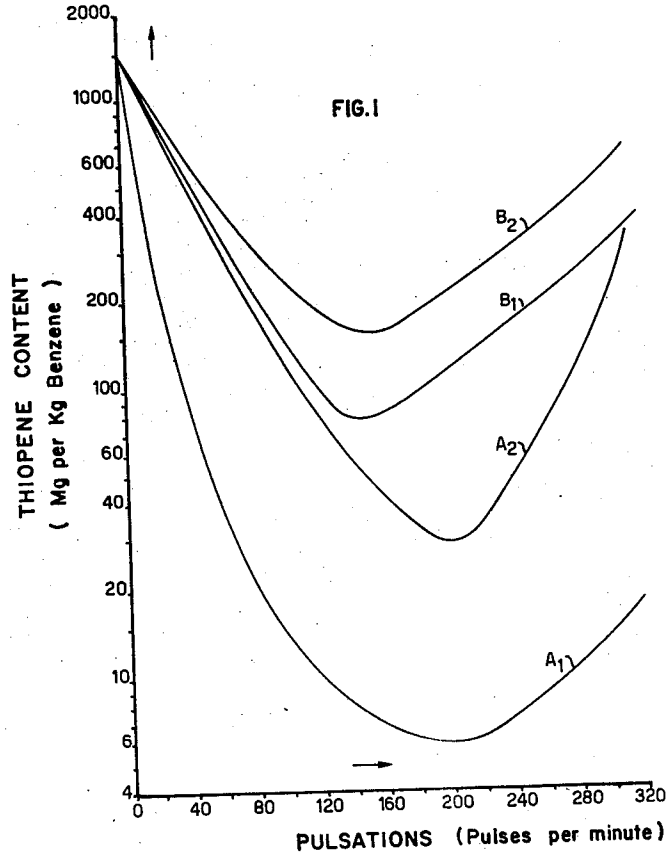
Aug. 9, 1960 A. P. OELE ET AL 2,948,764

PROCESS FOR REDUCING THE QUANTITY OF THIOPHENES IN AN AROMATIC HYDROCARBON

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FIG. 1



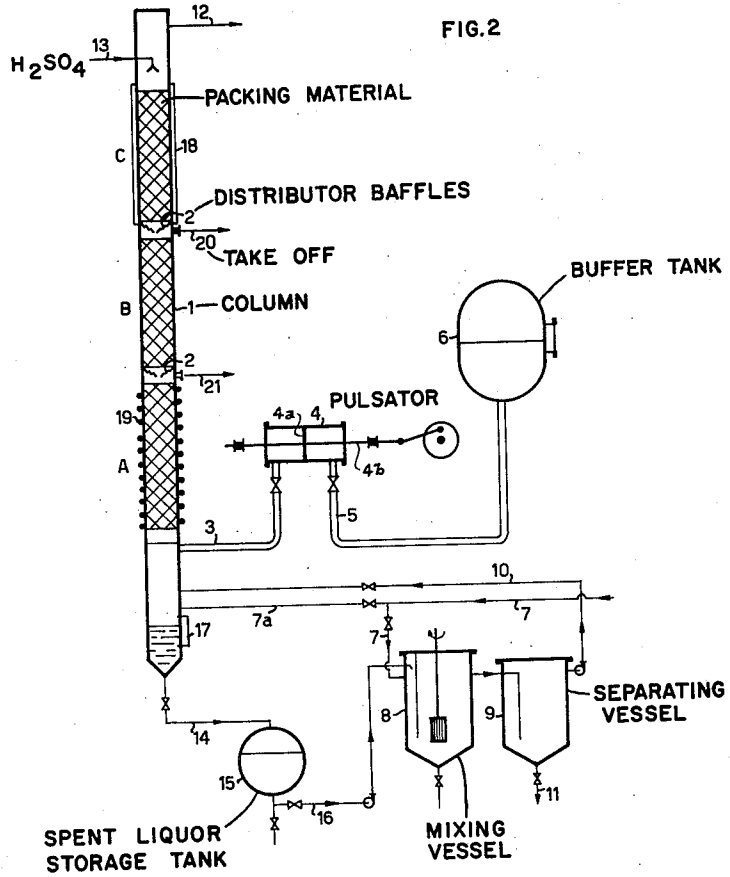
ADRIAAN P. OELE,
MATHIAS J.G. MUYTJENS and
JOHAN R. H. CORIS
BY: Cushman, Darby & Cushman
ATTORNEYS

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FIG.2



ADRIAAN P. OELE,
MATHIAS J.G. MUYTJENS, and
JOHAN R. H. GORIS

BY: Cushman, Darby & Cushman
ATTORNEYS

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2,948,764

PROCESS FOR REDUCING THE QUANTITY OF THIOPHENES IN AN AROMATIC HYDROCARBON

Adriaan P. Oele, Mathias J. G. Muytjens, and Johan R. H. Goris, all of Geleen, Netherlands, assignors to Stamicarbon N.V., Heerlen, Netherlands

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7 Claims. (Cl. 260—674)

This invention relates to the treatment of aromatic hydrocarbons with sulphuric acid for the removal of thiophenes.

Crude benzene and benzene homologues may be obtained by washing coke oven gas with a tar oil and subsequently steam distilling the tar oil to free the same from the mixture of aromatic hydrocarbons absorbed by the oil in the washing step. The absorbed mixture of hydocarbons mainly consists of benzene, toluene and xylene, but also contains various other substances such as cyclopentadiene. A further purification of the mixture of aromatic hydrocarbons is effected by rectification whereby, in addition to cyclopentadiene obtained in the first runnings, fractions consisting of benzene, toluene and xylene are obtained.

The abovementioned fractions containing benzene and/or its homologues are so strongly contaminated with undesirable impurities that they are unsuitable for many purposes, e.g., for use as motor fuel. Along with unsaturated compounds, which tend to cause gumming and discoloration, these fractions contain orgganic sulphur compounds, such as thiophene and methyl thiopene.

It is customary to remove the unsaturated compounds by treating the impure benzene, toluene and/or xylene with more or less concentrated sulphuric acid, e.g., 80–96% sulphuric acid by weight. This treatment, which may be carried out either discontinuously in stirring vessels, or continuously, e.g. in a packed column in which the impure aromatic hydrocarbons and the sulphuric acid are contacted while flowing in counter-current relation, results in the conversion of the unsaturated impurities into products of higher molecular weight. These high molecular weight products form, together with the sulphuric acid, a so-called acid tar which may be separated from the benzene and its homologues. The thus purified benzene and benzene homologues are then subjected to washing with caustic soda and again distilled.

The above described treatment with sulphuric acid leaves much to be desired in the way of simplicity of operations, cost, reduction of thiophene content and the like. Accordingly, the principal object of the present invention is to provide novel improvements in the continuous-type of process referred to above whereby the quantity of thiophenes in aromatic hydrocarbons may be effectively reduced by treating the same with sulphuric acid. Other objects will also be apparent from the following description of the invention.

Broadly stated, the improved process of the present invention comprises passing the sulphuric acid and the hydrocarbon liquid continuously and in countercurrent through a vertical column filled with packing bodies, the hydrocarbon liquid being passed upwardly through the column, and pulsating the liquids during their passage through the column.

The extent to which the thiophene content of a hydrocarbon is reduced by countercurrent treatment with sulphuric acid depends on various factors including the

strength of the sulphuric acid and the quantities of hydrocarbon and sulphuric acid passing in contact per unit time. However, other things being equal, the step of imparting pulsations to the liquid, according to the present invention, has been found to lead to a significant improvement in the thiophene removal. Moreover with appropriate choice of the acid strength and other treatment conditions, including the frequency of the pulsations and the ratio of hydrocarbon to sulphuric acid flowing in countercurrent contact, the thiophene content can be reduced to a greater extent with the present invention than is possible when carrying out the acid treatment in accordance with the known techniques described above. Thus, for example, by a continuous process according to the present invention, it is possible to reduce the thiophene content of benzene containing as much as 6500 mg. of thiophene per kg. of benzene, to below 13 mg. per kg. of benzene, using sulphuric acid with a concentration of 95% by weight. Hitherto it has only been possible to reduce the thiophene content of benzene or benzene homologues to an equivalent extent by treating the hydrocarbon discontinuously in stages, e.g., in two stages, with sulphuric acid, using very highly concentrated sulphuric acid having a strength of 99.5% by weight, in each stage. Discontinuous processes are laborious and cumbersome, particularly if large quantities of hydrocarbon are to be treated. Furthermore, apparatus for such discontinuous operations takes up a considerable amount of space and it is also essential to use a large quantity of energy to disperse the sulphuric acid in the material to be purified. Batch treatment is also relatively costly in sulphuric acid, as acid of the same strength must be used in each stage. Another disadvantage of the prior procedure is that an appreciable amount of benzene is sulphonated and thus lost.

In order to prevent fouling of the packing bodies in the column when operating according to the present invention, the aromatic hydrocarbon may be subjected to a pre-purification in a preceding stage in the form of a treatment with sulphuric acid, the acid being dispersed in the hydrocarbon by mechanical means. Whether it is advantageous to carry out such a pre-purification depends on the nature of the impurity and the degree to which the hydrocarbon to be purified is contaminated. If, for example, the hydrocarbon contains about 1 gram of cyclopentadiene per kg., pre-purification is advisable since cyclopentadiene forms an acid tar which is insoluble in sulphuric acid.

The sulphuric acid used in the countercurrent washing of the present process preferably has a concentration of 95% by weight or more. If a pre-purification is performed, the sulphuric acid used for such pretreatment need not have as high a concentration as that supplied to the washing column. For example, an acid concentration of from 75–95% is sufficient for the pretreatment. Thus, acid previously used in the countercurrent washing column, combined if necessary with fresh acid make-up, may be effectively used as the pretreating acid.

The pulsation rate influences the degree to which thiophenes are removed and the results obtainable with a given pulsation depend in part on the dimensions of the column. In order to reduce the quantity of thiophenes to less than 13 mg. of thiophenes per kg. of hydrocarbon, using a washing column of normal commercial dimensions (e.g., 5–10 metres in height and approximately 0.25 to 2 metres in width or diameter), the liquids are preferably subjected during their passage through the column to a pulsation having a frequency of 100–300 pulses per minute.

It has previously been proposed to countercurrently contact benzene and sulphuric acid in a horizontal appa-

ratus, while imparting pulsations to the contents of the apparatus (British patent Specification No. 404,005). According to said British patent, the apparatus is divided into a series of compartments in such a way that separation between benzene and sulphuric acid takes place in a number of these compartments due to the difference in specific gravity, while in adjoining compartments, the sulphuric acid is mixed again with the benzene as a result of the pulsation. However, it is not possible to remove thiophenes from the hydrocarbon to any substantial degree by the process described in this patent. In other words, it is critical to the success of the present process that the countercurrent hydrocarbon acid contact take place in a packed vertical column with the hydrocarbon passing upwardly through a column. The vertical column used in the invention described herein may be packed with any conventional packing bodies, typically Raschig rings, Berl saddles, or the like.

To prevent or reduce the deposition of acid tar on the packing bodies, the use of glazed porcelain packing bodies is recommended. As these bodies are considerably more expensive than unglazed porcelain packing bodies, it is advantageous to fill only the bottom part of the column, i.e., about one-third of the column length, with glazed packing bodies. The remainder of the column can be filled with unglazed packing bodies since deposition of acid tar only occurs in the bottom part of the column. Acid tar deposition may also be reduced or avoided if packing bodies in the form of unglazed packing rings are employed, the rings in the bottom part of the column having a relatively large diameter. Thus, for example, it is suitable to use 1" rings in the bottom third of the column length and .6" rings in the remaining part of the column. The packing bodies may comprise some other material than porcelain, e.g., a metal or metal alloy not attacked by concentrated sulphuric acid and/or acid tar.

If after a certain period of use the packing bodies should show some fouling, they may be cleaned by simply stopping the supply of benzene and continuing the sulphuric acid supply and the pulsation. The packing bodies may alternatively be cleaned with water, steam or an alkaline solution. It is also advantageous to place in the column some re-distributors, e.g. baffles, pans or the like on which the acid descending in the form of drops or a film is collected and automatically re-distributed over the packing bodies. In this way, possibly detrimental wall effects and channelling may be counteracted.

Preferably the packing bodies used herein are of such construction that the free space in the packed column amounts to 50–96% of the space occupied by the packing bodies. It is also preferable to pass the benzene or benzene homologues to be purified through the washing column as a continuous phase, i.e., in the form of an uninterrupted film or current while the sulphuric acid is distributed over the packing bodies as a discontinuous phase. When operating in this fashion, the sulphuric acid film is partly divided into drops as a result of the pulsation.

It is also possible to have the benzene or homologue thereof dispersed in drops, rising as the discontinuous phase through the sulphuric acid with the latter forming the continuous phase. With benzene as the continuous phase, however, the stroke of the pulsation may be greater and in order to obtain thorough removal of thiophenes, it is advisable to use the largest possible liquid displacement per pulsation. While the liquid volume displaced by the pulsations is, for a given plunger area, dependent on pulsation frequency and the stroke of the plunger effecting the pulsation, there is a limit to the volumetric displacement, viz. that displacement at which the packing bodies begin to move, and this happens sooner if the continuous phase is formed by the sulphuric acid.

The graph constituting Figure 1 of the accompanying drawing shows the relationship between the degree of thiophene removal and the frequency of the pulsations. The influences of the amount of benzene or the like fed to the column and the volume displaced by the pulsations are also shown.

Referring more particularly to Figure 1, the curves shown therein all relate to the purification of benzene containing 6500 mg. of thiophene per kg. of benzene. The treatment was carried out with 4% by volume of 95% by weight sulphuric acid in a column having a diameter of 10 cm., filled to a length of 6.8 metres with ½" Berl saddles. No pre-purification was employed. The temperature in the column was maintained at 18° C. The benzene was fed upwardly through the column as a continuous phase while the acid was in the discontinuous phase.

As indicated, the thiophene content of the purified benzene is shown on the ordinate (logarithmic scale) while the abscissa shows the pulsation frequency in pulses per minute, the latter corresponding with the number of revolutions per minute of the crank shaft actuating the pulsator.

In the tests represented by curves A_1 and A_2, the volume displaced by the pulsations was 600 litres per hour with ¼ and ½ litre of benzene, respectively, being supplied per hour and per sq. cm. of the column section.

In the cases represented by curves B_1 and B_2, the same amounts of benzene as for A_1 and A_2, respectively, were supplied but the volume displaced by the pulsations was 300 litres per hour. It will be noted that the larger volume displacement effected a substantially greater thiophene removal and in each case the amount of thiophene removed was greatest in the frequency range 100 to 300 pulses per minute.

The temperature utilized for contacting the acid and hydrocarbon may be varied but should be kept below about 45° C., otherwise an undesirably large quantity of the hydrocarbon to be purified may be lost due to sulphonation. Usually, a temperature range of about 20 to about 40° C., is preferred.

The amount of benzene or the like fed to the washing column can be rather widely varied and depends upon such factors as the temperature utilized, the amount of acid and the like. Usually, the higher the temperature, the greater the amount of benzene fed to the column. Typically, at a temperature of about 40° C., and an acid supply of 4% by volume (based on the volume of benzene) of 95% by weight sulphuric acid, a desirable benzene supply may be 1.5 litres per sq. cm. of the column section. If a stronger sulphuric acid, for example, 99% by weight is used, the supply of benzene may in this case amount to 2.5 litres per hour and per sq. cm. of the column section. Normally, from 1 to 3 litres of benzene or the like per hour and per sq. cm. of column section can be treated according to the invention. The data tabulated in Figure 1 and the specific reaction conditions set forth above are based on the use of a column about 7 metres in length. If a longer column is used, the load may be increased accordingly and other operating conditions may also be varied for optimum results.

One way of carrying out the invention is diagrammatically shown in Figure 2. As shown therein, the numeral 1 represents a column which may have a typical length and diameter of about 10 metres and 50 cm., respectively. Three layers of packing bodies, e. g., ½" Raschig rings, are positioned within column 1, these layers being designated as A, B and C. Between adjacent layers are positioned re-distributors 2 in the form of baffles. Column 1 is connected through a conduit 3 with a pulsator 4, the latter being, in turn, joined by means of conduit 5 to a buffer tank 6 partly filled with benzene or a benzene homologue. Pulsator 4 may comprise a cylinder wherein a disc 4*a* is mounted for reciprocal movement on a shaft 4*b*. Like the buffer vessel 6, pulsator 4 and the conduits 3 and 5 are filled with benzene or a benzene homologue.

Fresh sulphuric acid is sprayed onto the upper layer C of packing bodies in the top part of column 1 by means of conduit 13. Spent sulphuric acid is discharged from

the bottom of the column through a conduit 14 to a tank 15. If necessary as, for example, in the case where the hydrocarbons to be purified have a high cyclopentadiene content, the spent sulphuric acid can be pumped from tank 15 through a conduit 16 into a mixing vessel 8 equipped with suitable stirring means. Benzene or benzene homologues may be supplied to mixing vessel 8 through conduit 7.

From mixing vessel 8, the mixture of acid and benzene and/or benzene homologues flows over into a separating vessel 9, in which the sulphuric acid, with the impurities it has taken up, settles. The top layer comprising the pre-purified hydrocarbon is pumped through conduit 10 into the bottom part of column 1. The hydrocarbon flows upward through the column as the continuous phase and is discharged through conduit 12 to a caustic soda washery (not shown) for removal of acid residue.

Column 1 is fitted with a level indicator 17, by means of which the position of the boundary layer between the hydrocarbon and the spent sulphuric acid collecting in the bottom part of the column is checked and controlled.

The upper part of column 1 is fitted with a jacket 18 through which either cooling water or hot water may be circulated. Cooling water is used when the benzene and/or benzene homologues to be purified are supplied to the column in small quantities or if very strong sulphuric acid (e.g., 99% sulphuric acid) is used. Under other circumstances, the reaction temperature in the column may be raised by passing hot water through the jacket if this is desired. An induction heating spiral 19 is provided about the outer wall of the column, near the bottom part thereof.

If the hydrocarbon to be purified contains only a small amount of substances forming acid tars, the hydrocarbon can be fed directly into the column through conduits 7 and 7*a* without being pre-purified. It is also possible simultaneously to discharge purified hydrocarbon from the top of the column through conduit 12 and a less thoroughly purified product through conduits 20 or 21.

By means of the system illustrated in Figure 2, it will be appreciated that impure aromatic hydrocarbons, such as the crude benzene, toluene and xylene fractions obtained by washing coal gas with tar oil, expelling the absorbed hydrocarbons out of the tar oil and rectifying the expelled mixture, can be thoroughly freed of thiophenes. Thus, for example, the thiophene content of a crude benzene fraction, 5000–9000 mg. thiophene per kg. of benzene, can be reduced to less than 13 mg. per kg. of benzene, and usually 1–5 mg./kg. of benzene, by a process involving the following conditions: pre-purifying the crude benzene with 1% by volume of fresh acid, or with the spent acid from the washing column; supplying the pretreated benzene to the column at the rate of 4 cu. m. per hour; using 3–4% by volume of 98–99% by weight sulphuric acid, calculated on the amount of benzene, a temperature of 30° in the column, a frequency of the pulsator crank shaft of 200 r.p.m., a volume displacement of 1.25 litres per stroke, measured in the empty column, the column being 500 mm., with the stroke in the empty column being about 6 mm.

Using the conditions outlined in the preceding paragraph, benzene loss amounted to only 1.5%. When the benzene load of the column was reduced to 2.5 $m.^3$ per hour and the sulphuric acid supply amounted to 4–5% by volume of 98.5–99.5% by weight sulphuric acid, the thiophene content fell to below 0.2 mg. of thiophene per kg. of benzene, while the benzene loss was 2%.

By applying a discharge at ⅔ of the column height via conduit 20 and another at ⅓ of the column height through a conduit 21, it is possible to recover simultaneously benzene containing about 11 mg. thiophene per kg., and benzene with about 500 mg. of thiophene per kg., respectively.

It will be appreciated that various modifications may be made in the invention described herein without deviating from the scope thereof as set forth in the following claims.

We claim:

1. A process for reducing the quantity of thiophenes in an aromatic hydrocarbon by treatment thereof with sulphuric acid having a concentration of at least 95%, said process comprising the steps of counter-currently and continuously passing said sulphuric acid and said hydrocarbon in the liquid state at a temperature between 20 and 45° C., through a packed vertical column containing solid packing material and having a free space therein amounting to from 50 to 96% of the space occupied by the packing, the hydrocarbon being passed upwardly through said column, and pulsating the liquids during their passage through said column, from 100–300 pulses being imparted to the liquids per minute.

2. A process according to claim 1 wherein the hydrocarbon liquid is pretreated prior to being passed into said column by mechanically mixing the same with sulphuric acid having a concentration between 75 and 95% and allowing the acid to settle out.

3. A process according to claim 2 wherein said pretreatment is carried out with acid discharged from said column.

4. A process according to claim 1 wherein the hydrocarbon is conducted through the column as a continuous phase, and the sulphuric acid as a discontinuous phase.

5. A process according to claim 1 wherein the bottom part of the column is filled with glazed packing bodies and the remainder of the column is filled with unglazed packing bodies.

6. A process according to claim 1 wherein the column has a length of about 7 metres, the hydrocarbon to be purified is passed through said column at the rate of 1.0–2.5 litres per sq. cm. of the column section; the consumption of sulphuric acid is 3–5% by volume calculated on the volume of the hydrocarbon; and the pulsation stroke calculated as for the empty column is about 6 mm.

7. A process according to claim 1 wherein a fraction of the hydrocarbon is discharged at an intermediate position along the column and another fraction is discharged at the top thereof.

References Cited in the file of this patent

UNITED STATES PATENTS

1,991,843	Campbell et al.	Feb. 19, 1935
2,396,144	Anderson et al.	Mar. 5, 1946

FOREIGN PATENTS

404,005	Great Britain	Jan. 1, 1934