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REMOVAL OF THIOPHENES FROM AROMATIC HYDROCARBONS

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This invention relates to the desulfurization of hydrocarbon oils and is more particularly concerned with the removal of thiophenes and like cyclic sulfur compounds from hydrocarbon oils rich in aromatic hydrocarbons.

In the manufacture of industrial chemicals or chemical products from hydrocarbon oils, particularly oils of petroleum and coal-tar origin, the elimination of thiophenes and similar cyclic sulfur compounds which may be present as impurities, is a serious practical problem often encountered. Coal tar invariably contains sulfur compounds of this type and they are very frequently found in petroleum oils now commercially processed. Ever increasing proportions of petroleum crude oils of high sulfur content are finding their way into commercial channels and when these oils are used as a source of industrial chemicals, particularly aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, the xylenes, and other benzene homologs, the problem of removing cyclic sulfur compounds requires increasing consideration. It is desired to remove these cyclic sulfur compounds because of their odor, because of the corrosive products formed upon their degradation, because they act as severe poisons in many catalytic reactions, e. g., hydrogenation, or because of other considerations which arise by reason of the particular use to which the oils contaminated by the sulfur bodies are put.

This problem has been recognized for many years, particularly in the coal-tar industry, and many processes have been proposed for removing the undesired sulfur compounds. In some cases they are removed in part by fractional distillation. In many cases, however, the thiophenic compounds have boiling points so close to the boiling points of the aromatic hydrocarbons that they cannot be effectively removed by commercial fractional distillation procedures. For example, benzene, toluene, ethylbenzene, para-xylene, meta-xylene and ortho-xylene have boiling points, respectively, of 80.1, 110.8, 136, 138, 138.8 and 144° C., and thiophene, 2-methylthiophene, 3-ethylthiophene, 2,3-dimethylthiophene, 2,5-dimethylthiophene and 2,4-dimethylthiophene have boiling points, respectively, of 84, 113, 135–6, 136–7, 137–5 and 138° C. It will thus be seen that for each of the aromatic hydrocarbons there is a close-boiling thiophene.

Since thiophenes cannot be removed with sufficient effectiveness from aromatic hydrocarbons by ordinary fractional distillation, resort has been had to processes involving treatment with various reagents. The thiophenes are, however, relatively inert, and these methods are generally complex and costly, in many cases involving the loss of a substantial proportion of the aromatic hydrocarbons. For example, it has been proposed to treat the material contaminated by cyclic sulfur compounds with strong sulfuric acid, in an effort to effect selective sulfonation of the sulfur compounds, followed by fractional distillation to separate the sulfonated portion of the material from the non-sulfonated portion. Under the conditions of treatment, some sulfonation of

the aromatic compounds invariably occurs with resultant loss of the aromatic compounds. Because of the obvious deficiencies of this process, other processes involving chemical treatment have been proposed and have been used commercially to some extent. These processes call for treatment with aluminum chloride, or chlorination with gaseous or liquid chlorine, followed by distillation. In some cases, resort is even had to fractional crystallization.

In view of the complexity and high cost of the above types of sulfur-removal procedures, it is generally acknowledged that an important practical and economic problem still exists in this field.

It is a principal object of the present invention to provide an improved process for removing cyclic sulfur compounds from hydrocarbon oils rich in aromatic hydrocarbons and containing such sulfur compounds as contaminants.

It is another important object of the invention to provide a process of the character indicated which is efficient in operation and avoids the undesired destruction or conversion of the aromatic hydrocarbons.

It is a further object to provide a continuous process for desulfurizing hydrocarbon oils containing a high proportiton of aromatic hydrocarbons.

It is another object of the invention to provide a process for removing thiophenes and like cyclic sulfur compounds from oils derived from petroleum and coal tar and containing a predominant proportion of aromatic hydrocarbons.

It is a still further object to provide a desulfurizing process of the type described which avoids the drawbacks and deficiences of heretofore-proposed processes.

It is a feature of the invention that a hydrocarbon oil rich in aromatic hydrocarbons is treated at an elevated temperature and at a predetermined hydrogen partial pressure in the presence of a material having catalytic activity such that the objectionable cyclic sulfur bodies are converted into readily-separable forms, e. g., into hydrogen sulfide and gases such as butylene and butane, without adverse effect upon the aromatic hydrocarbons present. The process of the invention is effective to substantially eliminate the undesired sulfur bodies while permitting recovery of high yields of desulfurized aromatic hydrocarbons, even when the content of such sulfur bodies is very high, e. g., over 3% by volume.

In accordance with the inventiton, the aromatic hydrocarbon oil to be treated for removal of thiophenes and like cyclic sulfur compounds is introduced, together with hydrogen, into a treating zone maintained at a temperature of 900 to 1300° F., preferably at a temperature of 925 to 1200° F., in contact with particulate material of the character hereinbelow described. The total pressure in the treating zone and the introduction of hydrogen and hydrocarbon oil are controlled in known manner to provide a hydrogen partial pressure of 100 to 750 p. s. i. (pounds per square inch), preferably 150 to 600 p. s. i. The total pressure of the system may vary over a relatively wide range, generally not exceeding 3000 p. s. i. g. (pounds per square inch gage) and preferably not exceeding 1000 p. s. i. g.

The term "aromatic hydrocarbon oil" as used herein is intended to include individual aromatic hydrocarbons, e. g., benzene, toluene, and other benzene homologs, as well as mixtures of one or more of these aromatic compounds with other hydrocarbons and related compounds as found in fractions derived from petroleum, petroleum conversion products, coal tar, water-gas tar, and the like sources of aromatic hydrocarbons. The process of the invention is particularly valuable in the treatment of hydrocarbon oils which are predominantly aromatic in nature, especially such oils which comprise at least 80%

by volume of armoatic hydrocarbons and aromatic hydrocarbons in substantially pure form, except for the presence of cyclic sulfur bodies. The process of the invention is particularly suitable for the removal of cyclic sulfur bodies from commercial aromatic hydrocarbon fractions such as those known as "1° benzene," "2° benzene," "90% benzene," "2° toluene," "solvent naphtha," and the like.

The particulate contact material employed in the treating zone in an alumina of high surface area, viz., a surface area of at least about 100 square meters per gram, preferably at least 125 square meters per gram, as measured by low-temperature nitrogen adsorption. The alumina of high surface area employed in accordance with this invention comprises bauxite, activated alumina, and preparations of high surface area derived from alumina gels.

Bauxite is a well known, native aluminum oxide in hydrated form, often containing iron. In commercial practice, bauxite is ground to the desired particle size and dehydrated by heat treatment, the bauxite then being said to be "activated." This heat treatment is carried out at temperatures within a wide range, generally 600 to 1400° F. Activation of bauxite sometimes includes one or more additional processing steps like acid washing, and mechanical or magnetic separation of admixed minerals. While activated bauxite is a preferred contact material for the process of this invention, it is possible to charge ordinary bauxite into the reaction zone because at reaction temperatures of 900 to 1300° F. and at even higher regeneration temperatures the bauxite will undergo dehydration and, thus, become activated. Commercially available activated bauxite, such as is sold under trade names like "Porocel" and "Cyclocel," is a preferred catalyst for the purposes of this invention.

Activated alumina is a commercial product well known in the petroleum treating art and is described, for example, in "Chemical Engineers' Handbook" (John H. Perry, ed.), third edition (1950), page 905. Alumina gels prepared by precipitation of aluminum hydroxide from an aqueous solution of a soluble salt such as the nitrate, followed by filtration, washing, drying and calcining of the precipitate by conventional procedures are also suitable contact materials for the process of this invention.

While substantially pure hydrogen is advantageously used, a gas mixture containing hydrogen and inert gases, such as nitrogen or methane, may be employed with efficacy. In the latter case it is preferable to use a gas mixture having at least about 30% by volume of hydrogen in order to avoid the necessity of passing excessively large amounts of gas through the reaction zone to provide the desired hydrogen partial pressure of 100 to 750 p. s. i. and in order to avoid the necessity of raising the total pressure of the system to a high value.

The hydrocarbon-oil treating process of the invention is suitably carried out in conventional oil treating apparatus wherein an oil is introduced into a reaction zone in contact with a catalyst. The apparatus shown in the copending application of Percival C. Keith, Serial No. 139,758, filed January 20, 1950, now U. S. Patent 2,606,862, is advantageously used, although it is generally preferred to carry out the process in a fluidized bed such as is used commercially in the catalytic cracking of hydrocarbon oils, the hydrogen or hydrogen-containing gas being advantageously employed as the fluidizing medium. The contact material is continuously or intermittently withdrawn from the treating zone and regenerated in any convenient manner, as by treating it at elevated temperature with oxygen or air and, if desired, other gaseous materials such as steam.

The particular apparatus used for the process and the particular method of regenerating the catalyst form no part of the present invention and any convenient apparatus and method of catalyst regeneration may be employed. In regenerating the catalyst care must be taken, however, in accordance with commercial regeneration techniques, to avoid the use of temperatures which destroy or adversely affect the catalyst. In the regeneration of the catalyst of the present process, temperatures in excess of 1400° F. are generally to be avoided.

In order to facilitate the maintenance of the desired temperature in the reaction zone, the hydrocarbon oil to be treated is advantageously preheated to a temperature of 400 to 1000° F., preferably about 500 to 800° F., before being fed into the reaction zone. The hydrogen or hydrogen-containing gas may also be preheated to about the same temperature as the hydrocarbon oil.

Treatment of the hydrocarbon oil in the reaction zone under the specified conditions is carried out to an extent sufficient to reduce the sulfur content of the oil to the desired degree. Advantageously, the desired reaction is insured by employing a hydrocarbon oil feed rate in the range of 0.2 to 3, preferably not higher than about 1, volumes of liquid per hour per volume of catalyst, while employing a hydrogen flow rate of 500 to 2500 standard cubic feet (calculated as pure hydrogen) per barrel of aromatic hydrocarbon oil fed.

The effluent from the treating zone will contain vapors of the aromatic hydrocarbons and other hydrocarbons in the oil charged, admixed with more volatile compounds such as hydrogen sulfide and hydrocarbon gases formed by the breakdown of thiophenes and like refractory sulfur compounds in the reaction zone, and a small amount of catalyst which may sometimes be carried out of the reaction zone by the gases. The effluent is condensed and distilled to separate the desired desulfurized hydrocarbon oil.

The desulfurized aromatic hydrocarbon oil thus produced has had its content of thiophene or other cyclic sulfur bodies substantially eliminated or reduced to the desired degree without adverse effect upon the aromatic hydrocarbons present, which are recovered from the reaction in very high yield. The process of the invention may be effectively used to produce so-called "thiophene-free benzene" from benzene-rich hydrocarbon oil fractions derived from coal-tar and to effectively remove substantially all of the sulfur bodies, even when present to the extent of 5% by volume and more, from all types of aromatic hydrocarbon-containing oils.

For a further understanding of the invention, reference is now made to the following illustrative example.

A so-called 1° benzene, i. e., a benzene fraction boiling entirely within 1° C., including the boiling point of benzene, is mixed with a quantity of thiophene sufficient to provide a fraction comprising 95.1% by weight of benzene and 4.9% by weight of thiophene, corresponding to 1.87% by weight of sulfur. This is a greater proportion of thiophene than is normally found in commercial benzene fractions and has been selected to highlight the efficacy of the process. The thus prepared benzene fraction is preheated to a temperature of 600° F. and discharged into a reaction zone containing fluidized particles of activated alumina and maintained at a temperature of 975° F. The gaseous treating atmosphere is provided and the fluidization of the catalyst particles is effected simultaneously by introducing a stream of hydrogen into the bottom of the reaction zone. A portion of the fluidized catalyst is continuously returned to the reaction zone. The preheated benzene fraction is introduced at a rate to provide a space velocity in the reaction zone of 1 volume of liquid per hour per volume of catalyst in the reaction zone. The total pressure in the reaction zone is 210 p. s. i. g. and the hydrogen partial pressure is maintained at 175 p. s. i. The effluent is condensed to separate the benzene (over 98% by volume recovery) from the more volatile constituents and upon analysis for sulfur is found to contain only 0.16% sulfur by weight. Examination of the more volatile products formed in the reaction zone shows them to comprise

hydrogen sulfide and a mixture of hydrocarbon gases predominantly butylene and butane.

The foregoing example involved a relatively low temperature and low hydrogen partial pressure to show how readily thiophenic sulfur is eliminated under even the milder conditions specified by this invention. Obviously, a greater reduction in thiophene contact, and in fact substantially complete elimination of the sulfur initially present in the hydrocarbon oil, results at the higher and more favorable levels of hydrogen partial pressure and and temperature, within the specified ranges.

In similar manner, other aromatic hydrocarbon oils are desulfurized when treated in accordance with the invention and like results are obtained when other aluminas of high surface area are substituted for the activated alumina used in the above example. Thus, a like reduction in sulfur is effected when another portion of the same benzene-thiophene fraction is treated under essentially the same conditions in the presence of activated bauxite. It has been found that the process of the invention is effective to desulfurize hydrocarbon oils containing all types of aromatic hydrocarbons, and when, for example, the procedural steps set forth in the above example are repeated using a hydrocarbon fraction rich in toluene or the xylenes similar substantial reductions in sulfur content are realized.

In view of the various modifications of the invention which will occur to those skilled in the art upon consideration of the foregoing disclosure without departing from the spirit or scope thereof, only such limitations should be imposed as are indicated by the appended claims.

What is claimed is:

1. A process of desulfurizing an aromatic hydrocarbon oil, which comprises bringing hydrogen and an aromatic hydrocarbon oil containing cyclic sulfur compounds into contact with an alumina of high surface area and free of added catalysts and promoters in a reaction zone maintained at a temperature in the range of 900 to 1300° F., the contact of said hydrogen and said aromatic oil resulting in a net consumption of hydrogen, passing said aromatic oil through the reaction zone at a space velocity in the range of about 0.2 to 3 liquid volumes per hour per volume of said alumina, maintaining the partial pressure of hydrogen in said reaction zone in the range of 100 to 750 p. s. i., and recovering from the resulting reaction effluent said aromatic oil with a substantially reduced sulfur content.

2. A process as defined in claim 1 wherein said temperature is between 925 and 1200° F.

3. A process as defined in claim 1 wherein the space velocity of said aromatic oil in said reaction zone is in the range of 0.2 to 1 volume of liquid per hour per volume of said alumina.

4. A process of desulfurizing an aromatic hydrocarbon oil, which comprises bringing hydrogen and an aromatic hydrocarbon oil containing at least about 1% by volume of cyclic sulfur compounds and at least about 80% by volume of aromatic hydrocarbons into contact with an alumina of high surface area and free of added catalysts and promoters in a reaction zone maintained at a temperature in the range of 900 to 1300° F., the contact of said hydrogen and said aromatic oil resulting in a net consumption of hydrogen, passing said aromatic oil through the reaction zone at a space velocity in the range of about 0.2 to 3 liquid volumes per hour per volume of said alumina, maintaining the partial pressure of hydrogen in said reaction zone in the range of 100 to 750 p. s. i., and recovering from the resulting reaction effluent an aromatic hydrocarbon oil containing substantially less than 1% by volume of cyclic sulfur compounds and at least about 80% by volume of aromatic hydrocarbons.

5. A process of desulfurizing an aromatic hydrocarbon oil, which comprises bringing hydrogen and an aromatic hydrocarbon oil containing a troublesome amount of cyclic sulfur compounds into contact with an alumina of high surface area and free of added catalysts and promoters in a reaction zone maintained at a temperature in the range of 900 to 1300° F., the contact of said hydrogen and said aromatic oil resulting in a net consumption of hydrogen, passing said aromatic oil through the reaction zone at a space velocity in the range of about 0.2 to 3 liquid volumes per hour per volume of said alumina, maintaining the partial pressure of hydrogen in said reaction zone in the range of 100 to 750 p. s. i., and recovering from the resulting reaction effluent said aromatic oil containing not more than a minor portion of said cyclic sulfur compounds.

6. A process as defined in claim 5 wherein said aromatic oil is substantially wholly benzene.

7. A process as defined in claim 5 wherein said aromatic oil is substantially wholly toluene.

8. A process as defined in claim 5 wherein said partial pressure of hydrogen is between 150 and 600 p. s. i.

9. A process of preparing thiophene-free benzene, which comprises bringing hydrogen and benzene containing thiophene but essentially free of other hydrocarbons into contact with activated alumina free of added catalysts and promoters in a reaction zone maintained at a temperature in the range of 925 to 1200° F., the contact of said hydrogen and said benzene resulting in a net consumption of hydrogen, passing said benzene through the reaction zone at a space velocity in the range of about 0.2 to 3 liquids volumes per hour per volume of said alumina, maintaining the partial pressure of hydrogen in said reaction zone in the range of 150 to 600 p. s. i., and recovering from the resulting reaction effluent said benzene substantially free of said thiophene.

10. A process as defined in claim 4 wherein the space velocity of said aromatic oil in said reaction zone is in the range of 0.2 to 1 volume of liquid per hour per volume of said alumina.

References Cited in the file of this patent

UNITED STATES PATENTS

1,955,297	Jennings	Apr. 17, 1934
2,315,506	Danner et al.	Apr. 6, 1943
2,340,922	Bent et al.	Feb. 8, 1944
2,345,575	Burk et al.	Apr. 4, 1944
2,371,298	Hudson et al.	Mar. 13, 1945
2,419,029	Oberfell	Apr. 15, 1947
2,498,559	Layng et al.	Feb. 21, 1950
2,500,146	Fleck et al.	Mar. 14, 1950
2,516,877	Horne et al.	Aug. 1, 1950
2,574,448	Docksey et al.	Nov. 6, 1951