. Because of the freedom from caking and the free-flowing character of the product, it may be readily distributed throughout the body of water in which it is to be dissolved and does not agglomerate and form lumps in the water.

Our product possesses a remarkably high rate of solution in water as compared with the rate of solution shown by the same material dried by other drying methods, e. g., based on comparative tests hereinafter described it was found to dissolve in about one-tenth of the time required to dissolve other forms of alkyl aryl sulfonates not embodying our invention.

Our product takes up substantially less water than products chemically the same but not embodying our invention, i. e., our product is substantially less hygroscopic. In part, because of its low hygroscopicity as well as absence of fines and spaced arrangement of particles, our product shows substantially no tendency to cake. It should also be noted the content of volatile material in our product is less than 3%, generally less than 2%. This contrasts with the spray-dried product shown in Figures 3 and 4 of the drawing made by conventional spray-drying means in which the content of volatile material is substantially above 3%. The volatile content is determined by accurately weighing a $\frac{3}{4}$ gram sample of the product in a flat glass weighing dish, placing the sample in a hot air oven (electrically heated) maintained at a temperature of

110–115° C. not less than 18 hours and then reweighing the sample; loss of weight constitutes the volatile content.

It will be noted from the above, we have prepared alkyl aryl sulfonates in which the aryl radical is mononuclear and the alkyl radical contains from 12 to 23 carbon atoms, in a new physical form with remarkably advantageous properties as above described.

The following example is illustrative of our invention. All parts are by weight.

A kerosene fraction of Pennsylvania petroleum distillate, substantially all of which boiled between 180° and 300° C., having a specific gravity of 0.79 at about 25° C., and consisting principally of saturated hydrocarbons, was chlorinated by passing into it a stream of chlorine gas in the presence of a small amount of iodine as a catalyst while maintaining the temperature of the mixture around 55° to 60° C., until the specific gravity of the liquid had increased by 0.125. At this stage, about 1½ times the amount of chlorine theoretically necessary to yield the monochlor substitution products of the hydrocarbon mixture had been absorbed. The resulting chlorination product consisted of a mixture of monochlor hydrocarbons together with more highly chlorinated hydrocarbons and unchlorinated hydrocarbons.

10 parts of the resulting chlorination product comprising a mixture of monochlor hydrocarbons together with more highly chlorinated hydrocarbons and unchlorinated hydrocarbons, were reacted with 6 parts of benzene in the presence of 0.8 part of anhydrous aluminum chloride, for about 45 minutes with vigorous agitation at 42° to 45° C. The reaction mixture was then allowed to stand for about 2 hours. It separated into two layers. The upper oily layer was decanted. It contained a mixture of higher alkyl benzenes resulting from the condensation, together with unreacted benzene, unreacted petroleum hydrocarbons and chlorinated petroleum hydrocarbons, and by-products of the reaction. The oil was heated in a still until the liquid temperature reached 150° C. After cooling slightly, vacuum was applied and heating and distillation were continued until the vapor temperature reached 115° C. at an absolute pressure corresponding to 40 to 45 mm. mercury pressure, to remove a distillate comprising chiefly unreacted benzene, with some other low-boiling hydrocarbons. The receiver was then changed and distillation was continued until the vapor temperature reached 240° C. at 20 mm. mercury pressure, whereby a distillate was obtained comprising the alkyl benzene.

7.5 parts of the resulting distillate (comprising a mixture of the higher alkyl benzenes, together with other high-boiling constituents and by-products of the foregoing procedure) were agitated at 30° to 40° C. with 1 part of 100 per cent sulfuric acid for about 45 minutes. After standing quiescent for 1 to 2 hours the lower layer of spent wash acid was withdrawn. The remaining acid-washed oil was agitated with 6.5 parts of 100 per cent sulfuric acid at 60° C. for about 1 hour. The reaction mixture was then allowed to stand quiescent until it separated into three layers (about 1 hour). The upper layer, consisting of oily material and containing substantially all of the residual petroleum hydrocarbons and chlorhydrocarbons, as well as the greater portion of the water-insoluble by-products formed in the condensation and sulfonation operations, was re-

moved by decantation. The bottom sulfuric acid layer, containing principally spent sulfuric acid, was removed and discarded. The original middle layer, containing the alkyl benzene sulfonic acids and some sulfuric acid, was drowned in about 32 parts of cold water and neutralized with aqueous sodium hydroxide; for example, by treatment with a 50 per cent aqueous solution of caustic soda in an amount sufficient to render the resulting solution neutral to Brilliant Yellow and Congo Red. The inorganic salt content of the resulting neutralized solution amounted to about 40% by weight of the total solute. To the neutralized solution sufficient sodium sulfate was added to bring the inorganic salt content of the solute up to 60%; thus, the organic sulfonate content of the solute was 40%.

The solution was concentrated by evaporation until the concentration of solute reached about 32%. The liquor at a pressure of 125 pounds per square inch was then fed to spray nozzles having 2 millimeter orifices at the top of a 20-foot tower. 35 pounds of liquor per minute were sprayed. Drying air at a temperature of 700° F. was also introduced at the top of the tower at a rate of 450 pounds per minute. The air was introduced into the tower between vertical vanes designed to maintain the air in straight-line uni-directional vertical flow and avoid any whirling movement. Spent drying air was withdrawn from peripheral outlets at the bottom of the tower at a temperature of about 225° F. The spray-dried product was permitted to fall into a hopper below the tower and was withdrawn therefrom for storage and shipment.

The product thus obtained consisted of a mass of translucent hollow beads essentially spherical and with very thin walls as shown on Figures 1 and 2 of the drawing. The properties of this product were compared with a flake product and the spray-dried product not embodying our invention shown on Figures 3 and 4 of the drawing. Samples of these materials were tested for (1) particle size and uniformity, (2) bulk density, (3) rate of solution in water, and (4) hygroscopicity at 52%, 70%, 81% and 91% relative humidity. The results of the test were as follows:

(1) Particle size and uniformity as shown by screen analysis

Retained on—	Flake product	Spray-dried product not embodying our invention	Product of this invention
	Per cent		Per cent
10 mesh.....	24.0		0.0
20 mesh.....	32.5		0.1
40 mesh.....	32.8		54.4
60 mesh.....	9.0		37.0
100 mesh.....	0.5	0.0	2.3
200 mesh.....	1.2	1.2	5.1
Thru 200 mesh.....	Trace	93.8	1.1

(2) Bulk density

	Apparent specific gravity (water=1.00)	
	Not tamped	Tamped
Flake product.....	.475	.600
Spray-dried product not embodying our invention.....	.168	.247
Product of this invention.....	.090	.110

(3) *Rate of solution*

In this test 5 gram samples of each product were dissolved in 500 cc. of soft water. In each case the same mechanical agitation was used and the test was carried out at room temperature (25° C.). The following table shows the time required for complete solution in seconds:

	Seconds
Flake product.....	40-45
Spray-dried product not embodying our invention	35-40
Product of this invention.....	4-5

(4) *Hygroscopicity*

2 gram samples of each product, accurately weighed, were placed in 50 cc. beakers and exposed at room temperatures in desiccators to various relative humidities maintained by the use of appropriate saturated solutions of inorganic salts, viz.:

	Per cent relative humidity
Sodium dichromate $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	52
Potassium nitrate and ammonium chloride $\text{KNO}_3 + \text{NH}_4\text{Cl}$	70
Ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$	81
Sodium tartrate $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$	91

Samples were dried overnight at 105° C. so that all would be anhydrous at the start of the test. The following table shows the gain in weight of the samples tested:

Relative humidity	Days of exposure	Flake product	Spray-dried product not embodying our invention	Product of this invention
Per cent				
52	1	2.75	1.30	1.25
70	1	4.40	2.90	2.65
70	7	4.15	3.00	2.45
81	1	6.85	6.40	5.85
81	10	8.65	9.30	7.30
91	1/4	4.85	3.80	3.60

The above tests show that our product has a substantially lower hygroscopicity than either of the other forms tested. Moreover, due to the smooth, rounded outer surface and hollow bead structure of our product, it tends to remain free-flowing for a longer time under adverse humidity conditions than either the flake or the other spray-dried product.

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

What is claimed is:

1. A detergent composition consisting essentially of a neutral water-soluble salt of an alkyl aryl sulfonic acid and from about 40% to about 65% by weight of a water-soluble sulfate selected from the group consisting of alkali metal and alkaline earth metal sulfates, in which alkyl aryl sulfonic acid salt the aryl group is mononuclear and the alkyl group contains, on the average, from about 12 to 23 carbon atoms, the product being in the form of a mass of separate approximately globular hollow particles, at least about 85% of the mass consisting of particles of such size that they pass through a 20 mesh screen but are retained on a 60 mesh screen, the product in mass having a bulk density in the range of about .07 to .15.

2. A detergent composition consisting essentially of sodium benzene sulfonate and from about 40% to about 65% by weight of sodium sulfate, said sodium benzene sulfonate containing as a nuclear substituent an alkyl group derived from a petroleum fraction of the kerosene boiling range, said product being in the form of a mass of separate approximately globular hollow particles, at least about 85% of the mass consisting of particles of such size that they pass through a 20 mesh screen but are retained on a 60 mesh screen, the product in mass having a bulk density in the range of about .07 to .15.

3. A detergent composition consisting essentially of a neutral water-soluble salt of an alkyl aryl sulfonic acid and from about 55% to about 65% by weight of a water-soluble sulfate selected from the group consisting of alkali metal and alkaline earth metal sulfates, in which alkyl aryl sulfonic acid salt the aryl radical is mononuclear and the alkyl radical is derived from a kerosene fraction boiling in the range of about 180° to 300° C., said product being in the form of a solid containing no more than about 3% volatile material, made up of separate approximately globular hollow particles substantially all of the same order of magnitude and substantially all passing through a 20 mesh screen, at least 90% of the mass consisting of particles which are retained on a 60 mesh screen, no more than about 5% of the mass consisting of particles which pass through a 100 mesh screen, and no more than about 1½% of the mass consisting of particles which pass through a 200 mesh screen, the product in mass having a bulk density in the range of about .09 to .11.

4. A detergent composition comprising about 40% by weight sodium benzene sulfonate which contains as a nuclear substituent an alkyl group derived from a petroleum fraction of the kerosene boiling range and about 60% sodium sulfate, said product being in the form of a solid containing no more than about 3% volatile material, made up of separate approximately globular hollow particles substantially all of the same order of magnitude and substantially all passing through a 20 mesh screen, at least 90% of the mass consisting of particles which are retained on a 60 mesh screen, no more than about 5% of the mass consisting of particles which pass through a 100 mesh screen, and no more than about 1½% of the mass consisting of particles which pass through a 200 mesh screen, the product in mass having a bulk density in the range of about .09 to .11.

5. A free-flowing detergent composition comprising 35 to 45% by weight sodium benzene sulfonate which contains as a nuclear substituent an alkyl group derived from a petroleum fraction of the kerosene boiling range and about 55 to 65% by weight sodium sulfate, said composition being substantially non-caking and in the form of a mass of material made up of separate approximately globular hollow particles, substantially all of the same order of magnitude, at least about 85% of the mass consisting of particles of such size they pass through a 20-mesh screen but are retained on a 60-mesh screen, the composition in mass having a bulk density of about .07 to .15 and containing not more than 3% volatile material.

6. A detergent composition consisting essentially of a neutral water-soluble salt of an alkyl aryl sulfonic acid and from about 40% to 65% by weight of a water-soluble sulfate selected from

the group consisting of alkali metal and alkaline earth metal sulfates, in which alkyl aryl sulfonic acid salt the aryl radical is mononuclear and the alkyl radical contains, on the average, from 12 to 23 carbon atoms, said product being in the form of a mass of material in solid form made up of discrete megascopic particles substantially all of the same order of magnitude, the individual particles being hollow shells having smooth rounded contours and being approximately globular in shape and the product in mass being characterized by its low bulk density, low hygroscopicity, rapid water solubility, substantial freedom from caking by adhesion of particles, substantial freedom from a tendency to pack into a dense mass upon handling, its ability to flow freely and assume a smooth surface of repose, and the readiness with which it may be distributed in a body of water without substantial agglomeration of particles.

7. A detergent composition consisting essentially of sodium benzene sulfonate and from about 40% to 65% by weight of sodium sulfate, said sodium benzene sulfonate containing as a nuclear substituent an alkyl group derived from a petroleum fraction of the kerosene boiling range, said product being in the form of a mass of material in solid form made up of discrete megascopic particles substantially all of the same order of magnitude, the individual particles being hollow shells having smooth rounded contours and being approximately globular in shape and the product in mass being characterized by its low bulk density, low hygroscopicity, rapid water solubility, substantial freedom from caking by adhesion of particles, substantial freedom from a tendency to pack into a dense mass upon handling, its ability to flow freely and assume a smooth surface of repose, and the readiness with which it may be distributed in a body of water without substantial agglomeration of particles.

8. A detergent composition consisting essentially of sodium phenol sulfonate and from about 40% to 65% by weight of sodium sulfate, said sodium phenol sulfonate containing as a nuclear substituent an alkyl group derived from a petroleum fraction of the kerosene boiling range, said product being in the form of a mass of material in solid form made up of discrete megascopic particles substantially all of the same order of magnitude, the individual particles being hollow shells having smooth rounded contours and being approximately globular in shape and the product in mass being characterized by its low bulk density, low hygroscopicity, rapid water solubility, substantial freedom from caking by adhesion of particles, substantial freedom from a tendency to pack into a dense mass upon handling, its ability to flow freely and assume a smooth surface of repose, and the readiness with which it may be distributed in a body of water without substantial agglomeration of particles.

9. A detergent composition consisting essentially of a neutral water-soluble salt of an alkyl aryl sulfonic acid and from about 40% to 65% by weight of a water-soluble sulfate selected from the group consisting of alkali metal and alkaline earth metal sulfates, in which alkyl aryl sulfonic acid salt the aryl group is mononuclear and the alkyl group is derived from a petroleum fraction of the kerosene boiling range, said composition being in the form of a mass of separate approximately globular hollow particles, at least about 85% of the mass consisting of particles of such size that they pass through a 20 mesh screen but are retained on a 60 mesh screen, the product in mass having a bulk density in the range of about .07 to .15.

PAUL T. ZIZINIA.
THOS. L. MCKENNA.

CERTIFICATE OF CORRECTION.

Patent No. 2,384,767.

December 12, 1944.

PAUL T. ZIZINIA, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 12, for "compositions" read --composition--; page 3, second column, line 70, for "concurrently" read --cocurrently--; page 6, second column, line 41, claim 4, after "60%" insert --by weight--; 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 20th day of March, A. D. 1945.

Leslie Frazer

(Seal)

Acting Commissioner of Patents.