

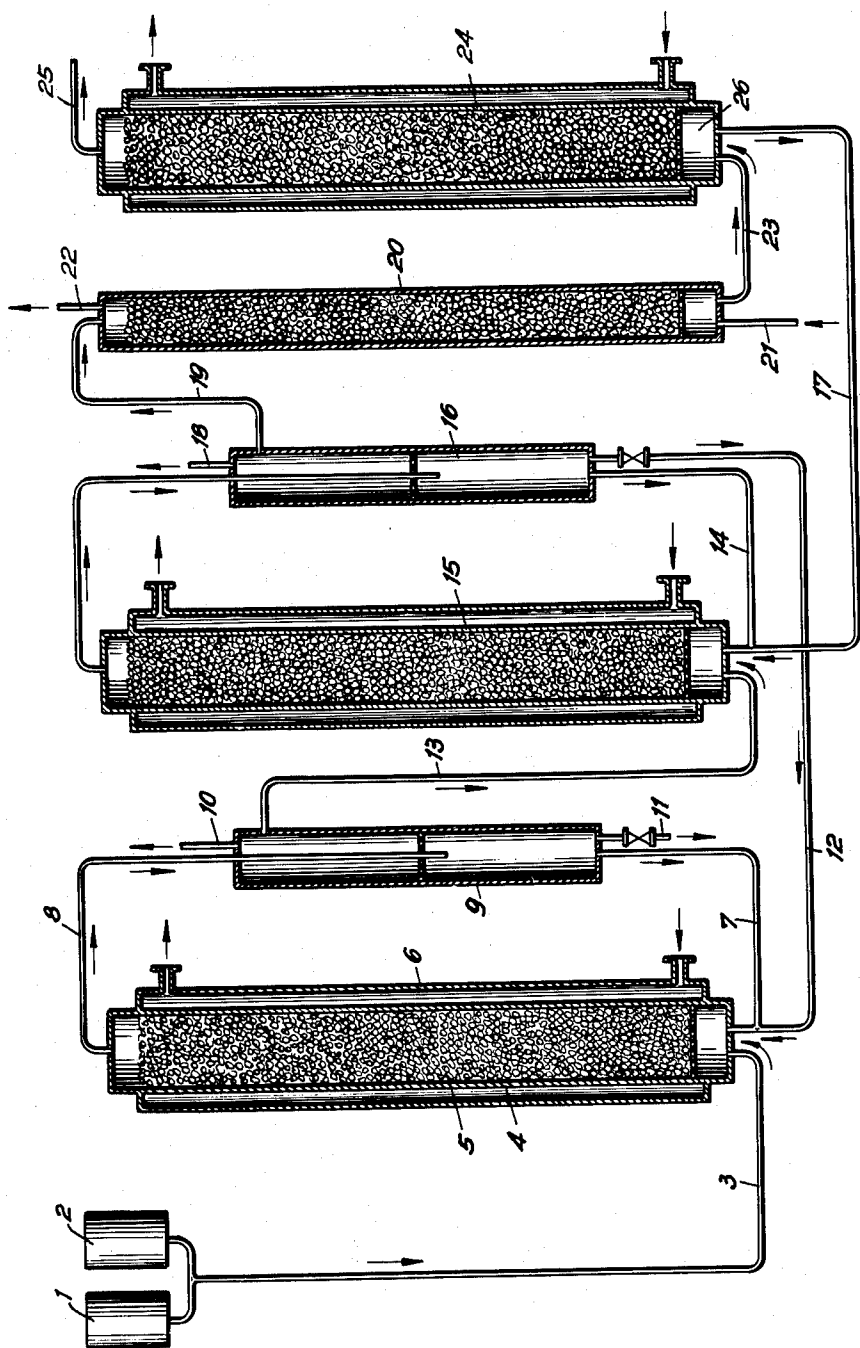
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PREPARATION OF PURE WHITE ALKYL ARYL SULFONATES

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PREPARATION OF PURE WHITE ALKYL ARYL SULFONATES

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5 Claims. (Cl. 260—505)

This invention relates to pure white alkyl aryl sulfonates. It more particularly relates to a process for the production of these sulfonates.

Alkyl aryl sulfonates which are used for detergents may be prepared from aliphatic and mixed aliphatic-naphthenic hydrocarbons by first separating these hydrocarbons into fractions of uniform carbon number, chlorinating these fractions in the known manner, separating by distillation pure alkyl monochlorides from the chlorination product, reacting the pure alkyl monochlorides with aromatic hydrocarbons, recovering pure monoalkyl benzenes from the alkylation mixture by distillation, sulfonating these pure monoalkyl benzenes with sulfuric acid and neutralizing them with alkali hydroxides or alkali carbonates. This process, as contrasted with the conventional process for the preparation of alkyl aryl sulfonates, results in almost white and nearly unhygroscopic detergents which are suitable as starting materials for the preparation of valuable light duty or heavy duty detergents.

When using aliphatic hydrocarbons of a molecular size lower than about C₁₀ in the above-mentioned process, the alkyl aryl sulfonates obtained are pure white. If, however, the aliphatic hydrocarbons contain more than 10 carbon atoms and less than 15 carbon atoms, as, for example, 12 carbon atoms, the color of the sulfonates prepared in accordance with the above-mentioned process, is still slightly yellow. Although this color is not by far as intensive as that of sulfonation products which are obtained when using alkyl chlorides containing di- and polychlorides, it is still objectionable. Absolutely pure white alkyl aryl sulfonates containing more than 10 carbon atoms in their aliphatic chain are highly desirable for several purposes, such as, for example, for the preparation of light-duty detergents as being used for washing wool and silk or for physical culture where neutrally reacting detergents are customarily employed.

One object of this invention is to obtain pure white alkyl aryl sulfonates which contain more than 10 carbon atoms and less than 15 carbon atoms in their aliphatic chain. This, and still further objects will become apparent from the following description:

It has been found that the yellow color appearing in the processing of hydrocarbons having more than 12 carbon atoms is caused by small quantities of a polycyclic organic compounds which form in the reaction of alkyl monochlorides with aromatic hydrocarbons, primarily with benzene, toluene or xylene, according to the method of Friedel-Crafts. The method of Friedel-Crafts is carried out with the use of aluminium chloride or addition compounds which form from anhydrous aluminium chloride and hydrocarbons and are referred to in the following description and in the claims as "contact oil." It is not possible to remove these impurities by distillation, since they distil in the range of the monoalkyl benzenes prepared. Also, a treatment with extracting or absorbing agents or an after-purification of the alkyl aromatics

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to be sulfonated or of the sulfo acids recovered therefrom is ineffective.

It has now been found that the objectionable coloring matters may be removed and practically completely white alkyl aryl sulfonates may be obtained by reacting the pure alkyl monochlorides with aromatic hydrocarbons so far that no unreacted alkyl chlorides remain in the alkylation mixture, and by aftertreating the alkylation mixture, after separation of the contact oil formed, with solid aluminium chloride. The alkylation product to be purified must be completely free from unreacted alkyl chlorides because otherwise the aluminium chloride used as purifying agent would cause any residual alkyl chloride to react with aromatic hydrocarbons. This reaction would result in the formation of larger quantities of contact oil and in a disturbance of the purifying process in such a degree that it is not possible to obtain pure white alkyl aryl sulfonates.

If alkyl monochlorides are condensed with aromatic hydrocarbons according to Friedel-Crafts, this reaction will not proceed to completion, but a residue of unreacted alkyl chlorides remains in the reaction mixture, the quantity of these unreacted alkyl chlorides reaching generally a magnitude of 10% of the alkyl chlorides charged. The complete reaction of the alkyl chlorides can only be obtained by larger quantities of aluminum chloride. However, under these reaction conditions, a considerably reduced yield of monoalkyl aromatics is obtained.

When C₁₂ monochloride which had been obtained by chlorinating a C₁₂ petroleum fraction freed from aromatic hydrocarbons is reacted with benzene at a mole ratio of 1:8 in a vessel with stirrer at a temperature of 20° C., the following results are obtained with different quantities of aluminium chloride:

TABLE I

Aluminum chloride, calculated on alkyl monochloride charged, percent by wt.	Unreacted alkyl monochloride in the alkylation mixture, percent by wt.	Yield of monoalkyl benzene, calculated on alkyl monochloride charged, percent by wt.
4	7	83
6	3	74
8	1	68
10	0	62

For reasons of economy it is not advantageous to react the alkyl monochlorides completely in one stage. Considerably higher yields of monoalkyl aromatics and a practically complete conversion of the alkyl monochlorides are obtained by carrying out the alkylation in two stages. The upper layer formed in the first alkylation stage is mixed, after separation of the contact oil, with additional quantities of aluminium chloride and subjected again to an alkylation under the same conditions. So much aluminium chloride is added to the first alkylation stage that 5 to 10% of the alkyl monochloride remain unreacted. Less than 5% of aluminium chloride, calculated on the alkyl monochloride, is generally sufficient for this purpose.

In the second alkylation stage, the addition of 3 to 6% of aluminium chloride is generally sufficient for the complete conversion of the products which contain still 5-10% of alkyl monochloride. The following Table II shows the results obtained in the second alkylation stage with a reaction product obtained in the first alkylation stage with the addition of 4% of aluminium chloride.

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TABLE II

Aluminum chloride, calculated on alkyl monochloride charged, percent by wt.	Unreacted alkyl monochloride in the alkylation mixture, percent by wt.	Yield of mono-alkyl benzene, calculated on alkyl monochloride charged, percent by wt.
2	2	80
4	0	77
6	0	73

The data of Tables I and II indicate that complete conversion of the alkyl chlorides is obtainable either in the first stage by the addition of 10% of aluminium chloride, or, in two-stage operation, by the addition of 4% of aluminium chloride to each stage. In the two-stage operation, a yield of 77% of mono-alkyl benzene is obtained as compared with only 62% in single-stage operation.

The reaction products obtained by means of a two-stage alkylation process and being free from unreacted alkyl chlorides are treated in a final stage with additional quantities of aluminium chloride in order to remove the objectionable polycyclic compounds which cause the undesirable color of the finished products. For this purpose, the reaction product of the second stage is separated from the contact oil formed and treated as the upper layer with aluminium chloride in a vessel with stirrer at a temperature of 20° C. In this final stage the quantity of aluminium chloride added must be at least 2% of the alkyl monochloride charged to the first alkylation stage. In general, the quantity of aluminium chloride added need not be higher than 5%. The use of the purification of the mono-alkyl aromatics according to the invention will generally cause a loss of approximately 12%.

When the quantity of aluminium chloride used for the treatment of the alkyl monochloride to be processed into alkyl aryl sulfonates is, for example, 4% in the first stage, 4% in the second stage, and 3% in the final stage, the yield of mono-alkyl aromatics will be $0.77 \times 88 = 68\%$. When carrying out the alkylation in single-stage operation with 10% of aluminium chloride, and the purification of the alkyl aromatics with 3% of aluminium chloride, the yield will be only $0.62 \times 0.88 = 54\%$, i. e. considerably lower than in three-stage operation.

It is known to carry out the reaction of alkyl chlorides with aromatic hydrocarbons in two stages in such a manner that, calculated on the alkyl monochloride charged, less than 5% of aluminium chloride are used in the first stage and up to 20% in the second stage. Although an increased yield is obtained in this way, no pure white sulfonates are obtained. The reason for this is that no complete conversion of the alkyl chlorides is effected in the first stage with less than 5%, so that the objectionable polycyclic compounds cannot be removed in a sufficiently large extent by the subsequent treatment with additional quantities of aluminium chloride. When operating in the first stage with sufficiently large quantities of aluminium chloride as to have no unreacted alkyl chlorides present in the reaction mixture, for instance, with 10% of aluminium chloride, and then, in a subsequent stage, with additional quantities of aluminium chloride, white sulfonates will be obtained, but the yield will decrease, as indicated by Tables I and II, by almost 20%.

An additional increase of the yield of mono-alkyl aromatics is possible by working in the first two stages not only with the addition of aluminium chloride, but by utilizing the contact oil separated after completion of the reaction for further alkylation reactions. The contact oil to be reused is freshened by small quantities of fresh aluminium chloride and/or by removing small portions of the used contact oil. The final stage of the

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process according to the invention can only be operated with solid aluminium chloride.

The best way to carry out the different stages of the alkylation and the purification of the alkylation products is by continuous operation.

For the continuous operation of the process according to the invention, it is most expedient to use vertically arranged reaction vessels lined with corrosion-resistant material and filled with a suitable aluminium chloride contact oil. These reaction vessels are equipped with a cooling jacket and filled with Raschig rings or other suitable distributing solids. The mixture consisting of alkyl monochloride and aromatic hydrocarbons is admitted at the lower end of the contact oil column. It rises within the contact oil layer and is passed over at the upper end, mixed with contact oil, into a settling vessel where a complete separation of the contact oil carried along can take place. To obtain better mixing of the reactants, part of the hydrogen chloride escaping at the top of the reaction vessel may be recycled to the bottom of the reaction tube.

One part by volume of the reaction mixture consisting of alkyl monochloride and aromatic hydrocarbons is suitably admitted for each part by volume of contact oil. The reaction temperature is generally maintained at approximately 20° C. The residence time of the reactants in the first alkylation stage should be approximately 2 hours. The second stage is operated with a reaction time of 30 to 60 minutes.

The upper liquid layer from the settling vessel connected in series to the first stage is passed over into the second alkylation stage, while the contact oil separated returns into the first stage. Approximately 3-5% of the circulating contact oil are hourly withdrawn from the contact oil cycle and replaced by contact oil drawn off from the second stage or by regenerated contact oil from the first stage.

Apart from a shortened reaction time, the second alkylation stage operates in the same manner as the first alkylation stage. Also in this stage the rate at which the mixture consisting of alkyl chloride and aromatic hydrocarbon is added is 1 part by volume for each part by volume of contact oil. The quantity of contact oil continuously drawn off from the contact oil cycle is equal to that supplied by the third stage which is connected in series to the second stage for the purpose of purifying the alkyl aromatics. It is also possible, if necessary or desired, to regenerate part of the contact oil drawn off from the second stage and to return this part into the second stage. In general, approximately 3 to 8% of the contact oil circulating in the second stage are hourly interchanged.

Continuous operation is also possible for the final stage of the aluminium chloride treatment, which is connected to purify the upper layer obtained in the second alkylation stage, which is free from unreacted alkyl chlorides. This is accomplished by separating the upper layer of the second alkylation stage from the contact oil and passing it from below through a vertically standing and cooled reaction tube of adequate length, which is filled with solid lumpy aluminium chloride. A contact oil forms which runs off in downward direction through the aluminium chloride bed in counter-current to the reaction mixture passed through. The formation of contact oil occurs chiefly in the lower layers of aluminium chloride. In this way, the aluminium chloride is gradually used up.

In the course of this operation, the aluminium chloride bed settles gradually and must be supplemented continuously or batchwise by fresh aluminium chloride without the necessity of interrupting the operation of the purification stage.

The contact oil accumulating at the lower end of the aluminium chloride column used for the purification of the reaction mixture from polycyclic compounds is used

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to make up the contact oil cycle of the second alkylation stage.

At the top of the aluminium chloride tower, an upper layer runs off which, after separation of any entrained contact oil quantities, no longer contains polycyclic compounds. After distillation, sulfonation and neutralization, it furnishes pure white alkyl aryl sulfonates.

In the purification according to the invention, the reaction mixture is maintained at a temperature of, for example, 10–20° C., and the residence time of the reaction mixture being purified is 30 to 60 minutes.

The yields obtainable in the continuous alkylation and purification in accordance with the invention are very good. When processing a C₁₂ monochloride, a yield of 87% of mono-alkyl aromatics, calculated on the alkyl monochloride charged, is reached in the first alkylation stage. No reduction of this yield occurs in the second alkylation stage. In contrast with the use of solid aluminium chloride, the continuous operation gives a considerable increase of yield, because in this case no upper layer is consumed in the two first alkylation stages for the formation of contact oil. Also, in the third stage, i. e. in the purification of the alkyl aromatics with solid aluminium chloride, the continuous operation gives a better yield than a batchwise operated stirring process. In the continuous operation, the loss in yield of mono-alkyl aromatics remains generally below 10%.

When processing a C₁₂ monochloride obtained from a petroleum fraction free from aromatics, the continuous operation gives a yield of at least $0.87 \times 90 = 78\%$ by weight of mono-alkyl benzene, calculated on the alkyl monochloride charged. As opposed to that, batchwise operation of the three-stage aluminium chloride treatment according to the invention gives $0.77 \times 88 = 68\%$ of mono-alkyl benzene, and the batchwise operated two-stage process even only $0.62 \times 88 = 54\%$ of mono-alkyl benzene.

Instead, from the upper layer obtained in the alkylation and free from alkyl chlorides, the objectionable polycyclic compounds may be removed, if necessary or desired, from the mono-alkyl aromatics resulting in the distillation of the reaction mixture. For this purpose, the separated alkyl aromatic hydrocarbon is passed through a column of solid lumpy aluminium chloride or is stirred up with aluminium chloride. The mono-alkyl aromatics treated in this manner yield, in the subsequent sulfonation and neutralization, pure white products.

The purification of the isolated alkyl aromatic hydrocarbons has the disadvantage, however, that the aromatic hydrocarbon is seriously attacked by the aluminium chloride, which causes partially aliphatic hydrocarbons to split off. Apart from a decrease of yield, which, with a C₁₂ mono-alkyl benzene, will reach approximately 20% in this case, an additional distillation is required to separate undesirable hydrocarbons from the condensation products recovered.

An additional increase of the yield of mono-alkyl benzene to about 85% may be reached without a reduction of the quality, especially without a deepening of color of the alkyl aryl sulfonates produced as the finished products, if the alkylation mixture obtained in the first two stages of the process is freed as completely as possible from its content of hydrogen chloride before the final treatment with solid aluminium chloride. In the third stage, the formation of contact oil depends essentially on the content of hydrogen chloride in the entering alkylation mixture. When the alkylation product of the second stage charged to the third stage of the process is freed from the hydrogen chloride dissolved, the quantity of contact oil formed in the third stage will reduce to about half that of the values usual so far, thereby reducing correspondingly the losses in mono-alkyl benzene. The previous removal of the content of hydrogen chloride does in no way affect the purifying action of the solid aluminium chloride.

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The alkylation mixture entering the third operation stage may be freed in any optional way from its content of hydrogen chloride. A treatment with soda and/or bleaching clay carried out in vessels with stirrer may be used, or air or other inert gases may be blown through the alkylation mixture. It is also possible to combine the two procedures by blowing at first inert gases or air through the mixture and removing the residual portions of hydrogen chloride with soda or sodium hydroxide by passing the alkylated products over these materials.

The reduction of contact oil formation obtained in the third operation stage occurs in the same manner for the aftertreatment carried out batchwise in a stirring process or continuously in a tube filled with solid aluminium chloride.

In the continuous operation in which a separate contact oil cycle is used in each of the first and second operation stages, the quantity of contact oil formed in the third stage is not sufficient to regenerate the contact oil cycle in the first two stages. Freshly prepared contact oil must therefore be used for the regeneration of the contact oil cycle of the first two stages.

It is of particular advantage to regenerate the contact oil drawn off from the first stage and to charge the regenerated contact oil to the second alkylation stage together with the contact oil formed in the final stage. The best way to regenerate the contact oil is to separate the contact oil with water into aluminium chloride and hydrocarbons. The hydrocarbon mixture is freed by distillation from its resinous polymerization products and then used for the preparation of fresh contact oil.

When, for example, 6.5% of the circulating contact oil are drawn off from the first stage, about 4.5% of contact oil are recovered in the regeneration. In the final stage, after removal of the hydrogen chloride, only about 2% of contact oil are obtained, calculated on the contact oil quantity circulating in the first or second stage. Since also from the contact oil cycle of the second alkylation stage 6.5% of contact oil must be interchanged and given into the first stage, the quantity of 2% forming in the third stage together with the 4.5% resulting in the contact oil regeneration is just sufficient to meet the contact oil requirement.

The process in accordance with the invention may be carried out, for example, by means of the apparatus represented in the drawing.

The aromatic hydrocarbon to be processed, preferably benzene, toluene or xylene, is in container 1. The alkyl monochloride to be converted is withdrawn from storage container 2. Both of the materials are mixed and fed through line 3 to the base of the reaction tube 4. The reaction tube 4 is filled with packing material 5, for example with Raschig rings, and surrounded at its outer surface with a jacket 6 by means of which the reaction tube 4 may be brought to the temperature required for the reaction, using cooling or heating media. The contact oil required for the reaction is admitted at the base of the reaction tube 4 through line 7.

The reaction mixture withdrawn at the top of tube 4 passes through line 8 into a settling vessel 9 from which the hydrogen chloride formed escapes through line 10. In vessel 9, a separation into two layers takes place. The contact oil separated as the lower layer returns through line 7 into the reaction tube 4. A part of the contact oil may be withdrawn from the separating vessel 9 through line 11. A quantity of contact oil corresponding to the quantity withdrawn is transferred from the contact oil cycle of the second alkylation stage to the contact oil cycle of the first alkylation stage by means of line 12.

The alkylation mixture separated in the settling vessel 9 from the contact oil is introduced through line 13 to the base of a second reaction tube 15. Contact oil is simultaneously admitted through lines 14 and 17 to the lower end of the reaction tube 15. The reaction tube 15 is likewise surrounded by a jacket to maintain optimum

reaction temperature by means of heating or cooling media.

The reaction mixture forming in reaction tube 15 is withdrawn at the top of the tube and passed into a separator 16. Here, the contact oil separates as lower layer and is returned through line 14 into the cycle of the reaction tube 15. As already mentioned, part of the contact oil withdrawn from separator 16 is transferred through line 12 into the contact oil cycle of the first alkylation stage. A portion corresponding to this quantity is freshly introduced through line 17. The hydrogen chloride formed in the second alkylation stage 15 escapes at the top of the settling vessel 16 through line 18.

The reaction mixture freed from the contact oil is charged from the separator 16 through line 19 to the top of a tube 20 filled with filling bodies. It trickles down through the filling bodies and collects at the base of the tube 20. Air or another inert gas is blown through line 21 into the lower end of tube 20 to blow out the hydrogen chloride still contained in the reaction mixture through line 22.

The reaction product freed from the hydrogen chloride is passed, through line 23, from below into a reaction tube 24 filled with solid lumpy aluminum chloride, and led off at the top of this tube through line 25. During the purification of the reaction product, contact oil forms in tube 24 from the solid aluminum chloride which contact oil collects in the lower part 26 of this reaction tube. This contact oil is passed through line 17 to the second alkylation stage to make up the contact oil cycle of this stage.

The reaction tube 24 may be provided with a jacket in which cooling or heating media are used to provide for optimum temperature conditions in the treatment with solid aluminum chloride.

Example 1

A C₁₂ fraction derived from petroleum and freed from the aromatics present, was chlorinated, and a pure C₁₂ monochloride fraction separated from the chlorination mixture. 250 gms. of this fraction were stirred for four hours at 20° C. with 760 gms. of benzene and 25 gms. of aluminum chloride in a glass flask of 2000 cc. capacity. Then 900 gms. upper layer and 90 gms. of contact oil were separated. The upper layer comprising 900 gms. was mixed with 7.5 gms. of aluminum chloride and stirred again for 3 hours at 20° C. in a glass flask of 2000 cc. capacity. Thereafter, 28 gms. of contact oil were separated from the reaction mixture. The end product was an upper layer of 879 gms. After purification with 5 gms. of bleaching clay (trademark Tonsil) and 5 gms. of soda, which purification was inserted to remove residual contact oil or residual quantities of hydrogen chloride, the excess benzene was at first distilled off; then the remainder was separated by vacuum distillation into 135 gms. of C₁₂ mono-alkyl benzene, 70 gms. of C₁₂ hydrocarbon, and 13 gms. of higher boiling products.

The yield of mono-alkyl benzene was 54% by weight, calculated on the C₁₂ monochloride charged. When this C₁₂ mono-alkyl benzene was sulfonated and neutralized in the conventional manner, pure white alkyl benzene sulfonates were obtained.

Example 2

250 gms. of the C₁₂ monochloride fraction used in Example 1 were stirred with 760 gms. of benzene and 10 gms. of aluminum chloride for 4 hours at 20° C. in a glass flask of 2000 cc. capacity. After completion of the reaction, 945 gms. upper layer and 35 gms. of contact oil were separated. The upper layer was mixed with 10 gms. of aluminum chloride and stirred for 3 hours at 20° C. in a glass flask of 2000 cc. capacity. The reaction product formed thereby was again separated from the contact oil and passed over into another

2000 cc. glass flask. After the addition of 7.5 gms. of contact oil, the agitation was continued for 3 hours at 20° C. After this treatment, an upper layer of 895 gms. and 27 gms. of contact oil were obtained. The upper layer was treated with 5 gms. of bleaching clay (trademark Tonsil) and 5 gms. of soda, freed from excess benzene by distillation, and then separated, by vacuum distillation, into 170 gms. of pure C₁₂ mono-alkyl benzene, 58 gms. C₁₂ hydrocarbons and 14 gms. higher boiling products.

The yield of C₁₂ mono-alkyl benzene was 68% by weight, calculated on the C₁₂ monochloride charged. The subsequent sulfonation and neutralization of the C₁₂ mono-alkyl benzene yielded pure white alkyl benzene sulfonates.

Example 3

A vertical tube 300 cm. long with an inside diameter of 150 mm. surrounded by a cooling water jacket and provided at the inside with acid-proof lacquer, was filled with porcelain rings 8 mm. in diameter, and then almost completely filled with aluminum chloride contact oil. The contact oil was derived from the second alkylation stage and had a volume of approximately 40 liters.

7.5 liters of benzene and 2.5 liters (2200 gms.) of C₁₂ monochloride of the origin mentioned in Example 1 together with 10 liters of contact oil were hourly fed from below into the reaction tube thus filled. Besides, 200 liters/hr. of the hydrogen chloride escaping at the upper end of the reaction tube were admitted at the lower end of the reaction tube. The reaction temperature was maintained at 20° C. The reaction mixture flowing off at the top of the reaction tube entered a settling tube of 3 m. in length and 150 mm. diameter, which was also protected with acid-proof lacquer. In this tube the mixture separated into the lighter hydrocarbon layer and the lower contact oil layer. The contact oil was drawn off at the bottom and recycled into the alkylation tube. 0.4 liter of contact oil was hourly drawn off from the cycle, and replaced by contact oil from the second alkylation stage. The upper layer separated from the reaction product of the first alkylation stage was passed into an alkylation tube of the same construction, but only 2.5 m. in length and 100 mm. inside diameter. This reaction tube, which was also filled with porcelain rings, was filled with aluminum chloride contact oil which had already been used in the third operation stage.

10 liters of contact oil and 200 liters of hydrogen chloride in addition to the alkylation products obtained in the first stage were hourly fed into this second alkylation tube at the bottom. The resulting reaction product passed from the top of the reaction tube into a settling tube of 3 m. in length and 150 mm. in diameter, where it separated into an upper layer and a lower contact oil layer. The contact oil was drawn off at the bottom of the settling tube and returned into the reaction tube. 0.4 liter of contact oil was hourly separated and used to make up the contact oil circulating in the first alkylation stage. The quantity of contact oil drawn off was replaced by the same quantity of contact oil from the third operation stage.

The upper layer of the second alkylation stage was fed from below into a vertical tube of 2.5 m. in length and 80 mm. in inside diameter, which was filled with lumpy aluminum chloride and externally cooled with water. After the passage through the aluminum chloride layer, the alkylation mixture fed in was drawn off at the top of the tube. The reaction temperature was 15° C. At the bottom of the tube the contact oil formed accumulated at a rate of approximately 0.4 liter/hr. This contact oil was passed over into the second alkylation stage to make up the contact oil cycle.

The liquid running off from the top of the tube filled with aluminium chloride was treated in the usual manner with bleaching clay and soda and clarified. Then it

was freed from excess benzene by distillation and separated into hydrocarbons, mono-alkyl benzene and higher boiling products. 1.75 kilos of C₁₂ mono-alkyl benzene, 0.36 kilo of C₁₂ hydrocarbon and 0.13 kilo of higher boiling products were obtained per hour. The yield of mono-alkyl benzene was 79.5% by weight, calculated on the C₁₂ monochloride charged. In a subsequent sulfonation and neutralization carried out in the usual manner, pure white alkyl benzene sulfonates were obtained from this material.

Example 4

C₁₀ monochloride was reacted with xylene by means of the reaction tubes used in Example 3. For this purpose, 8.3 liters of xylene and 1.7 liters (1500 gms.) of C₁₀ monochloride together with 10 liters of contact oil were hourly fed from below into the first reaction tube. Moreover, the working method was exactly the same as that of Example 3. 1.17 kilos C₁₀ mono-alkyl xylene were hourly obtained as the end product. Based on the C₁₀ monochloride charged, the yield of C₁₀ mono-alkyl xylene was 78% by weight of the theoretically possible yield.

Example 5

7.6 liters of toluene and 2.4 liters (2100 gms.) of C₁₄ monochloride were hourly reacted in the same way and using the same apparatus as described in Example 3. At the same time, 10 liters of contact oil and 200 liters of the hydrogen chloride escaping at the top of the reaction tube were hourly charged at the base of the first reaction tube. The reaction temperature was 22° C. 1.66 kilos C₁₄ mono-alkyl toluene were obtained per hour which, based on the C₁₄ monochloride charged, corresponded to a yield of 79% by weight.

Example 6

A vertical tube 3 m. long with an inside diameter of 150 mm. lined with acid-proof lacquer and surrounded by a cooling water jacket, was filled with porcelain rings of 8 mm. diameter and then nearly completely filled with aluminum chloride contact oil. The contact oil was taken from a second alkylation stage connected in series and had a volume of approximately 40 liters.

7500 cc. of benzene and 2500 cc. (2200 gms.) of C₁₂ monochloride together with 10 liters of contact oil were hourly fed from below into the reaction tube thus filled. The C₁₂ monochloride had been prepared by chlorination and subsequent distillation from a dearomatized C₁₂ fraction of an Arabian petroleum.

Besides, 200 liters of the hydrogen chloride escaping at the top of the reaction tube were hourly fed at the bottom of the reaction tube. The reaction temperature was maintained at 20° C.

The alkylation mixture flowing off at the top of the reaction tube was drawn off into a settling tube of 3 m. in length and 150 mm. in diameter connected in series, where the mixture separated into a lighter hydrocarbon layer and the lower contact oil layer. The contact oil was drawn off at the bottom and recycled into the reaction tube. 650 cc. of contact oil were hourly drawn off from the cycle and replaced by contact oil from the second alkylation stage.

The upper layer separated from the reaction product of the first alkylation stage was passed into an alkylation tube of the same construction but of only 250 mm. in length and 100 mm. inside diameter. This reaction tube was also filled with porcelain rings of 8 mm. diameter and with aluminum chloride contact oil. 10 liters of contact oil and 200 liters of hydrogen chloride in addition to the alkylation products obtained in the first alkylation stage, were hourly fed into the second alkylation tube at the bottom. The resulting reaction product was passed from the top of the reaction tube into a settling tube connected in series to the reaction tube, having 3 m. length and 150 mm. diameter, where it separated into an

upper layer and a lower contact oil layer. The contact oil was drawn off at the bottom and returned into the reaction tube of the second stage. 650 cc./hr. of contact oil were drawn off and used to regenerate the contact oil circulating in the first alkylation stage.

The quantity of contact oil drawn off from the second alkylation stage was compensated by 200 cc. of contact oil which formed in the third stage, and by 450 cc. of contact oil formed in the regeneration of the 650 cc. of contact oil drawn off from the first stage. The regeneration was effected by decomposition with water and subsequent distillation of the oil constituents. The resinous products present in the contact oil remained in the residue from distillation, while the distillate, with benzene and aluminum chloride, furnished new contact oil.

The upper layer from the second alkylation stage was trickled down through a vertical tube 200 cm. long with an inside diameter of 50 mm. filled with Raschig rings, while 200–300 liters/hr. of dried air were passed through from below in counter-current to remove the hydrogen chloride dissolved. The alkylation mixture freed from hydrogen chloride, was then passed from below into a vertical tube 250 cm. long and with an inside diameter of 80 mm. filled with lumpy aluminum chloride and externally cooled with water. The reaction temperature was 15° C.

After the passage through the aluminium chloride layer, the alkylation mixture was drawn off at the top of the tube. At the bottom of the tube, the contact oil formed accumulated at a rate of approximately 200 cc./hr. It was used in the manner mentioned above to make up the contact oil cycle of the second operation stage.

The liquid running off from the top of the tube filled with lumpy aluminium chloride, was treated in the usual manner with bleaching clay and soda and clarified. Then it was freed from excess benzene by distillation and separated into hydrocarbon, mono-alkyl benzene and higher boiling products.

The following end products were obtained per hour: 1.87 kilos of C₁₂ mono-alkyl benzene, 0.35 kilo of C₁₂ hydrocarbon and 0.11 kilo of higher boiling products. The yield of mono-alkyl benzene was 85% by weight, calculated on the C₁₂ monochloride charged. Sulfonation and neutralization of this mono-alkyl benzene in the usual manner yielded pure white alkyl benzene sulfonates.

We claim:

1. In a process for the preparation of alkyl aryl sulfonates by chlorinating a hydrocarbon fraction of uniform carbon number, separating pure alkyl monochlorides from the chlorination products, reacting the alkyl monochlorides with aromatic hydrocarbons selected from the group consisting of benzene, toluene and xylene, and a member selected from the group consisting of aluminium chloride and aluminium chloride contact oil in at least one stage, separating by distillation pure mono-alkyl aromatics from the reaction products, and sulfonating and neutralizing the mono-alkyl aromatics, the improvement for obtaining pure white alkyl aryl sulfonates containing more than 10 carbon atoms and less than 15 carbon atoms in their aliphatic chain which comprises completely reacting the pure alkyl monochlorides with the aromatic hydrocarbons whereby no unreacted alkyl chlorides remain in the alkylation mixture, separating the alkylation mixture from any contact oil present, and passing the alkylation mixture through a layer of solid aluminum chloride for contact therewith.

2. Improvement according to claim 1, which includes removing hydrogen chloride from said alkylation mixture before said passing in contact with solid aluminium chloride.

3. Improvement according to claim 1, in which said complete reacting of the alkyl monochlorides is effected in at least two stages with vertical reaction tubes filled with aluminium chloride contact oil; the mixtures to be

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alkylated being passed in from below, and the alkylation mixtures being drawn off toward the top, separated from the contact oil which is returned to the tube, and introduced into the succeeding stage; said passing in contact with solid aluminium chloride being effected by passing the alkylation mixture from the last alkyl monochloride reaction stage upward through a vertical reaction tube filled with lumpy aluminium chloride, the contact oil forming during said contact with solid aluminium chloride being cycled to said last alkyl monochloride reaction stage, a substantially equal quantity of contact oil being withdrawn from each alkyl monochloride reaction stage and cycled to the preceding alkyl monochloride reaction stage, a substantially equal quantity of contact oil being withdrawn from said first alkyl monochloride reaction stage.

4. Improvement according to claim 3, which includes

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withdrawing additional contact oil from said alkyl monochloride reaction stages, regenerating the contact oil and recycling it to the stages.

5. Improvement according to claim 1, in which the passing of the reaction mixture through the layer of solid aluminum chloride is carried out at a temperature not in excess of 30° C. with a residence time of at least 30 minutes.

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