

UNITED STATES PATENT OFFICE

2,332,370

RECOVERY OF ORTHO-XYLENE

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No Drawing. Application October 11, 1941,
Serial No. 414,601

5 Claims. (Cl. 260-674)

This invention is directed to a process for the recovery of orthoxylene from oils containing it and like-boiling olefins and other like-boiling, non-aromatic hydrocarbons, e. g. naphthenes or paraffins.

Ortho-xylene is present in oil fractions such as drip oil and fractions recovered from cracked petroleum products. By "drip oil" I refer to those condensates from carburetted water gas such as condensates formed in the gas distributing lines or holders or the light oil which may be condensed in cooling the carburetted water gas after removal of tar. Drip oils may contain about 5% ortho-xylene. A common characteristic of drip oils and cracked petroleum products is that in addition to the aromatic hydrocarbons they contain a substantial proportion of like-boiling, non-aromatic hydrocarbons including olefins and paraffins or naphthenes.

Distillation of drip oil or cracked petroleum products with efficient rectification of the vapors may be employed to recover a fraction in which the ortho-xylene is concentrated. However, even with efficient rectification a fraction containing more than about 80% to 85% ortho-xylene can rarely be obtained. Olefins together with paraffins and usually some naphthenes and traces of meta- and para-xylene make up the remaining 15% to 20% of the ortho-xylene fraction. These non-aromatic hydrocarbons individually may have boiling points ranging from considerably below to above the boiling point of ortho-xylene, e. g. their boiling points may range from 100° to 155° C., whereas ortho-xylene boils at about 144° C. Nevertheless, these non-aromatics cannot be separated from the ortho-xylene by fractional distillation of their mixtures, e. g. drip oil and cracked petroleum oils, under practical conditions. It appears that in the mixture the relative volatilities of the respective hydrocarbons are so modified by the presence of the other hydrocarbons as to prevent their separation by fractional distillation. Such hydrocarbons, those which cannot be separated by fractional distillation or are difficultly separable from each other by fractional distillation under practicable conditions for distilling oils, are referred to as "like-boiling" hydrocarbons.

Chemical treatment of oils such as referred to above has been used to recover pure ortho-xylene therefrom, but such methods have hitherto been cumbersome and expensive.

I have now discovered that a pure ortho-xylene may be recovered from an oil containing it together with like-boiling olefins and other non-

aromatic hydrocarbons (paraffins or naphthenes), by subjecting the oil to a series of three treatments. I have discovered that by chlorinating the oil the relative volatilities of the aromatic hydrocarbon and other constituents of the oil may be so changed with respect to each other that by fractionally distilling the chlorinated oil the non-aromatic hydrocarbon constituents can be selectively removed to an extent not possible prior to chlorination. I have found that the remainder of the like-boiling, non-aromatic hydrocarbons may be separated from the aromatic by azeotropically distilling the oil, either prior to its chlorination or after the fractional distillation of the chlorinated oil. While it is possible to recover from an ortho-xylene oil fraction a relatively pure ortho-xylene product by the foregoing combination of steps irrespective of whether the azeotropic distillation precedes or follows the steps of chlorination and fractional distillation, I have discovered that the aromatic hydrocarbon may best be recovered in high yields and of high purity by first azeotropically distilling the oil fraction and thereafter chlorinating the residue of the azeotropic distillation and fractionally distilling the chlorinated residue.

It is preferred that the aromatic oil fraction to be treated by the process of my invention be one from which constituents boiling from the oil fraction at temperatures higher and lower than the desired ortho-xylene boils therefrom have been removed. For example, in recovering ortho-xylene from drip oil it is preferred to first fractionally distill and wash with concentrated sulfuric acid the drip oil and to recover therefrom a close cut fraction in which the ortho-xylene is concentrated, such as a fraction boiling in the range 135° C. to 145° C. Less advantageously the industrial, acid-washed xylol fractions boiling in the range 135° C. to 155° C., or xylene oils of even broader boiling range, may be treated by the process of my invention.

This invention is not limited, however, to the distillation of xylene fractions of particular boiling ranges. In the treatment of oils containing xylene, like-boiling, non-aromatic hydrocarbons and lower and higher boiling constituents, the like-boiling, non-aromatic hydrocarbons are selectively separated from the xylene by the chlorination and distillation treatments as described above. When low boiling constituents are present in the oil subjected to the azeotropic distillation, they will be separated from the xylene by the azeotropic distillation together with like-boiling, non-aromatic hydrocarbons. High boiling con-

stituents left with xylene in the residue of the azeotropic distillation may be separated from the xylene by a fractional distillation of this residue either before or after the chlorination step of this process. I prefer, however, that the oil subjected to the azeotropic distillation be one containing but small amounts of lower boiling materials. The presence of large amounts of these materials involves the use of larger quantities of azeotropic agent to accomplish the separation of like-boiling, non-aromatic hydrocarbons from the xylene and increases the burden upon the equipment employed for this distillation.

For the azeotropic distillation of the ortho-xylene fraction I prefer to employ methanol as the azeotropic agent. My invention is not limited, however, to the use of particular azeotropic agents. Any material known to form azeotropes with non-aromatic hydrocarbons boiling from the oil fraction in the same temperature range as the ortho-xylene boils therefrom may be employed. Among the numerous materials which may be used are the following: an aliphatic monohydroxy alcohol containing 1 to 5 carbon atoms to the molecule (methanol, ethanol, etc.); monomethyl ether of ethylene glycol, pyridine or allyl alcohol.

In the azeotropic distillation the ortho-xylene is left in the residue separate from like-boiling paraffins and naphthenes which are distilled over as azeotropes with the methanol or other agent used. A portion of the olefins is likewise carried over in the distillate. The residue of this distillation contains the ortho-xylene and like-boiling olefins. It may also contain a residual small amount of paraffins or naphthenes not completely separated from the oil by the azeotropic distillation.

The oil residue of the azeotropic distillation is then chlorinated, preferably by passing chlorine gas into the oil until the oil turns yellow. The change of color to yellow takes place rather suddenly as the chlorine is bubbled into the oil and is a good indication that sufficient chlorine has reacted with the oil for treatment by the next step of my process. Although I prefer to treat the oil with chlorine gas, other chlorinating materials may be employed such as chlorine water or other material which will yield free chlorine for combination with hydrocarbons present. I prefer to chlorinate the oil at ordinary room temperatures, although somewhat higher or lower temperatures may be employed. Excessively high temperatures should be avoided, however, since they may cause undesirable reactions of chlorine with the oil.

The chlorinated oil is subjected to fractional distillation. Hydrochloric acid present in the oil is neutralized with an alkali before subjecting the oil to fractional distillation. It is also preferred to have present in the fractional distillation an alkali, such as sodium carbonate, to neutralize any hydrochloric acid formed during the fractional distillation. In this distillation the fraction of the distillate containing the relatively pure aromatic hydrocarbon is collected separate from the forerunnings and higher boiling materials, the latter of which may be left as a residue of the distillation when the aromatic hydrocarbon has been taken over and collected separate from the lower boiling materials.

The following examples are illustrative of the use of my invention for the treatment of particular oil fractions to recover the aromatic hydrocarbon contained therein:

Example 1.—A particularly pure, acid-washed,

commercial ortho-xylene concentrate had the following characteristics:

Specific gravity at 15.5° C.	0.862
Melting point	-31° C.
Francis Bromine No.	0.119
Distillation range	

92% distilling at 143°-144.1° C.

This ortho-xylene fraction was obtained from drip oil by fractionally distilling the drip oil, taking off that fraction in which the ortho-xylene was concentrated and washing this fraction with concentrated sulfuric acid. This is a conventional procedure heretofore followed for the recovery of concentrated ortho-xylene products from drip oil.

This ortho-xylene fraction was mixed with methanol in the proportions of 400 volumes of methanol for every 100 volumes of the ortho-xylene fraction. The mixture was then subjected to a fractional distillation. In the presence of the methanol the non-aromatics of the xylene fraction were in large part selectively distilled over as azeotropes leaving behind a residue which, after washing with water, had the following characteristics:

Specific gravity at 15.5° C.	0.880
Melting point	-27° C.
Francis Bromine No.	0.104
Ortho-xylene	92-93% by weight
Distillation range	

87% distilling at 138.8-144.7° C.

Chlorine was bubbled through the residue of the azeotropic distillation until the residue turned yellow. The chlorinated residue was neutralized with a 10% caustic soda solution and the neutralized oil separated from the aqueous solution. This oil was then fractionally distilled in the presence of a small amount of sodium carbonate. Distillation started with the vapors at the top of the fractionation column in which the vapors were rectified at 136.4° C. When 20% of the oil had been distilled over and the temperature of the vapors at the top of the rectification column was at 144.3° C., the succeeding distillate was collected separately from the preceding forerunnings. The distillation was continued until 70% of the oil had been distilled over and the vapor temperature at the top of the rectification column was 144.4° C. Towards the end of the distillation of the chlorinated residue to take over this ortho-xylene fraction, some hydrochloric acid was formed and not neutralized by the sodium carbonate initially added to the material being distilled. The distillate coming over containing this hydrochloric acid was washed with caustic soda solution to remove this hydrochloric acid. The distillate collected as described, separate from forerunnings and higher boiling materials left as residue, was a substantially pure ortho-xylene with a melting point -25.5° to -25° C., a Bromine No. 0.003 and a refractive index (Na 20°) 1.5047-1.5048.

By fractionally distilling the above chlorinated distillate under a reduced pressure of 100 mm. Hg, a fraction with a melting point of substantially -25.5° C. and consisting of substantially pure ortho-xylene may be obtained. However, the yield and purity of the ortho-xylene product are not as satisfactory as when the distillation is carried out at substantially atmospheric pressure.

Example 2.—The oil fraction of Example 1 containing 80% to 83% ortho-xylene was first

chlorinated by bubbling chlorine through the oil fraction until it turned yellow. The chlorinated oil was neutralized with caustic soda solution and the neutralized oil fractionally distilled in the presence of sodium carbonate. Distillation started with the vapors at the top of the fractionation column used for rectifying the vapors at 143.8° C. A distillate representing 70% of the oil charged was collected, with the temperature of the vapors at the top of the fractionation column rising to 144.2° C. This distillate was mixed with twice its volume of methanol and the mixture fractionally distilled. Non-aromatic hydrocarbons were azeotropically distilled over with the methanol at temperatures of about 64.2° C. to 64.6° C. The temperature then rapidly rose to 144° C. The residue left from this fractional distillation, after washing with water, had a melting point of -25.75° C. and an n_D^{20} of 1.5041. It represented a relatively pure ortho-xylene product as compared with the commercial products heretofore marketed as nitration grade ortho-xylene, although it was less pure than the product obtained employing the process of Example 1 above.

Example 3.—300 volumes of a closely fractionated drip oil distillate containing about 79% ortho-xylene, were mixed with 1200 volumes of methanol and the mixture fractionally distilled through a fractionating column. When the vapor temperature at the top of the column reached 140° C. the distillation was stopped. The residue was treated with chlorine gas until it turned yellow. Chlorination of the oil residue was checked by determining the Bromine No. of the chlorinated oil. With the Bromine No. 0.003 or less (grams of bromine absorbed per gram of oil), the chlorination was sufficiently complete for the subsequent steps of the process.

The chlorinated oil was washed with a 20% caustic soda solution to neutralize it and the washed oil was fractionally distilled in the presence of a small amount of sodium carbonate. Distillation started with the vapors at the top of the fractionation column at 144.0° C. The vapor temperature gradually rose to 144.2° C. The melting point of the initial distillate was -27.2° C. and as the distillation progressed the melting point of the distillate rose to -25.3° C., leaving a residue with a melting point below -30° C. By collecting separately from the forerunnings those cuts with melting points of -25.5° C. to -25.3° C., a substantially pure ortho-xylene product was obtained.

As an explanation of the reason for the above described process serving to recover the aromatic hydrocarbon separate from like-boiling, non-aromatic hydrocarbons, the following is offered. By the azeotropic distillation like-boiling paraffins and naphthenes are largely separated from the aromatic hydrocarbon, together with a portion of the like-boiling olefins. In chlorinating the oil, free chlorine reacts preferentially with the olefins to form therewith addition products. By this chlorination the distillation temperatures of the several constituents of the oil relative to one another, including the relative distillation temperatures of the aromatic hydrocarbon and small amounts of paraffinic and naphthenic hydrocarbons which may be present, are so altered that upon fractional distillation of the chlorinated oil the aromatic hydrocarbon may be taken over in a fraction, separate from forerunnings and higher boiling materials, which is substantially free from materials other than the aromatic hydrocarbon.

The herein described process for the recovery of ortho-xylene products from oils containing ortho-xylene together with like-boiling olefins and other like-boiling, non-aromatic hydrocarbons is particularly important because heretofore no economical method has been known for the recovery of pure ortho-xylene from such oils. While pure toluene and benzene may be obtained from certain drip oil fractions by washing the oil with concentrated sulfuric acid and fractionally distilling the washed material, this process is not satisfactory when applied to the recovery of ortho-xylene from drip oil concentrates. The recovery of ortho-xylene from drip oil presents a unique problem and this specific application of my invention is of particular importance because it provides an economical method for the recovery of the ortho-xylene.

The term "olefins" is used in this specification and in the appended claims in a broad sense to include unsaturated hydrocarbons having one double bond in the molecule or having a higher degree of unsaturation, e. g. diolefins.

I claim:

1. The process for the recovery of ortho-xylene from a sulfuric acid-washed oil containing the same and containing like-boiling olefins and other like-boiling, non-aromatic hydrocarbons formed by the high temperature decomposition of petroleum oil, which comprises subjecting said acid-washed oil to a series of three treatments comprising an azeotropic fractional distillation whereby like-boiling, non-aromatic hydrocarbons are selectively removed from a residue containing said aromatic hydrocarbon, a chlorination treatment whereby olefins are converted into chlorinated hydrocarbons, and a non-azeotropic fractional distillation of the chlorinated material, and in that fractional distillation to which the oil is last subjected in carrying out the aforedescribed series of steps, recovering an ortho-xylene having a melting point above -25.8° C. substantially completely separated from the non-aromatic hydrocarbons in said acid-washed oil.

2. The process for the recovery of ortho-xylene from a sulfuric acid-washed drip oil fraction containing the same together with like-boiling, non-aromatic hydrocarbons including like-boiling olefins, which comprises subjecting said oil to a series of three treatments comprising an azeotropic fractional distillation whereby like-boiling, non-aromatic hydrocarbons are selectively removed from a residue containing ortho-xylene, a chlorination treatment whereby olefins are converted into chlorinated hydrocarbons, and a non-azeotropic fractional distillation of the chlorinated material, and in that fractional distillation to which the oil is last subjected in carrying out the aforedescribed series of steps recovering an ortho-xylene having a melting point above -25.8° C. substantially completely separated from the non-aromatic hydrocarbons in said acid-washed oil.

3. The process for the recovery of ortho-xylene from a sulfuric acid-washed drip oil fraction containing ortho-xylene and like-boiling, non-aromatic hydrocarbons, including like-boiling olefins, which comprises first azeotropically distilling said drip oil fraction in the presence of a material which forms low boiling azeotropes with non-aromatic hydrocarbons present in the oil and thereby selectively separating from said ortho-xylene like-boiling, non-aromatic hydrocarbons present in said oil, including a portion of the like-boiling olefins, as a distillate leaving

a residue containing ortho-xylene and like-boiling olefins, chlorinating said residue, fractionally distilling the chlorinated residue and collecting as distillate a fraction having a melting point no lower than -25.5°C . which substantially consists of ortho-xylene separate from forerunnings and the higher boiling materials present in the chlorinated oil residue subjected to the fractional distillation.

4. The process for the recovery of ortho-xylene from a sulfuric acid-washed drip oil fraction containing ortho-xylene and like-boiling, non-aromatic hydrocarbons, including like-boiling olefins, which comprises first azeotropically distilling said drip oil fraction in the presence of methanol and thereby selectively separating from said ortho-xylene like-boiling, non-aromatic hydrocarbons present in said oil, including a portion of the like-boiling olefins, as a distillate leaving an oil residue containing ortho-xylene and like-boiling olefins, treating said oil residue with gaseous chlorine until the oil residue develops a yellow color, fractionally distilling the chlorinated oil residue and collecting as distillate a fraction having a melting point no lower

than -25.5°C . which substantially consists of ortho-xylene separate from forerunnings and the higher boiling materials present in the chlorinated oil residue subjected to the fractional distillation.

5. The process for the recovery of ortho-xylene from a sulfuric acid-washed oil containing the same and containing like-boiling olefins and other like-boiling, non-aromatic hydrocarbons, which comprises subjecting said acid-washed oil to a series of three treatments comprising an azeotropic fractional distillation whereby like-boiling, non-aromatic hydrocarbons are selectively removed from a residue containing said aromatic hydrocarbon, a chlorination treatment whereby olefins are converted into chlorinated hydrocarbons, and a non-azeotropic fractional distillation of the chlorinated material, and in that fractional distillation to which the oil is last subjected in carrying out the aforescribed series of steps, recovering an ortho-xylene having a melting point above -25.8°C . substantially completely separated from non-aromatics in the oil subjected to this distillation.

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