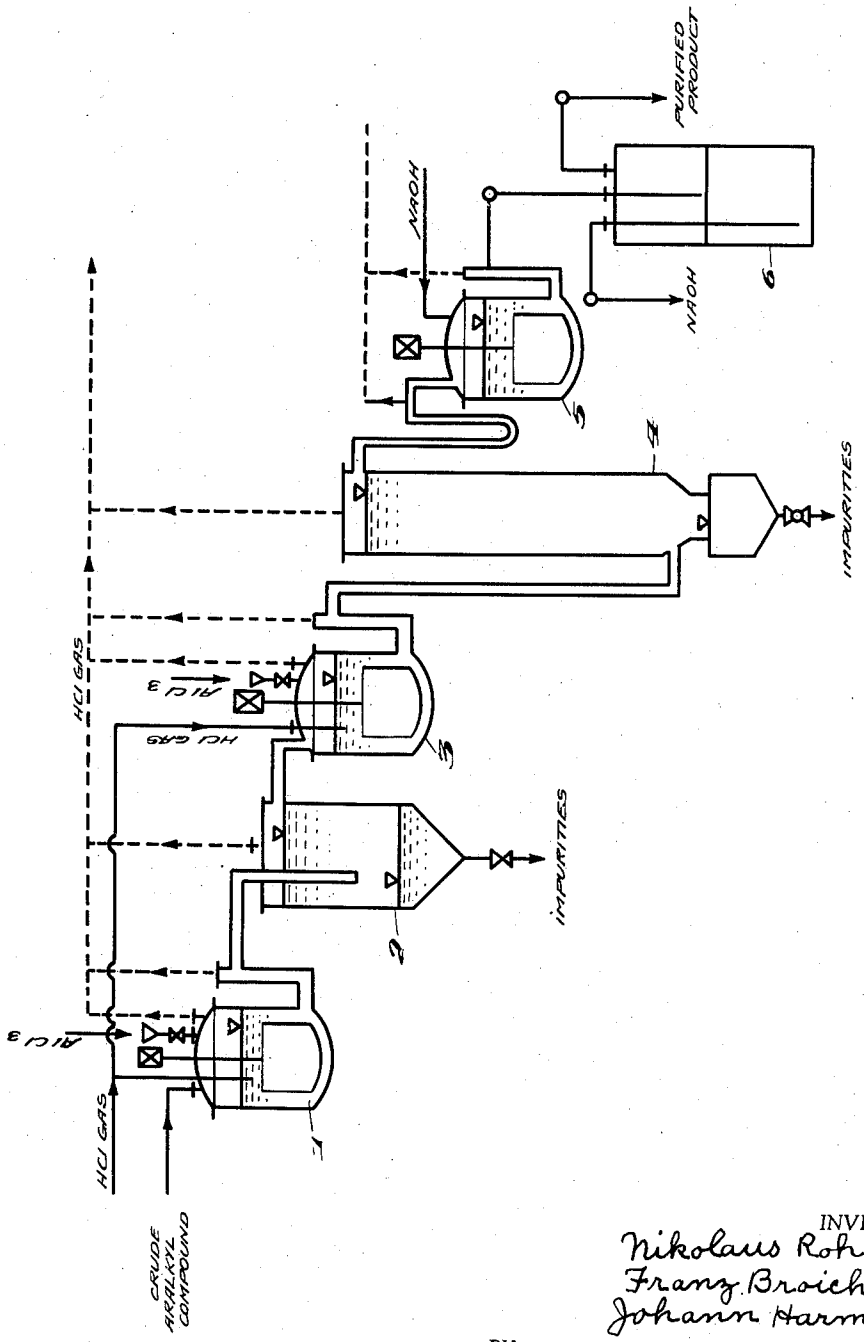
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PROCESS FOR THE PURIFICATION OF HIGH MOLECULAR WEIGHT ARALKYL COMPOUNDS

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PROCESS FOR THE PURIFICATION OF HIGH MOLECULAR WEIGHT ARALKYL COMPOUNDS

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2 Claims. (Cl. 260—674)

It is known that the monoalkyl aromatic compounds obtainable by the Friedel-Crafts synthesis from chlorinated aliphatic or mixtures of chlorinated aliphatic and naphthenic hydrocarbons having more than 10 carbon atoms per molecule and from benzene hydrocarbons constitute starting materials for detergents which are produced from mono alkyl aromatic compounds by sulfonation.

It is customary to produce the sulfonates as color-free as possible so that they will not discolor the material being washed. To this end alkylbenzenes as pure as possible generally have been used because their sulfonation does not give colored by-products. It has been attempted to accomplish this result by a special procedure for alkylating the aromatic compounds by the use of certain alkyl halogenides. It has been proposed also to refine the alkylbenzenes giving colored sulfonates with sulfuric acid or aluminum chloride but such processes have not proved to be satisfactory. By refining with sulfuric acid, sulfonic acids are obtained which, due to its solubility in the alkylbenzenes, give by washing with weak alkali emulsions which are very difficult to separate, while when the alkylbenzenes are refined with aluminum chloride considerable amounts thereof are consumed in splitting the alkylbenzenes and this results in a loss in yield.

It has been found that alkyl aromatic compounds which have been produced by the Friedel-Crafts synthesis from high molecular weight alkyl chlorides containing more than 10 carbon atoms and from benzene hydrocarbons such as benzene, toluene and xylene can be very satisfactorily purified by treating the separated and neutralized water-free crude alkyl aromatic compounds with an aluminum chloride in the presence of gaseous hydrogen chloride, separating the resulting aluminum chloride double compound and then working up the purified alkyl aromatic compound in the usual way. In the foregoing sentence high molecular weight alkyl chlorides includes the chlorides of aliphatic hydrocarbons and mixtures of aliphatic and naphthenic hydrocarbons.

In an example of the process the isolated and neutralized water-free crude alkyl aromatic compound is first fractionally distilled and only about the last 30% of the monoalkyl aromatic compound distillate fraction which contains the bulk of the colored impurities is treated with aluminum chloride in the presence of gaseous hydrogen chloride.

In the process of the present invention the maximum amount of aluminum chloride required is about 5% by weight calculated upon the weight of the alkyl aromatic compound to be purified. Generally 0.5–3% is sufficient depending upon the amount of undesired material present. It is important that the alkyl aromatic compound to be treated shall be free from the benzene hydrocarbon starting material because it will go along with the aluminum chloride double compound and increase the solubility of the double compound in the alkyl aromatic compound to be purified. Therefore the separation of the purified alkyl aromatic compound from the aluminum chloride double compound will be made difficult.

The loss of alkyl aromatic hydrocarbon in the aluminum chloride double compound which consists of about 65% of organic material, 30% of aluminum chloride and 5% of hydrogen chloride is relatively small and negligible.

Example 1

Benzene and a chlorinated crude oil fraction consisting of about 25% of normal paraffins, 35% of isoparaffins and 40% of cycloparaffins (boiling range 220–225° C.) and containing about 6% of chlorine are reacted by the Friedel-Crafts process in the presence of aluminum chloride. Then the aluminum chloride double compound is separated in the usual way, the reaction product washed to neutrality and the unreacted benzene etc. separated by distillation. The resulting product is a dark brown alkylbenzene which upon sulfonation yields a colored sulfonate. If the crude alkylbenzene is fractionated a fraction amounting to about 64% is obtained which has a boiling range of 175–195° C. at 20 Torr. (mm. of Hg). This fraction upon sulfonation gives a light colored sulfonate. The fractionation gives a second fraction amounting to about 20% having a boiling range of 195–203° C. at 20 Torr., which upon sulfonation gives a dark colored sulfonate.

2000 kg. of this second alkylbenzene fraction in a vessel equipped for stirring is saturated with hydrogen chloride at room temperature while excluding moisture and then 10 kg. of aluminum chloride is added and the mixture is stirred for 2 hours while introducing a small stream of hydrogen chloride. The aluminum chloride dissolves in a short time with the formation of a double compound. The mixture is then allowed to stand, the heavy aluminum chloride double compound 30 kg.) is separated and the so-purified alkylbenzene fraction is washed to neutrality with dilute water solution of sodium hydroxide. If necessary the alkylbenzene can be treated with a color absorbing material such as activated decolorizing earth before washing with alkali. The product is distilled and yields 1965 kg. of a purified alkylbenzene having a boiling range of 195–202° C. at 20 Torr., which by sulfonation yields a faultless sulfonate.

The purification treatment gives the following comparison. 100 g. samples of the crude and purified alkylbenzenes are treated at 50° C. for 3 hours with 250 g. of sulfuric acid monohydrate and 35 g. of water are then added, the oily sulfonic acid separates out and is neutralized with dilute sodium hydroxide solution and dissolved in water to a concentration of 7% calculated on the sodium salt. The color of the resulting solution is compared with a solution of iodine in potassium iodide solution and the number of milligrams of iodine per 100 $cm.^3$ of potassium iodide solution in a solution of equal color is determined. The crude alkylbenzene having the boiling range of 195–203° C. at 20 Torr., gives a reading of 14 while the purified alkylbenzene gives a reading of 6.

Example 2

The dark brown colored alkylbenzene having the boiling range 185–280° C. at 20 Torr. (97%) described in Example 1 is continuously purified in the apparatus illustrated in the accompanying drawing.

The drawing is a diagrammatic showing of the apparatus and will be described hereinafter in connection with the process which is carried out in it.

The stirring vessel 1 which has a capacity of 500 liters is maintained at 20–25° C. and supplied with crude alkyl-

benzene, hydrogen chloride and aluminum chloride at the rate of 500 liters of the crude alkylbenzene, 2500 liters of gaseous hydrogen chloride and 4.5 kg. of aluminum chloride per hour. The mixture flows from the vessel **1** at the rate of 500 liters of liquid per hour to the settling tank **2** which has a capacity of 1000 liters where the aluminum chloride double compound settles out and is withdrawn from time to time while 500 liters of alkylbenzene per hour flows from the tank **2** to the stirring vessel **3** which has 500 liters capacity. 500 liters of gaseous hydrogen chloride and 4.5 kg. of aluminum chloride are introduced per hour into the vessel **3** and 500 liters per hour of the resulting mixture is delivered from the vessel **3** to the settling tank 4 which has a capacity of 1500 liters. Aluminum chloride double compound settles in tank **4** and is removed from time to time. The alkylbenzene flows from tank **4** through a filter chamber (not shown) containing filling bodies and glass wool which serves to retain entrained aluminum chloride double compound and into another stirring vessel **5** where it is neutralized with a 20% aqueous solution of sodium hydroxide and the resulting mixture is delivered to the separating vessel **6** where the purified alkylbenzene is separated from the caustic soda solution. A treatment of the liquid with absorbing material may be interposed between the settling tank **4** and the stirring vessel **5** but this is necessary only if an alkylbenzene capable of giving a completely colorless sulfonate is required. The purified alkylbenzene is finally distilled under vacuum at 5–10 Torr. and gives, after separation of a fore running amounting to 2%, a water white oil having a bluish fluoresence and a boiling range of 305–390° C. at normal pressure. The distillation residue amounts to 4%. By the introduction of 66,750 liters of crude alkylbenzene, 1,200 kg. of aluminum chloride, and 400,000 liters of hydrogen chloride gas, 64,440 liters of purified alkylbenzene are produced, besides 3,400 kg. of aluminum chloride double compound containing 34% by weight of $AlCl_3$ and 3% by weight of HCl.

The color values are as follows:

Crude alkylbenzene	90
Purified alkylbenzene	8.5
Purified and distilled alkylbenzene	6.0

We claim:

1. Process of purifying crude, water-free alkyl aromatic compounds produced by reacting alkyl chlorides containing more than 10 carbon atoms with benzene hydrocarbons by the Friedel-Crafts method which comprises separating the crude alkyl aromatic compounds from aluminum chloride double compound, washing the resulting separated crude alkyl aromatic compounds to neutrality, separating unreacted benzene hydrocarbons therefrom, intimately contacting, the resulting separated, water-free and benezene hydrocarbon-free crude, alkyl aromatic compounds with from about 0.5% to about 5% by weight of aluminum chloride in the presence of gaseous hydrogen chloride at about room temperature and separating the resulting purified alkyl aromatic compounds from the resulting liquid aluminum chloride double compound.

2. Process as defined in claim 1 in which the separated and neutralized water-free crude alkyl aromatic compounds are fractionally distilled to produce a residual fraction amounting to about 30% which is treated with the aluminum chloride in the presence of gaseous hydrogen chloride.

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