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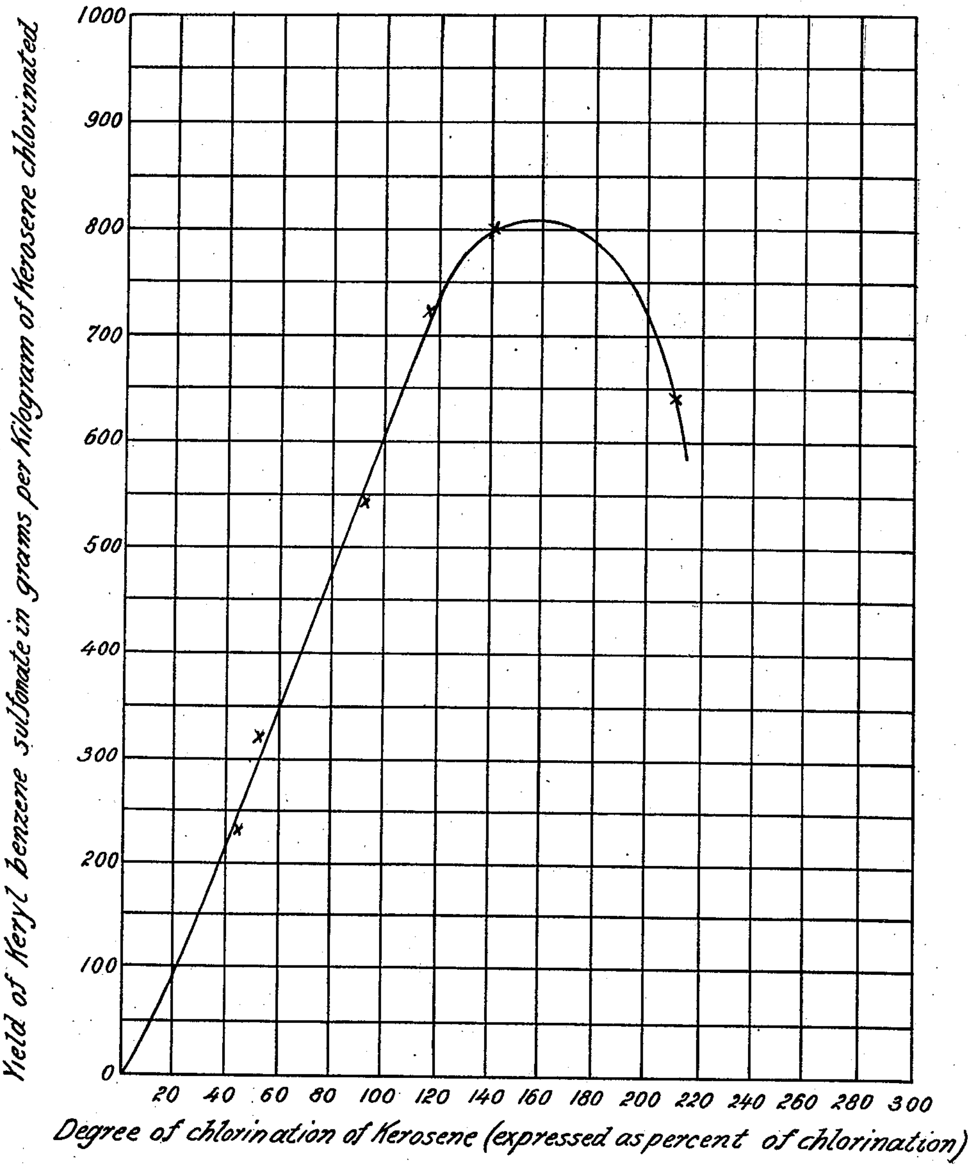

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MANUFACTURE OF SIDE-CHAIN AROMATIC SULPHONATES

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The present invention relates to improvements in the manufacture of side-chain aromatic sulphonates which are valuable detergents and wetting, emulsifying, and the like agents. One process for the manufacture of these products involves chlorinating a hydrocarbon mixture of the type of a petroleum distillate, preferably a paraffinic petroleum hydrocarbon distillate; condensing resulting chlorinated hydrocarbons with an aromatic compound with the aid of a condensation catalyst of the Friedel-Crafts type, such as anhydrous aluminum chloride or anhydrous zinc chloride, to form a mixture containing aromatic compounds having nuclear side-chains; sulphonating resulting mixed side-chain aromatic compounds; and recovering the resulting mixed sulphonic acids, preferably in the form of their salts, such as their salts with alkali metals. The invention particularly relates to improvements in the chlorination step of said process for the manufacture of the mixed side-chain aromatic sulphonates.

It is an object of the invention to provide improvements in the step of the above process in which the hydrocarbon mixture of the type of a petroleum distillate is chlorinated, whereby mixed side-chain aromatic sulphonates possessing excellent properties may be obtained in high yields. A more specific object of the invention is to provide improvements in the chlorination step of the process of preparing mixed side-chain aromatic sulphonates involving chlorinating a paraffinic petroleum hydrocarbon distillate in which the hydrocarbons contain an average of 7 to 35 carbon atoms, condensing resulting chlorinated hydrocarbons with benzene, phenol, or naphthalene, sulphonating the resulting mixed condensation products, and recovering the mixed sulphonation product, preferably in the form of an alkali metal salt; the improvement resulting in products of high quality which are obtained in excellent yields.

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

The mixed side-chain aromatic sulphonates with which the present invention is concerned are preferably derivatives of aromatic compounds of the benzene, naphthalene, and diphenyl series. Thus the products may be derivatives of benzene, naphthalene, diphenyl, or substituted members of the series to which these compounds belong, such as, for example, compounds containing nuclear substituents of which halogens and hydroxyl, alkoxy, alkyl, and carboxyl radicals are examples. Where the aromatic compounds are substituted, they preferably contain but one substituent. As suitable substituted aromatic compounds there may be mentioned phenol, cresol, chlorbenzene, toluene, xylene, resorcinol, hydroxydiphenyl, phenetole, and benzoic acid. As pointed out above, the side chains present in the sulphonates are derived from a hydrocarbon mixture of the type of a petroleum distillate; for example, a kerosene or "white oil" fraction of petroleum, and preferably a paraffinic petroleum hydrocarbon distillate. Thus the side chains are predominantly alkyl, cycloalkyl, or aralkyl radicals. Preferred products are composed predominantly of mono side-chain aromatic sulphonates in which the side chains are alkyl radicals.

It is obvious that in order to produce superior products of the above type it is important to make certain that the side chains are of the desired character. It is also important, if the object is to prepare products adapted for general use, to obtain the mixed side-chain aromatic sulphonates substantially free from the hydrocarbon mixture (e. g., the kerosene or "white oil" fraction) used in manufacturing the products.

In the manufacture of mixed side-chain aromatic sulphonates having the desired type of side chains and therefore having desirable properties, the manner in which the chlorination of the hydrocarbon mixture is carried out is important. References in the literature disclose that when chlorinating a hydrocarbon mixture for the purpose of finally replacing a hydrogen atom of the hydrocarbon molecules with some other radical such as the hydroxyl group, the best yields of the desired products are obtained when at the end of the chlorination reaction, the amount of organically combined chlorine in the chlorinated hydrocarbon mixture is much less than that which corresponds to one atom of chlorine per molecule of hydrocarbon. For example, Ayres (Ind. Eng. Chem. 21, 899–904 (1929)) in discussing the chlorination of pentane for the purpose of preparing amyl alcohol points out that one of the most important objects in the chlorination is the production of a minimum amount of polychlorides. According to Ayres, the ideal method for preventing reaction of more than one molecule of chlorine with a pentane molecule would be to mix chlorine with an infinite excess of pentane and then allow reaction to take place. In actual practice, Ayres was able to restrain the formation of polychlorides very satisfactorily by using ratios of 20 parts of pentane to 1 part of chlorine. That chlorination of this nature, which is conveniently termed "underchlorination," should result in a high proportion of desired products from hydrocarbon mixtures is also supported by theoretical considerations. In processes wherein a hydrocarbon mixture is chlorinated so as to obtain from the mixture radicals of the hydrocarbon molecules, it has been considered that the useful products are obtained substantially entirely from the monochlorinated molecules, the polychlorinated molecules having been regarded as undesired impurities. It is known that the first chlorine atom introduced into a hydrocarbon molecule at least does not seriously retard the introduction of further chlorine atoms into this molecule. For this reason, as chlorination is continued up to and beyond the point which corresponds to the introduction of one chlorine atom for each molecule of hydrocarbons, it was to be expected that a large proportion of the hydrocarbons present in the mixture would be converted into undesirable polychlorides. Thus, while at first, say at the point where the chlorine which has become combined organically in the mixture corresponds to about one-fifth of the amount of chlorine which would be so combined if each molecule of hydrocarbon in the mixture were converted to a monochlor hydrocarbon, the chlorinated hydrocarbons in the mixture would be predominantly monochlorides, as the chlorination proceeded a proportion of these monochlorides would be converted into polychlorides. Although it would be expected that continued chlorination would convert some of the unchlorinated hydrocarbons to the desired monochlorides, it would be expected that this action would be accompanied by the conversion of the monochlorides first formed into the undesired polychlorides, resulting in a final mixture containing a high proportion of the polychlorides. On condensing the mixture containing the polychlorides with an aromatic compound, it would be expected that the condensation taking place between the polychlorides and the aromatic compound would defeat the securing of desirable side-chain aromatic sulphonates upon the eventual sulphonation of the condensation products.

The present invention is based upon the discovery that the foregoing teachings and theoretical considerations do not hold true in the above-outlined general process for the manufacture of mixed side-chain aromatic sulphonates which are valuable for their detergent properties. Thus it has been found that by chlorinating a hydrocarbon mixture of the type of a petroleum distillate, such as a kerosene or "white oil" fraction of petroleum, and preferably a paraffinic petroleum hydrocarbon distillate, to such an extent that the amount of chlorine which has become combined organically in the mixture is more than that which would be so combined if each hydrocarbon molecule present in the mixture were converted to its corresponding monochloride, a chlorinated mixture is obtained which can be used successfully for the production of desirable mixed side-chain aromatic sulphonates with exceptional surface active properties. Hereinafter a chlorinated mixture containing an amount of organically combined chlorine which exceeds that which would be present if the mixture consisted of monochlorinated hydrocarbons only is said to be overchlorinated. It has further been found that by using an overchlorinated hydrocarbon mixture not only is it possible to obtain desirable mixed side-chain aromatic sulphonates, but these sulphonates are obtainable in greatly increased yields, based on the amount of hydrocarbon mixture employed, than when an underchlorinated hydrocarbon mixture is used.

A further advantage flowing from the overchlorination procedure is that the desired mixed side-chain aromatic sulphonates can be obtained more easily in a form substantially free from unchlorinated hydrocarbons. By underchlorinating a petroleum distillate, a chlorination product is obtained which is composed to a large extent of unchlorinated hydrocarbons. Because of the similarity of the boiling points of the unchlorinated and chlorinated hydrocarbons in the mixture it is not feasible as a practical matter to separate them prior to condensation. After condensation it is difficult to remove the unchlorinated hydrocarbons from the condensation products because these hydrocarbons boil over a wide range which is not sufficiently different from and usually overlaps the boiling range of the complex condensation products. By carrying out the chlorination of the hydrocarbon mixture to a degree greater than that corresponding to the introduction of one atom of chlorine for each atom of hydrocarbon (that is, greater than 100 per cent chlorination on a molar basis), the unchlorinated hydrocarbons in the mixture are reduced to a minimum and may be removed by means not entirely successful when greater quantities of unchlorinated hydrocarbons are present.

There can be obtained at the present time special petroleum fractions which boil within relatively narrow ranges. However, such fractions are specialty products and are generally more expensive than the ordinary petroleum fractions which boil over wide ranges. The chlorination step of the present invention is particularly valuable, as compared with underchlorination, when used in a process for the manufacture of side-chain aromatic sulphonates from peroleum fractions which boil over relatively wide ranges, such as kerosene fractions of petroleum. For example, in a case where a kerosene is used which boils over a range of 100° C. and the resulting chlorination product is condensed with benzene, the individual compounds in the condensation product boil only about 40° C. higher than the individual hydrocarbon compounds from which they were derived. Thus, some of the hydrocarbons in the unchlorinated hydrocarbon mixture have boiling points above the boiling points of some of the compounds in the condensation product. Consequently, separation of the unchlorinated hydrocarbons from the condensed products and from the side-chain aryl sulphonates which are made by sulphonating these condensed products is difficult. But where the proportion of unchlorinated hydrocarbons to condensed compounds is low, as where the present chlorination method is practiced, the difficulties created by the presence of these unchlorinated hydrocarbons are greatly lessened. Thus, when an overchlorinated mixture of hydrocarbons is used for the condensation, the fraction of the condensation product which contains the desirable side-chain aromatic compounds may be separated by distillation with lesser amounts of unchlorinated hydrocarbons therein; furthermore, when such a fraction is sulphonated, the resulting side-chain aromatic sulphonate mixture retains less unsulphonatable hydrocarbons; and upon being subjected to a drying operation on a drum drier or in a spray drier, for example, some of these hydrocarbons in the mixture are removed so that the amount of hydrocarbons remaining in the final desired side-chain aryl sulphonate mixture is relatively small, and its detrimental effects upon the washing action of the sulphonates are greatly lessened.

As stated above, the chlorination of the hydrocarbon mixture in accordance with the present invention is carried out to a degree such that the final chlorinated mixture contains more than one atom of organically combined chlorine for each hydrocarbon molecule which was present in the mixture before chlorination. As a feature of the invention it has been found that the yields of the desired mixed side-chain aromatic sulphonates generally increase with increase in the degree of chlorination until the hydrocarbon mixture contains an amount of organically combined chlorine corresponding to about one and one-half atoms of chlorine per molecule of hydrocarbon; that is, the hydrocarbon mixture has been chlorinated to a degree which conveniently may be said to correspond to about "150 per cent chlorination." Throughout this specification and the claims, per cent chlorination is on a molar basis; it refers to the per cent ratio between the actual increase in weight due to chlorination of an amount of hydrocarbon distillate corresponding to the average molecular weight of the hydrocarbons in the distillate and the expected increase in weight of the same amount and kind of hydrocarbon distillate if every hydrocarbon in the amount of hydrocarbon distillate were converted to its corresponding monochlor hydrocarbon. Thus, the percent chlorination may be expressed by the formula:

$$\frac{(34.5+D)\times 100}{34.5}$$

where 34.5 represents the increase in weight of an average molar quantity of hydrocarbon mixture if all the hydrocarbons in this quantity of mixture were converted to monochlor hydrocarbons only and (34.5+D) represents the actual increase in weight of an average molar quantity of hydrocarbon mixture due to chlorine which is caused to become organically combined in the hydrocarbons of the quantity of mixture by the chlorination. Beyond the maximum point, which varies somewhat depending upon the specific hydrocarbon mixture treated and the conditions of chlorination, the yields of side-chain aromatic sulfonates derived from the resulting chlorinated hydrocarbon mixture begin to fall off. It has been determined that if chlorination of the hydrocarbon mixture is continued beyond the point corresponding to 200 per cent of chlorination on a molar basis, the yields of derived side-chain aromatic sulphonates fall off to such an extent as not to justify, from an economic standpoint, the use of the chlorine required. Accordingly, in accordance with the invention, the hydrocarbon mixture is chlorinated to a degree corresponding to more than 100 per cent, and not more than 200 per cent chlorination. Within these limits it is preferred to chlorinate the hydrocarbon mixture to a degree corresponding to not more than 175 per cent chlorination. Especially valuable results are obtained when the chlorination is carried out to a degree corresponding to from 110 per cent to 150 per cent chlorination, or more specifically to a degree corresponding to about 120 per cent chlorination. By chlorinating to from 110 to 150 per cent chlorination, nearly maximum yields of high-quality products are obtained, and the consumption of chlorine is kept at a reasonable level.

The chlorination can be carried out in any desired manipulative manner; for example, it may be carried out by chlorinating the hydrocarbon mixture in batches or by subjecting the mixture to continuous chlorination. Thus the chlorination may be effected by passing chlorine gas into a batch of the hydrocarbon mixture while agitating the batch or by contacting a stream of chlorine gas with a stream of the mixture. The extent of chlorination may be determined by the increase in the specific gravity of the hydrocarbon mixture chlorinated. The temperature at which the chlorination is effected may be varied over relatively wide limits. Although the temperature maintained has an effect upon the amount of side chain aromatic sulphonates obtained from a given quantity of a hydrocarbon mixture, yet at all temperatures at which it is feasible to carry out the chlorination of hydrocarbon mixtures the yields of the desired side-chain aromatic sulphonates, based on the amount of hydrocarbon mixture employed, are highest when the chlorination is carried out to a degree corresponding to more than 100 per cent and not more than 200 per cent chlorination.

It will be understood, of course, that the chlorination is ordinarily effected at the temperatures at which such operations are usually carried out; for example, at temperatures within the range of 0° to 135° C., and preferably within the range 50° to 80° C. The optimum chlorination temperature varies with the hydrocarbon mixture being chlorinated. In general, the higher boiling mixtures, such as "white oil," are chlorinated more efficiently at about 80° C. Also, the chlorination may be carried out with the aid of chlorine carriers, catalysts, or adjuvants such as, for example, phosphorus trichloride, iodine, sunlight, etc.

The hydrocarbon mixtures employed in the present process are complex mixtures, such as petroleum distillates, whose compositions are not definitely known. The approximate composition of petroleum distillates is determined by reference to the boiling points and the other physical properties of the compositions. Ordinarily, the petroleum distillates employed in the making of the side-chain aromatic compounds will boil over ranges, the lower boiling points of which are not below 80° C. at atmospheric pressure, and the upper boiling points of which are not above 350° C. at 25 mm. absolute pressure. For the manufacture of products designed for general detergent use it is preferred to employ petroleum fractions derived from Pennsylvania, or Mount Pleasant, Michigan, petroleums which fractions boil for the most part within the range 180° to 300° C., and are preferably composed predominantly of saturated hydrocarbons which boil within the range of 180° to 280° C. Thus the preferred hydrocarbon mixtures are composed predominantly of saturated hydrocarbons, including saturated acyclic and saturated alicyclic hydrocarbons, containing an average of 7 to 35 carbon atoms, or, better, 10 to 19 carbon atoms, and especially 12 to 16 carbon atoms.

In order that the invention may be understood more fully reference should be had to the following examples. For convenience, where a kerosene fraction of petroleum is used in the processes disclosed in the examples, the product obtained by chlorinating this fraction is termed "keryl chloride" and the product obtained by condensing the keryl chloride with benzene, for example, is termed "keryl benzene." It will be understood that the specific character of the keryl chlorides and keryl benzenes or other keryl aryl products will be dependent upon the particular kerosene used and the manner in which the process is carried out.

Example 1.—In order to demonstrate the advantageous yields of keryl benzene sulphonates obtainable by means of the present invention, the following series of experiments was made:

At each of the temperatures 40° C., 60° C., 100° C., 120° C., and 140° C., a series of chlorinated kerosenes was prepared. The chlorinated kerosenes in any series differed from each other in the extent of their chlorination. Each chlorinated kerosene was condensed with benzene to form keryl benzene which was sulphonated by a procedure uniformly applied to each keryl benzene. It was found that at any temperature level of chlorination, the maximum yield of keryl benzene sulphonates was obtained when the amount of organically combined chlorine in the chlorinated kerosene was between amounts required theoretically for complete monochlorination and dichlorination of all the hydrocarbons in the kerosene. This conclusion is supported by the data in Table 1 following. Details of the experimental procedure were as follows:

Part A.—0.2 gram iodine was dissolved in 500 grams of Pennsylvania kerosene having a boiling range of 185° to 275° C. While this kerosene containing iodine was vigorously agitated in a glass vessel and maintained at 40°±1° C., a stream of chlorine gas was conducted into it at the rate of about 2.5 grams per minute until the desired degree of chlorination was reached. This was determined by blowing air through the chlorinated kerosene for a short time to remove dissolved chlorine and hydrogen chloride, and measuring the increase in weight of the kerosene caused by the organically combined chlorine therein.

Except for simple changes necessitated by the temperature at which the chlorination was made, the foregoing procedure was repeated with 500-gram portions of the same kerosene at temperature levels of 60° C., 100° C., 120° C., and 140° C.

At 100° C., 120° C., and 140° C., chlorine gas was introduced into the kerosene through a fine glass capillary to obviate tendencies towards flashing and soot-formation at the point of contact of chlorine gas and kerosene.

The chlorinated kerosenes prepared at 140° C. were not aerated, but were agitated for several minutes to remove dissolved chlorine and hydrogen chloride; it was observed that air passing through the chlorinated kerosene at about 140° C. impaired the quality of the preparation. The gain in weight by each of the several kerosene fractions due to their accession of organically combined chlorine ranged from about 20 per cent to about 200 per cent of the weight of chlorine which theoretically would have been combined in the kerosene fraction if it had been monochlorinated. The keryl chlorides thus prepared are shown in Table 1.

Part B.—From each batch of chlorinated kerosene a keryl benzene was then prepared by adding at room temperature during 20 minutes a definite weight of a batch of chlorinated kerosene to an agitated mixture of double the said weight of benzene and one-twentieth of the said weight of anhydrous aluminum chloride. When the mixture of chlorinated kerosene, benzene and aluminum chloride was complete, its temperature was raised to 44° to 46° C. for 90 minutes during which the mixture was agitated continuously. It was then transferred to a separatory funnel and allowed to stand for about 16 hours. The lower tarry layer of the settled mass was drawn off and discarded. The upper layer of reaction product was fractionally distilled.

The excess benzene present in the distilland was stripped by the distillation, first at atmospheric, and then at reduced pressure. The pressure was then adjusted to 4 mm. of mercury and a small fraction of distillate boiling up to 80° was collected and discarded. The next fraction, containing the monokeryl benzenes, and consisting of all the material boiling between 80° and 250° C. under 4 mm. of mercury, was then collected. A small amount of undistilled residue consisting largely of poly-phenylated kerosene was discarded.

Part C.—Each of the keryl benzene fractions so obtained was then acid washed and sulphonated as follows: A 100-gram portion of the keryl benzene fraction was stirred for 45 minutes with 10 ccs. of 100 per cent sulphuric acid in a glass flask without external heating or cooling. The resulting mixture was transferred to a separatory funnel, allowed to stand for a half hour, and the separated lower, colored, acid layer was drawn off and discarded. The upper, acid-washed keryl benzene layer was then placed in a glass sulphonating flask and agitated with 100 ccs. of 100 per cent sulphuric acid which was run in during 10 minutes. Sulphonation of the keryl benzene was completed by warming the mixture to 55° to 60° C. and maintaining the agitated mass at that temperature for about one hour. The mixture was transferred to a separatory funnel and allowed to stratify for one hour; the middle layer of keryl benzene sulphonic acid was separated from the lower layer of spent sulphonating acid and the top layer of unsulphonated hydrocarbon. The sulphonic acid layer was drowned in about 200 grams of ice, neutralized with 50 per cent aqueous caustic soda using additional ice as necessary to keep the temperature below 35° C. The neutral solutions were analyzed as follows: A 25 cc. aliquot portion of the neutralized solution was placed in a tared beaker and evaporated to constant weight at 90° to 95° C., first at atmospheric pressure and then in vacuo in which the vacuum was gradually increased to about 22 to 25 inches of mercury. From the weight of dry sample in the beaker, the total solids present in the solution were calculated. The sodium keryl benzene sulphonate content of the solids was determined by dissolving in 5 to 10 ccs. of water with gentle warming a one-gram sample of a drum-dried sample of the neutralized solution. To this solution, 100 ccs. of anhydrous ethyl alcohol were then added; the alcoholic mixture was stirred thoroughly, then allowed to stand for 15 minutes, after which the precipitated inorganic salts were collected on a tared Gooch crucible, washed with five 10 to 20 cc. portions of anhydrous alcohol, dried for three hours at 100° C. and weighed. The difference between the weight of salt and weight of sample was the weight of keryl benzene sulphonate in the sample. Therefrom, the proportion of sodium keryl benzene sulphonate in the solids, and the amount of the former produced in the solution were then readily calculated.

The effect upon yield of sodium keryl aryl sulphonates, of variations in amount of organically combined chlorine in the chlorinated kerosenes from which they are derived, is seen in the following table:

Table 1

Temperature of chlorination	Degree of chlorination (expressed as per cent of chlorination) assuming the av. M. W. of the kerosene hydrocarbons = 189	Yield expressed as grams of sodium keryl benzene sulphonate obtained per kilo of kerosene chlorinated
40° C	27	71
	47	154
	78	366
	95	526
	119	620
	136	704
	157	776
	186	873
60° C	21	87
	41	262
	82	610
	102	720
	120	850
	142	950
	160	900
	199	870
100° C	23	167
	42	348
	81	636
	103	805
	121	858
	145	890
	161	915
	203	830
120° C	41	386
	63	516
	83	670
	104	829
	125	924
	144	990
	170	985
	192	990
140° C	45	384
	82	626
	103	740
	122	770
	139	722
	160	794
	183	805
	198	772
	243	716

Example 2.—This example illustrates the improved process of the present invention, using chlorkerosenes made by a continuous chlorination process. A series of samples were chlorinated to different degrees in the following manner.

A continuous stream of Pennsylvania kerosene (boiling range 185° to 275° C., specific gravity 0.792) was chlorinated by contacting it with a stream of chlorine in a reaction zone and continuously removing and cooling the chlorinated kerosene. The rate of kerosene flow was varied from about 4 to about 12 ccs. per minute and the rate of chlorine flow about 5 to about 0.8 grams per minute. The temperature of the reaction in the reaction zone was about 130° C.

Depending on the amount of heat generated (which increased with the degree of chlorination attained), the temperature in the reaction zone was controlled by preheating the kerosene or by passing cold air through an air jacket disposed about the chlorination apparatus to cool the reaction zone. By varying the rate of flow of the chlorine and of the kerosene, portions of kerosene were chlorinated to varying degrees. The chlorination was carried out in the absence of light.

The chlorinated kerosene samples so obtained were worked up into keryl benzene sulphonate by the methods described in Parts B and C of Example 1.

The yields of sodium keryl benzene sulphonate, determined in the manner described in Example 1, and obtained from the continuously chlorinated kerosene chloride samples are summarized in Table 2. In order to illustrate more clearly the effect of the degree of chlorination on the yields of sodium keryl benzene sulphonate, the degree of chlorination (expressed as per cent of chlorination) was plotted against the yields of sodium keryl benzene sulphonate. The resulting graph appears in the drawing, which is believed to be self-explanatory. It is pointed out that the products obtained with the use of overchlorination were at least equal in quality to those obtained using underchlorination. For example, the 724 grams of sodium keryl benzene sulphonate obtained by chlorinating the kerosene to 117 per cent chlorination were at least equal in quality on a gram for gram basis to the 229 grams obtained by chlorinating the kerosene to 45 per cent chlorination.

As in Example 1, the results indicate clearly the advantageous effect on yield of sodium keryl benzene sulphonates of chlorinating the kerosene portion to an extent between the chlorination corresponding to mono- and di-chlorination of all the hydrocarbons in the kerosene portion.

Table 2

Degree of chlorination (expressed as per cent of chlorination) assuming the average M. W. of the kerosene hydrocarbons = 189	Yield expressed as grams of sodium keryl benzene sulphonate obtained per kilo of kerosene chlorinated
45	229
53	322
93	548
117	724
141	800
210	647

Example 3.—A hydrogenated petroleum fraction which was derived from Louisiana crude oil and, to the extent of 85 per cent, boiled between 200° and 355° C. at atmospheric pressure was fractionated under an absolute pressure of 4 mm. of mercury. The distillate boiling from 90° to 140° C. was collected. This "cut" of distillate had a specific gravity of 0.837 at 29° C. and had an average molecular weight of about 219. Each of two 219-gram portions of this cut was chlorinated in a glass flask exposed to diffused daylight. The chlorine was run in at a rate of about 2.0 to 2.5 grams per minute. The temperature of the chlorinating mixture during chlorination rose from room temperature to around 45° to 50° C. where it was maintained until the end of the chlorination period.

After the two batches had been chlorinated for 45 and 90 minutes, respectively, chlorination was stopped, and air was passed through the mixtures to drive out HCl or chlorine dissolved in the two chlorinated batches. The latter were then weighed. Weight increases were 29 and 39 grams, respectively, corresponding to a degree of chlorination of 84% and 113% chlorination.

Each batch of chlorinated kerosene was then condensed with an amount of phenol corresponding to one molecule of phenol per atom of combined chlorine in the batch. Thus, 80 grams and 106 grams of phenol were reacted with the hydrocarbon batches chlorinated to 84% and 113%, respectively. 15 grams of anhydrous zinc chloride were used in each case as condensation catalysts. The condensation was carried out by agitating and heating the mixture of chlorinated kerosene, phenol, and zinc chloride to around 170° C. for about 7 hours. At the end of this time, the reaction mixture was allowed to settle and the crude reaction product was poured off the zinc chloride residues. The crude reaction product was then washed successively with 100 cc. portions of 10 per cent hydrochloric acid, hot water, and saturated aqueous sodium chloride solution. The washed crude product was then dried with anhydrous calcium chloride and distilled. The desired keryl phenol product boiled between 140° C. and 220° C. at 5 mm. of mercury. The yields of desired products were 78 and 86 grams, respectively, for the batches of petroleum fraction chlorinated to 84% and 113%.

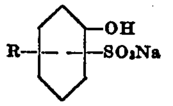
The two keryl phenol products were then separately sulphonated as follows: A 15-gram portion of the keryl phenol preparation was placed in a glass flask, cooled to below 15° C., and 8.3 cc. of 100% sulphuric acid were run in. After agitating the mixture for one hour and allowing it to reach room temperature, the sulphonating mixture was warmed to 45° C. for one hour more, then it was poured onto about 200 grams of cracked ice and the aqueous mixture so obtained was neutralized with 50% caustic soda solution. The resulting solution was then drum dried.

On testing, it was found that the dried product made from the 113% chlorinated petroleum fraction was considerably superior to the dried product made from the 84% chlorinated batch. The superiority consisted in freedom from turbidity of the dilute solution of the product.

Example 4.—Commercial kerosene derived from Pennsylvania petroleum was fractionally distilled and the fraction boiling between 220° and 240° C. was collected. This fraction consisted of hydrocarbons which have a probable average carbon and hydrogen content corresponding to a formula: $C_{12}H_{26}$ to $C_{13}H_{28}$. A 199-gram portion was cooled to 0° C. and treated with a stream of dry chlorine in a glass flask fitted with a glass agitator. Introduction of chlorine was stopped when the weight of the chlorinated mixture had increased by about 45 grams, of which 44 grams represented chlorine combined with the kerosene hydrocarbons. This degree of chlorination corresponded to about 115 per cent chlorination. The mixture was maintained at about 0° C. during the chlorination, which required about an hour and a half.

150 grams of this chlorinated kerosene were mixed with 65 grams of phenol and 50 grams of anhydrous zinc chloride, and the mixture was heated gradually. Voluminous amounts of hydrogen chloride gas were evolved at 60° to 110° C. On heating the mixture to 135° C., the evolution of hydrogen chloride abated; the mixture was then held at 135° C. for one hour to complete the reaction. The oily portion of the reaction mass was decanted from the zinc chloride, and washed once with water to remove any zinc salts; it was then fractionally distilled under reduced pressure. The distillate, which boiled from 180° C. to 250° C. at 8 mm. was collected as product; yield was 53 grams of oil.

50 ccs. of the keryl phenol distillate thus obtained were stirred, and thereto 35 ccs. of 100 per cent sulphuric acid were added slowly, the temperature of the mixture being kept at about 30° C. The sulphonation mixture was then warmed to 75° C. and held at that temperature (about 20 minutes) until a sample gave only a very slight precipitate of calcium salts from a calcium chloride solution containing the equivalent of 0.224 calcium oxide per liter. The sulphonation mixture was then diluted with water to about 500 parts by weight and neutralized with 50 per cent aqueous sodium hydroxide. The solution was evaporated to dryness on a drum drier. The final product was a mixture of sodium salts of keryl phenol sulphonic acid of the type:



in which R represents the organic residue derived from the petroleum fraction which was chlorinated and condensed with phenol as previously described. Yield of product was 115 parts of dry flaked material.

Example 5.—10,620 lbs. of Pennsylvania kerosene (boiling range 185° to 275° C.) were charged into a lead-lined kettle fitted with lead-covered agitator, thermometer well and other accessories. 4.4 lbs. of iodine were dissolved in the agitated kerosene charge which was warmed to about 60° C. and maintained between 60° C. and 70° C. while chlorine gas was passed into the liquid at an average rate of about 300 lbs. per hour until the specific gravity of the chlorinated kerosene had changed from 0.788 at 24° C. before to 0.918 at 24° C. after the chlorination. The amount of chlorine required for the purpose was about 4,825 lbs. The final chlorinated kerosene mixture weighed about 12,834 lbs. The degree of chlorination corresponded to 114 per cent of chlorination.

A mixture of 13,272 lbs. of benzene and 332 lbs. anhydrous aluminum chloride was agitated and 6,636 lbs. of the foregoing chlorinated kerosene mixture were added thereto, over a period of 3 hours, during which the temperature of the mass rose to about 35° C. The mixture was then heated to 45° C. and held there for about an hour and a half. Agitation was then stopped and the mixture was allowed to stand for about 2 hours; thereafter the lower tarry layer was withdrawn. The upper layer was conveyed to a stripping kettle in which the liquid was stripped of low-boiling hydrocarbons, chiefly benzene, by boiling the liquid at 150° C. first under atmospheric pressure and finally under reduced pressure of 3 to 4 inches of mercury absolute pressure. The material left after this stripping was distilled in vacuo until about 7 per cent of the charge in the still had been removed as distillate. The remaining distilland was distilled, and distillate therefrom was collected separately until the boiling point of the distilland was 250° C. at 14 mm. mercury pressure. This last distillate was chiefly the condensation product of the chlorinated hydrocarbons of the kerosene fraction and the benzene; i. e., a keryl benzene.

The keryl benzene was washed with 100 per cent sulphuric acid by mixing it with about 15 per cent of its weight of acid, and agitating the mixture in an enamel-lined kettle for about one hour at 30° to 35° C. The mixture was allowed to stand for about one-half hour to permit separation into layers. The spent sulphuric acid, which constituted the lower layer, was withdrawn and discarded.

The upper acid-washed layer of keryl benzene was mixed in an enamel-lined kettle with about 1.25 times its weight of 100 per cent sulphuric acid at a temperature between 30° and 35° C. The mixture was then warmed to 55° C. and agitated at that temperature for one hour. It was then allowed to stand for 2 hours during which time three layers of material separated. The upper layer was chiefly unsulphonated material, the middle portion was chiefly sulphonated keryl benzene, and the lower layer was spent sulphuric acid. The middle layer was separated from the others, drowned in ice water, neutralized with an aqueous solution of caustic soda and dried on a rotary drum drier.

Example 6.—The petroleum fraction used in this example is known commercially as "white oil" and is a purified distillate of which under an absolute pressure of 10 mm. of mercury more than 98 per cent distils over the range 157° to 278° C. and more than 85 per cent distils over the range 195° to 260° C. For convenience, the condensation products from white oil and benzene are called "white-oil-benzene" compounds.

2,270 lbs. of white oil were agitated in a vessel lined with lead. 1.75 lbs. of iodine were dissolved in the agitated white oil. Chlorine gas was then passed through the oil with continued agitation until the specific gravity of the sample showed an increase of 0.09 over that of the original white oil. During chlorination, the temperature was adjusted to 70° to 86° C. by suitably heating or cooling the batch. The chlorinated white oil weighed approximately 2,651 lbs. The degree of chlorination corresponded to about 150% chlorination.

617 lbs. of benzene and 62 lbs. of anhydrous aluminum chloride were agitated in an Allegheny metal kettle, warmed to 35° to 40° C. and held at that temperature for about an hour and a quarter during which period 617 lbs. of the chlorinated white oil (prepared as above-described) were run in. The agitated mixture was then warmed to 55° C. and agitated at 55° to 59° C. for an hour. The agitation was then stopped and the batch was allowed to settle for about 18 hours. During this period, the batch was allowed to cool down to about 30° C. Some 248 lbs. of tar which settled out were discarded.

The crude condensation product was transferred to a stripping kettle, and unreacted benzene was stripped off by gradually heating the batch to 150° C. and holding it at that temperature until distillation ceased and then simultaneously increasing the vacuum in the still to approximately 27 inches of mercury and gradually heating the distilland to about 175° C. The remaining stripped white-oil-benzene weighed 433 lbs.

200 lbs. of stripped white-oil-benzene were charged into an enamel-lined kettle fitted with an enameled agitator and other suitable accessories. The batch was then cooled to 16° C. and 266 lbs. of 100 per cent sulphuric acid were run in during an hour and a quarter. The temperature was then raised to 50° to 55° C. and held there for about an hour and a half. 120 lbs. of water were then added slowly to the batch, which was cooled so that the final and highest temperature thereof was 66° C. To the mixture, 80 lbs. of Stoddard solvent were added. After agitating the batch for 15 minutes, and then allowing it to stand for one hour, the lower spent acid layer was drawn off. Then 80 lbs. more of Stoddard solvent were added to the batch which was agitated for 15 minutes and allowed to stand for about 18 hours before the rest of the spent acid was drawn off.

The sulphonation mixture was then neutralized with 50 per cent aqueous caustic soda solution. The resulting product, which was a solution of white-oil-benzene-sodium-sulphonate in Stoddard solvent, is adapted for use in preparing highly efficient detergent compositions for dry cleaning.

Example 7.—A large batch of the kerosene used in Example 4 was rectified and the fraction boiling up to 91° C. under a pressure equal to 13 mm. of mercury was collected. Approximately one gram of iodine was dissolved in 1000 grams of this kerosene fraction which was adjusted to a temperature of 50° to 55° C. and chlorinated directly, while it was agitated, with a stream of chlorine gas. Chlorination was interrupted when the weight increase of the chlorinated kerosene fraction indicated that it contained an amount of organically combined chlorine corresponding to 110 per cent of that theoretically required for monochlorination of all the hydrocarbons in the kerosene. A mixture of 300 grams of this chlorinated kerosene, 180 grams of naphthalene, and 30 grams of anhydrous zinc chloride was agitated and heated to 170° C. for 16 hours. The condensation mixture was allowed to stand and settle; the oily layer was decanted from solid residue and distilled. The distillate boiling between 150° and 250° C. at 13 mm. of mercury was collected as the desired keryl naphthalene.

20 grams of distilled keryl naphthalene were agitated for one-half hour at room temperature, with an equal volume of 80 per cent sulphuric acid. The mixture was allowed to separate, and the lower, colored acid layer was withdrawn and discarded. The acid-washed keryl naphthalene was sulphonated by agitating it with 20 ccs. of 100 per cent sulphuric acid for an hour and a half at 30° C. The sulphonation mixture was drowned in about 300 ccs. of water, and neutralized with aqueous caustic soda solution, the temperature being kept below 40° C. during neutralization. The neutral aqueous solution of sodium keryl naphthalene sulphonate was drum dried to obtain a dry composition which dissolved readily in water to form substantially water-white solutions which had valuable detergent properties.

In the following examples, the parts are by weight:

Example 8.—A kerosene fraction of Pennsylvania petroleum distillate having a boiling range of about 172° to about 250° C., which, on the basis of its source and properties, was considered to be a mixture of hydrocarbons (mainly open-chain aliphatic hydrocarbons) having a range from about 10 to about 15.5 carbon atoms per molecule, was chlorinated in diffused daylight at a temperature between 50° and 60° C. until about 21 parts of chlorine had been absorbed per 100 parts of kerosene (corresponding to about 109 per cent chlorination). 200 parts of this mixture of chlorinated hydrocarbons were reacted at ordinary temperature with 150 parts of monochlorbenzene and 20 parts of anhydrous aluminum chloride. The temperature of the mixture was allowed to rise to about 60° C. with agitation and this agitation was continued for about one additional hour after this temperature was reached. The mixture was allowed to stand and separate into two layers of which the upper was decanted, washed with dilute hydrochloric acid and distilled until a vapor temperature of 120° C. at 5 mm. was reached. The residue (85 parts) was an amber-colored oil comprising chiefly a mixture of alkyl chlorbenzenes in which the alkyl groups contained from about 10 to 15.5 carbon atoms. 20 parts of the oil were sulphonated by mixing it with 25½ parts of 26° Bé. oleum at a temperature from about 10° to 15° C. for about 3 hours. The mixture was then heated to 40° to 55° C., where it was held for about one-half hour. The mixture was then diluted by drowning it in 6 to 7 times its weight of ice and water, neutralized with concentrated aqueous caustic soda and dried. The resulting product was an almost white solid soluble in water to form substantially colorless solutions having desirable wetting and washing properties. The product was chiefly a mixture of nuclearly alkylated chlorbenzenes in which the alkyl groups contained from about 10 to about 15.5 carbon atoms.

Example 9, Part 1.—Chlorine was passed into a kerosene (a purified Pennsylvania petroleum distillate) which boiled from 245° to 315° C., and of which 90 per cent distilled between 260° and 305° C., and had a specific gravity of 0.815, contained in a closed, lead-lined vessel which was equipped with a vent for hydrogen chloride produced by the chlorination. The chlorination was carried out in the dark, but to facilitate the chlorination the kerosene initially contained about 0.45 part of iodine per 1000 parts of kerosene. The temperature of the reaction mass was preferably maintained at about 45° to 50° C. The introduction of chlorine was continued until the weight of the mass increased to an extent which corresponded substantially with 115 per cent chlorination. The specific gravity of the reaction mixture reached about 0.915.

Part 2.—300 parts of the above chlorinated kerosene was mixed with 30 parts of anhydrous aluminum chloride and 150 parts of commercial diphenyl. The mixture was agitated under reflux at room temperature (that is, at about 15° to 30° C.) for about one hour and thereafter at about 75° C. for about one and a half hours. The mass was then cooled to about 20° to 30° C. and poured into a mixture of 600 parts of ice water and 30 parts of commercial muriatic acid. The aluminum salts dissolved in the cold dilute acid while the organic matter, which contained the alkylated diphenyl compounds, was precipitated in a semi-liquid, pasty form. Small amounts of benzene and/or ether were added to the agitated aqueous mixture to dissolve the organic products. Upon standing, the mixture separated into an upper layer which was a solution of the organic matter in the organic solvent, and a lower aqueous acid layer which was withdrawn and discarded. The benzol and/or ether solution of organic matter was washed with water until it was reasonably free of acid, and was then distilled in vacuo. The fraction of the distillate which boiled at about 170° to about 260° C. at 5 mm. pressure was collected separately. It was a light-yellow viscous oil which was insoluble in water, but soluble in benzene and in ether. It was a mixture comprised chiefly of alkylated diphenyl compounds in which the alkyl groups corresponded with the kerosene hydrocarbons employed. It also contained some chloralkyl diphenyl compounds derived from the dichlor hydrocarbons.

Part 3.—25 parts of the oil obtained according to Part 2 of this example were mixed with 15 parts of 100 per cent sulphuric acid and stirred at about 90° C. for about 20 minutes, or until a 1 cc. sample was practically completely soluble in about 10 ccs. of water at about 25° C. The sulphonation mass was poured into 300 parts of water and the aqueous acid mixture was neutralized with caustic alkali or a water-soluble carbonate (e. g., sodium carbonate), and the resulting neutral solution was dried. The product was chiefly a mixture of the salts (e. g., alkali metal salts) of alkyl-diphenyl sulphonic acids. It was a light-brown to white solid which was soluble in water, and in aqueous solutions of mineral acids and of water-soluble alkalies.

Example 10, Part 1.—Chlorine was passed into a kerosene (a purified Pennsylvania petroleum distillate) boiling from 245° to 315° C., and of which 90 per cent distilled between 260° and 305° C., and had a specific gravity of 0.815, contained in a closed, lead-lined vessel which was equipped with a vent for hydrogen chloride produced by the chlorination. The chlorination was carried out in the dark, but to facilitate the chlorination the kerosene initially contained about 0.45 part of iodine per 1000 parts of kerosene. The temperature of the reaction mass was preferably maintained at about 45° to 50° C. The introduction of chlorine was continued until the weight of the mass increased to an extent corresponding substantially with 115 per cent chlorination. The specific gravity of the reaction mixture reached about 0.915.

Part 2.—560 parts of the resulting mixture of chlorinated hydrocarbons, 350 parts of phenol and 28 parts of granular anhydrous zinc chloride were agitated at room temperature for about 3 hours and then heated, with agitation, at about 135° C. for about 5 hours. The resulting reaction mass was cooled and added to about 600 parts of water, the mixture was heated to 70° C. with agitation, allowed to settle, and the upper, oil layer was separated and washed with hot water to remove zinc chloride and residual phenol. The washed oil was then treated with a small amount of alkali (7 parts of a 50 per cent solution of sodium hydroxide) and distilled in vacuo (e. g., 4 mm. pressure) in a still equipped with a fractionating column. Fractions boiling between about 140° and 230° C. at 4 mm. pressure were collected as separate products or as one product.

Part 3.—262 parts of one of the resulting mixtures of alkyl phenols (the resulting product or one of the fractions thereof) were sulphonated by agitating well with 262 parts of 100 per cent sulphuric acid, while maintaining the temperature at 20° to 30° C. When the sulphonation had been effected, the reaction mass was drowned in 1500 parts of water, treated with sufficient caustic soda to render it neutral to delta paper (about 260 parts of a 50 per cent solution of caustic soda), and evaporated to dryness.

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that changes can be made without departing from the scope of the invention.

Thus, in using the chlorinated hydrocarbon mixtures prepared in accordance with the present invention the proportion of the aromatic compound employed may be varied. Generally, the optimum amount of aromatic compound to be employed is dependent upon the amount of chlorine combined in the hydrocarbon mixture. In order to obtain complete reaction, one mol of aromatic compound should be used for each atom of combined chlorine in the hydrocarbon mixture. Preferably, an excess of the aromatic compound is used as this favors complete reaction of the chlorinated hydrocarbons in the mixture.

The particular manner in which the sulphonation is carried out forms no part of the present invention; this step can be carried out in any suitable manner. For example, sulphuric acids of various strengths such as 66° Bé. sulphuric acid, 100 per cent sulphuric acid, 26 per cent oleum and 65 per cent oleum, and chlorsulphonic acid may be used as sulphonating agents. The sulphonation may be carried out in the presence of inert solvents or diluents, and sulphonation assistants as, for example, the lower fatty acids and their anhydrides, such as acetic acid and acetic anhydride, or the alkali metal sulphates, such as sodium or potassium sulphate, may be employed. Also, the temperature at which the sulphonation 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 sulphonating agent the lower is the preferred temperature. In most cases the sulphonation is carried out most efficiently at temperatures between 5° and 90° C. For complete sulphonation the sulphonating agent in terms of 100 per cent sulphuric acid may be employed in amounts which range from 0.3 to 5 times or more the weight of the condensation product to be sulphonated. Ordinarily, the extent to which the sluphonation is carried out will vary with the individual material being sulphonated, the duration of the sulphonation, and the use to be made of the sulphonated product.

The side-chain aromatic sulphonates may be prepared in the form of their free sulphonic acids or in the form of their salts. Thus they may be prepared in the form of their alkali metal, alkaline earth metal, ammonium, or organic base salts (e. g., amine salts). They are of particular value in the form of their alkali metal and especially sodium salts.

This application is a continuation-in-part of my applications Serial No. 737,777, filed July 31, 1934; Serial No. 93,521, filed July 30, 1936; and Serial No. 186,231, filed January 21, 1938.

Since certain changes may be made in the process described above without departing from the scope of the invention it will be understood that the description should be interpreted as illustrative and not in a limiting sense.

I claim:

1. In the manufacture of side-chain aromatic sulphonates by chlorinating a hydrocarbon mixture of the type of a petroleum distillate, condensing resulting chlorinated hydrocarbons with an aromatic compound, and sulphonating resulting side-chain aromatic compounds, the improvement which comprises chlorinating the hydrocarbon mixture to a degree corresponding to more than 100 per cent and not more than 200 per cent chlorination.

2. In the manufacture of side-chain aromatic sulphonates by chlorinating a hydrocarbon mixture of the type of a petroleum distillate containing an average of 7 to 35 carbon atoms, condensing resulting chlorinated hydrocarbons with an aromatic compound, and sulphonating resulting side-chain aromatic compounds, the improvement which comprises chlorinating the hydrocarbon mixture to a degree corresponding to more than 100 per cent and not more than 175 per cent chlorination.

3. In the manufacture of side-chain aromatic sulphonates by chlorinating a hydrocarbon mixture of the type of a petroleum distillate containing an average of 7 to 35 carbon atoms, condensing resulting chlorinated hydrocarbons with an aromatic compound, and sulphonating resulting side-chain aromatic compounds, the improvement which comprises chlorinating the hydrocarbon mixture to a degree corresponding to from 110 to 150 per cent chlorination.

4. In the manufacture of side-chain aromatic sulphonates by chlorinating a petroleum distillate containing an average of 10 to 19 carbon atoms per molecule, condensing resulting chlorinated hydrocarbons with an aromatic compound, and sulphonating resulting side-chain aromatic compounds, the improvement which comprises chlorinating the petroleum distillate to a degree corresponding to more than 100 per cent and not more than 175 per cent chlorination.

5. In the manufacture of side-chain aromatic sulphonates by chlorinating a hydrocarbon mixture of the type of a petroleum distillate containing an average of 7 to 35 carbon atoms, condensing resulting chlorinated hydrocarbons with an aromatic compound of the benzene series, and sulphonating resulting side-chain aromatic compounds, the improvement which comprises chlorinating the hydrocarbon mixture to a degree corresponding to more than 100 per cent and not more than 200 per cent chlorination.

6. In the manufacture of side-chain benzene sulphonates by chlorinating a petroleum distillate containing an average of 7 to 35 carbon atoms, condensing resulting chlorinated hydrocarbons with benzene, and sulphonating resulting side-chain benzene compounds, the improvement which comprises chlorinating the petroleum distillate to a degree corresponding to more than 100 per cent and not more than 200 per cent chlorination.

7. In the manufacture of side-chain phenol sulphonates by chlorinating a petroleum distillate containing an average of 7 to 35 carbon atoms, condensing resulting chlorinated hydrocarbons with phenol, and sulphonating resulting side-chain phenol compounds, the improvement which comprises chlorinating the petroleum distillate to a degree corresponding to more than 100 per cent and not more than 200 per cent chlorination.

8. In the manufacture of side-chain naphthalene sulphonates by chlorinating a paraffinic petroleum hydrocarbon distillate containing an average of 7 to 35 carbon atoms, condensing resulting chlorinated hydrocarbons with naphthalene, and sulphonating resulting side-chain naphthalene compounds, the improvement which comprises chlorinating the petroleum distillate to a degree corresponding to more than 100 per cent and not more than 200 per cent chlorination.

9. In the manufacture of side-chain aromatic sulphonates by chlorinating a paraffinic petroleum hydrocarbon distillate containing an average of 10 to 19 carbon atoms, condensing resulting chlorinated hydrocarbons with an aromatic compound, and sulphonating resulting side-chain aromatic compounds, the improvement which comprises chlorinating the hydrocarbon mixture to a degree corresponding to from 110 to 150 per cent chlorination.

10. In the manufacture of side-chain benzene sulphonates by chlorinating a paraffinic petroleum hydrocarbon distillate boiling for the most part within the range 180° to 300° C., condensing resulting chlorinated hydrocarbons with benzene, and sulphonating resulting side-chain benzene compounds, the improvement which comprises chlorinating the petroleum distillate to a degree

corresponding to more than 100 per cent and not more than 175 per cent chlorination.

11. In the manufacture of side-chain phenol sulphonates by chlorinating a paraffinic petroleum hydrocarbon distillate boiling for the most part within the range 180° to 300° C., condensing resulting chlorinated hydrocarbons with phenol, and sulphonating resulting side-chain phenol compounds, the improvement which comprises chlorinating the petroleum distillate to a degree corresponding to more than 100 per cent and not more than 175 per cent chlorination.

12. In the manufacture of side-chain benzene sulphonates by chlorinating a paraffinic petroleum hydrocarbon distillate containing an average of 10 to 19 carbon atoms, condensing resulting chlorinated hydrocarbons with benzene, and sulphonating resulting side-chain benzene compounds, the improvement which comprises chlorinating the petroleum distillate to a degree corresponding to from 110 to 150 per cent chlorination.

13. In the manufacture of side-chain phenol sulphonates by chlorinating a paraffinic petroleum hydrocarbon distillate containing an average of 10 to 19 carbon atoms, condensing resulting chlorinated hydrocarbons with phenol, and sulphonating resulting side-chain phenol compounds, the improvement which comprises chlorinating the petroleum distillate to a degree corresponding to from 110 to 150 per cent chlorination.

14. In the manufacture of side-chain benzene sulphonates by chlorinating a paraffinic petroleum hydrocarbon distillate boiling for the most part within the range 180° to 300° C., condensing resulting chlorinated hydrocarbons with benzene in the presence of anhydrous aluminum chloride, and sulphonating resulting side-chain benzene compounds, the improvement which comprises chlorinating the petroleum distillate to a degree corresponding to about 120 per cent chlorination.

15. The process for manufacturing side-chain aromatic sulphonates which comprises chlorinating a paraffinic petroleum hydrocarbon distillate containing an average of 7 to 35 carbon atoms to a degree corresponding to more than 100 per cent and not more than 175 per cent chlorination, condensing the resulting chlorinated mixture with an aromatic compound with the aid of a Friedel-Crafts condensation catalyst to form a mixture of side-chain aromatic compounds, and sulphonating the mixture of side-chain aromatic compounds.

16. The process for manufacturing side-chain benzene sulphonates which comprises chlorinating a paraffinic petroleum hydrocarbon distillate containing an average of 10 to 19 carbon atoms to a degree corresponding to more than 100 per cent and not more than 175 per cent chlorination, condensing the resulting chlorinated mixture with benzene with the aid of anhydrous aluminum chloride to form a mixture of side-chain benzene compounds, and sulphonating the mixture of side-chain benzene compounds.

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