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PURIFICATION OF AROMATIC HYDROCARBONS

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This invention is concerned with the purification of aromatic hydrocarbons, and more particularly with the reduction of the "paraffin" content of such hydrocarbons. This application is a continuation in part of my application Serial No. 57,839, filed June 16, 1949, and now abandoned.

An object of my invention is the provision of an improved process of hydrocarbon purification using aluminum chloride. Another object is the improvement of the efficiency of such processes by the use of promoters. Another object is to reduce the cost of such processes. Other objects will appear in the course of the disclosure of my invention.

The common aromatic hydrocarbons benzene, toluene, and xylene, which may be recovered as by-products in the coking of coal, find considerable use as raw materials in further chemical manufacture. For these purposes it is generally required that the content of unwanted constituents be quite low. One class of unwanted constituents is the "paraffins," which some toluene specifications, for example, require to be held below 0.2% when the toluene is to be used in the manufacture of hydrogenated and chlorinated compounds. It is also useful to reduce the "paraffin" content of toluene to a minimum percentage when the toluene is to be used in the manufacture of TNT. In the present state of the art it is impossible to produce the aromatic hydrocarbons with this degree of purity without some auxiliary purifying treatment.

The term "paraffins" as here used is a trade expression referring to nonaromatic compounds which are unsulfonatable and have boiling points close to that of the aromatic hydrocarbon. For example, in benzene of commercial grade produced from coal-coking operations, these "paraffins" have been found to be primarily naphthenic and to include the following compounds [see John R. Anderson and Carl J. Engelder, Industrial and Engineering Chemistry, vol. 37, pp. 541–3 (1945), and Chemical Abstracts, vol. 39, p. 3146/3 (1945)]:

(1) Cyclohexane;

(2) Methylcyclohexane;

(3) 3-methylhexane or 3-ethylpentane or both;

(4) Heptane or 2,2,4-trimethylpentane or both;

(5) 1,1-dimethylcyclopentane; and

(6) Trans-1,2-dimethylcyclopentane or trans-1,3-dimethylcyclopentane or both.

A considerable number of methods for reducing

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the percentage of these "paraffins" have been devised, including adsorption of the "paraffins" on sold adsorbents, solvent extraction, azeotropic distillation, extractive distillation, and chemical reaction, particularly treatment of the "paraffins" to produce less undesirable lower or higher boiling point compounds. Of these various methods the last has been found to reduce the "paraffin" content to lowest values.

The said treatment is generally carried out by reacting the "paraffins" with an acid-reacting metal halide, such as aluminum chloride. Under favorable conditions, the "paraffin" content of a commercially refined hydrocarbon so treated can be reduced to the 0.2% limit imposed by a number of users, provided that the temperature is kept closely below the boiling point of the aromatic hydrocarbon. Repeated treatment may be necessary in some instances to reduce the "paraffin" content to the maximum limit of 0.2%; for example, if the initial "paraffin" content happens to be high as a result of the particular operating conditions of the coke oven which produced the aromatic hydrocarbon. I have discovered, however, a process by which reaction of the "paraffins" in aromatic hydrocarbons can be carried out in one stage so completely that the unreacted "paraffin" content lies well below the lowest limits so far set by industrial users of toluene and other aromatic hydrocarbons.

My invention consists, essentially, in reacting the hydrocarbon with aluminum chloride to which is added, as promoter, alpha picoline. Olefins and any tar formed are afterwards removed by known means. A single treatment, by the process of my invention, of toluene, for example, containing upwards of 0.50% "paraffins," not only produces purified toluene containing less than 0.10% of these compounds, but does so with full speed and effectiveness at relatively reduced temperatures such as 80° C. and 50° C. This is well below the reaction temperature of close to 110° C. necessary for maximum effectiveness when treating toluene with aluminum chloride alone.

The following examples illustrate the operation of my invention. In these examples a sample of "paraffin" containing toluene stock was obtained from a batch of toluene produced as a regular by-product of coal-coking operations and of commercially refined grade, sulphuric acid washed, which is not fully purified but meets the test for "nitration grade" toluene in A. S. T. M. Specification D841–47 as determined by the procedure described in A. S. T. M. Specification D851–47 (see vol. 5, A. S. T. M. Stand-

ards, 1949, pp. 1292 and 1313). The test sample of toluene was determined to contain 0.9% "paraffins" (by volume) by using an Abbé refractometer to determine its refractive index and that of a standard sample of thoroughly purified toluene; and comparing the readings to obtain a measure of the percentage by volume of "paraffin" impurities, with an accuracy within one-tenth of one per cent.

Example I

200 ml. of the test sample of toluene was mixed with 5.22 grams of anhydrous aluminum chloride, and 2 ml. of alpha picoline, the reagents being mixed together first and then added to the toluene. The mixture was maintained at 80° C. and agitated in a vessel at atmospheric pressure for about two hours. The resultant mixture was subsequently washed with water to remove the aluminum chloride and with concentrated sulphuric acid to remove any olefins formed in the course of the reaction. After distillation to remove any tar the distillate was tested for its refractive index and found to contain no detectable amount of "paraffins" by comparison of the refractive index of the distillate with that of the standard sample.

Example II

Another 200 ml. of the same test sample of toluene was treated as described above in Example I, except that the reaction temperature was maintained at 50° C. instead of 80° C. The distillate was again found to contain no detectable amount of "paraffins."

Although the above described process is preferred by me, a reasonable latitude is permissible in the practice of my invention without substantial impairment of its effectiveness. It is not necessary that the quantity of aluminum chloride added be limited to 3%; the quantity may be reduced to about 1% if care is exercised, or increased up to about 9% without encountering trouble. It is, of course, uneconomic to use more than necessary, and I find 3% to be perhaps the optimum amount. The time of the reaction may vary between about one-half and three hours, the lower figure being at the expense of some yield. The time of reaction depends to a considerable extent on the degree of agitation achieved.

The maximum temperature is the boiling point of the hydrocarbon being treated, which, for toluene, is 110° C. This temperature appears to be the optimum when a metal halide is used alone; for example, comparative tests at 110° C., 80° C. and 50° C., at atmospheric pressure, using aluminum chloride alone as the purifying agent, showed an increase of 0.1% impurities at 80° C., and an increase of 0.2% impurities at 50° C., as compared with results under otherwise like conditions at 110° C. On the other hand, when alpha picoline is used as a promoter, according to the practice of my invention, the optimum temperature for the reaction is considerably lower, the value depending to some extent on the amount of alpha picoline used. I have found that a high degree of purification can be obtained at a temperature as low as 50° C. At these lower reaction temperatures the formation of tar is greatly reduced, and this in itself is an important advantage of my process over those of the prior art.

As mentioned, I have found the optimum amount of aluminum chloride to be about 3% by weight, and the optimum amount of alpha picoline under these conditions to be about one-fifth or 20% of the weight of the aluminum chloride. The minimum amount of alpha picoline which is effective is about one-tenth or 10% of the weight of the aluminum chloride, when the aluminum chloride addition is in the region of the optimum figure.

It will be understood that my invention is limited, not by the foregoing description, but rather by the appended claims.

I claim:

1. A method of reducing the percentage of "paraffin" hydrocarbons in a mixture of a small percentage of "paraffin" hydrocarbons dissolved as normally occurring impurities in a liquid aromatic hydrocarbon produced from coal, said "paraffin" hydrocarbons being unsulfonatable, nonaromatic and of such nature as to distill over with the aromatic hydrocarbon, comprising treating the said mixture with anhydrous aluminum chloride and alpha picoline, at a temperature and pressure below the boiling point of the aromatic hydrocarbon, until the percentage of said "paraffin" hydrocarbons in the mixture is reduced to about 0.2% or less by volume.

2. A method of reducing the percentage of "paraffin" hydrocarbons in a mixture of a small percentage of "paraffin" hydrocarbons dissolved as normally occurring impurities in a liquid aromatic hydrocarbon which is produced from coal and is from the group consisting of benzene, toluene and xylene, said "paraffin" hydrocarbons being unsulfonatable, nonaromatic and of such nature as to distill over with the aromatic hydrocarbon, comprising treating the said mixture with anhydrous aluminum chloride and alpha picoline at a temperature and pressure below the boiling point of the aromatic hydrocarbon and agitating the mixture, until the percentage of said "paraffin" hydrocarbons in the admixture is reduced to about 0.2% or less by volume in a single treatment.

3. A method of reducing the percentage of "paraffin" hydrocarbons in a mixture of a small percentage of "paraffin" hydrocarbons dissolved as normally occurring impurities in liquid toluene produced from coal, said "paraffin" hydrocarbons being unsulfonatable, nonaromatic and of such nature as to distill over with the toluene, comprising treating the said mixture with anhydrous aluminum chloride and alpha picoline at atmospheric pressure and below 110° C. and agitating the mixture, until the content of "paraffin" hydrocarbons is reduced to about 0.2% by volume or less in a single treatment.

4. A method of reducing the percentage of "paraffin" hydrocarbons in a mixture of a small percentage of "paraffin" hydrocarbons dissolved as normally occurring impurities in a liquid aromatic hydrocarbon which is produced from coal and is from the group consisting of benzene, toluene and xylene, said "paraffin" hydrocarbons being unsulfonatable, nonaromatic and of such nature as to distill over with the aromatic hydrocarbon, comprising treating the said mixture with anhydrous aluminum chloride and alpha picoline in amount not less than 10% by weight of the aluminum chloride, at a temperature and pressure below the boiling point of the aromatic hydrocarbon, and agitating the mixture, until the content of "paraffin" hydrocarbons is reduced to about 0.2% or less by volume in a single treatment.

5. A method of reducing the percentage of "paraffin" hydrocarbons in a mixture of a small percentage of "paraffin" hydrocarbons dissolved as normally occurring impurities in a liquid aromatic hydrocarbon which is produced from coal and is from the group consisting of benzene, toluene and xylene, said "paraffin" hydrocarbons being unsulfonatable, nonaromatic and of such nature as to distill over with the aromatic hydrocarbon, comprising treating the said mixture with anhydrous aluminum chloride in amount between about 1% and 9% by weight of the aromatic hydrocarbon and alpha picoline in amount not less than 10% by weight of the aluminum chloride, at a temperature and pressure below the boiling point of the aromatic hydrocarbon, and agitating the mixture, until the content of "paraffin" hydrocarbons is reduced to about 0.2% or less by volume in a single treatment.

6. A method of reducing the percentage of "paraffin" hydrocarbons in a mixture of a small percentage of "paraffin" hydrocarbons dissolved as normally occurring impurities in liquid toluene produced from coal, said "paraffin" hydrocarbons being unsulfonatable, nonaromatic and of such nature as to distill over with the toluene, comprising treating the said mixture at a temperature of about 50° C. to 80° C. at about atmospheric pressure with anhydrous aluminum chloride in amount about 3% by weight and alpha picoline in amount about 20% by weight of the anhydrous aluminum chloride, and agitating the mixture, until the content of "paraffin" hydrocarbons is reduced to about 0.1% or less by volume in a single treatment.

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