

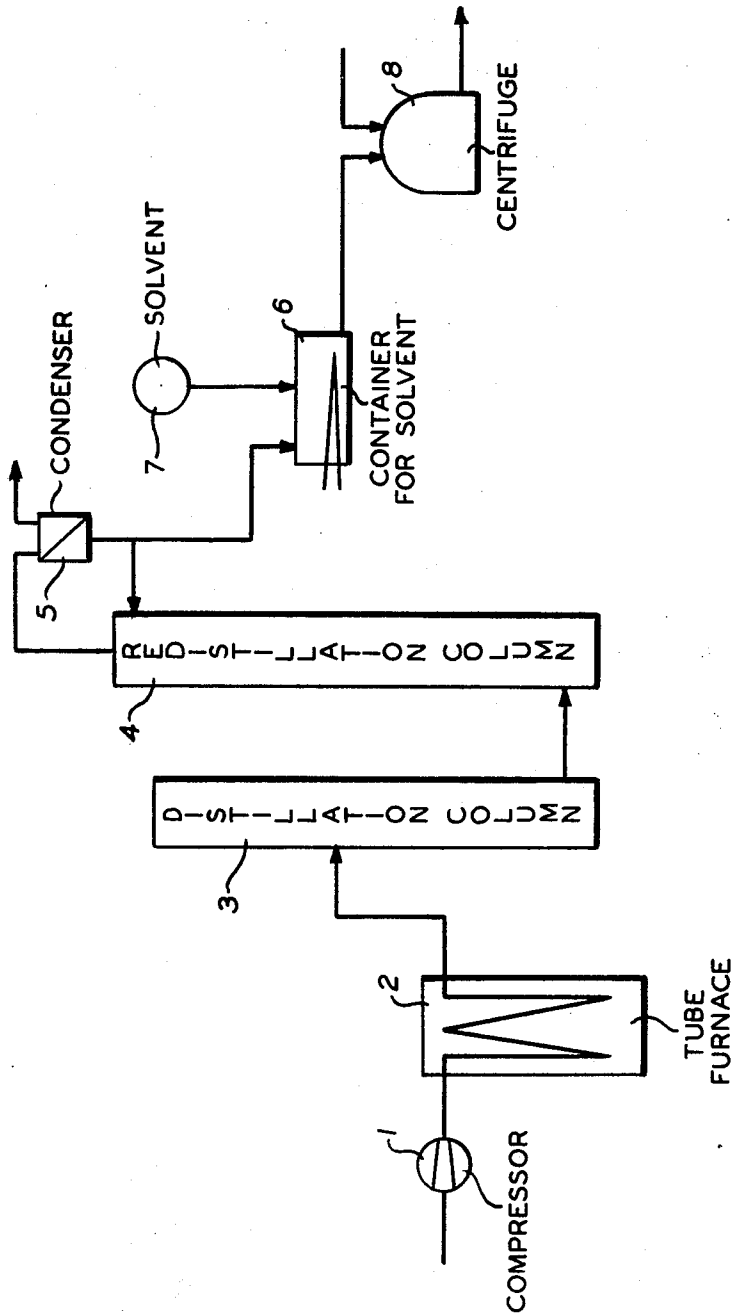
Nov. 28, 1972

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3,704,331

PROCESS FOR THE PRODUCTION OF ANTHRACENE

Filed Dec. 15, 1970



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PROCESS FOR THE PRODUCTION OF ANTHRACENE

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Filed Dec. 15, 1970, Ser. No. 98,426

Claims priority, application Germany, Jan. 7, 1970,

P 20 00 351.4

Int. Cl. C07c 15/28, 15/30

U.S. Cl. 260—675

5 Claims

ABSTRACT OF THE DISCLOSURE

Oils rich in aromatic substances or residues from the pyrolysis of gasoline or similar hydrocarbon mixtures are used for the production of anthracene through enrichment by distillation and recrystallization from an aryl-alkyl-ketone, preferably acetophenone.

This invention relates to a process for the production of anthracene from oils, which are rich in aromatic ingredients, or residues from the pyrolysis of gasoline or similar hydrocarbon mixtures through enrichment by distillation and recrystallization.

Anthracene is an economically important raw material for the production of anthraquinone-dyestuffs in the textile industry. It has been previously obtained practically exclusively from coal tar, which has an anthracene content of above 1%. Up to date, no processes for the recovery of anthracene from pyrolysis oils or pyrolysis residues of the ethylene-production and acetylene-production—which in general contain only 0.1 to 1% anthracene—have become known. However, such oils or residues are obtained in growing amount as the production of ethylene and acetylene continues to develop and they can, therefore, enlarge the raw material basis for anthracene in the future.

The main object of the present invention consists in recovering the anthracene from these starting materials of novel and unconventional composition in technically progressive and economical manner. This object is attained as follows.

The anthracene present in the starting material—i.e. in oils rich in aromatic compounds, or in residues from pyrolysis of gasoline, or in similar hydrocarbon mixtures—is first concentrated, in a manner known by itself, by distillation to a concentration of 1–4% of anthracene and subsequently further enriched redistillation and/or crystallization to 10 to 25%. Subsequently, the anthracene-fraction thus obtained may be recrystallized to any desired purity, from an aryl-alkyl-ketone.

Suitable starting materials for carrying out the present invention are, for example, oils rich in aromatic ingredients, or residues from gasoline pyrolysis to ethylene and/or acetylene, containing 0.1 to 1% anthracene. Thereby these raw materials are first preferably subjected to a brief treatment at increased temperature and under increased pressure, described in pending application Ser. No. 6,574, Herbert Buffleb et al., filed Jan. 28, 1970 in group 116.

According to a preferred embodiment of the invention the aryl-alkyl-ketone used for recrystallization is acetophenone, in a proportion of anthracene fraction (which may be enriched) to acetophenone of 1:1 up to 1:6.

The anthracene yield according to the present inven-

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tion is in the range of 80–90%, based on the anthracene fraction of 10–25%; about 80%, based on anthracene oil containing 2–4% and about 60% on the anthracene present in the crude pyrolysis oil or pyrolysis residue, which contains anthracene in a concentration of 0.1–1.0%. The product obtained according to the process of this invention contains 95–99% pure anthracene.

The solvents used according to this invention for recrystallizing the enriched anthracene i.e. the aryl-alkyl-ketones, particularly the acetophenone, have been found to be extraordinarily selectively effective. The German Pat. 389,878 describes cyclohexanone and its homologues, for the purification of crude anthracene. However, comparative experiments described in the present specification have clearly shown the considerable superiority of the aryl-alkyl-ketones over the cyclohexanone.

The following examples serve to illustrate the invention.

EXAMPLE 1

20 tons per hour of a residual oil which is rich in aromatic ingredients, obtained in the pyrolysis of gasoline to ethylene, and contains 0.8% anthracene, is passed under a pressure of 4–10 atmospheres through a tube furnace, and is heated in the furnace with a time of stay of 45 minutes to a final temperature of 380° C. It is subsequently allowed to expand into a distillation column operated at 100 torr at the sump of the column. As a lower side stream of the distillation column—in an amount of 15% calculated on the residual oil charged—anthracene oil containing 3.8% anthracene is drawn off.

This anthracene oil is redistilled in a column having about 30 calculated trays in the column with a return reflux ratio of 7:1 and at a vacuum of 20 torr at the head of the column. Thereby in an amount of 25%—calculated on the anthracene oil charged—an anthracene fraction containing 13.5% of anthracene is obtained.

50 parts by weight of this fraction are dissolved in 60 parts by weight of acetophenone at 120° C., the solution is allowed to cool off and the crystals are centrifuged at 20° C. The crude centrifuged material is washed with 20 parts by weight of acetophenone and dried. 6.4 parts by weight of anthracene containing 95.8% by weight of anthracene, according to Montecatini, are thus obtained.

The yield of anthracene amounts to 91% based on the anthracene fraction; based on the anthracene oil it amounts to 81% and about 60% based on the amount of anthracene present in the residual oil.

EXAMPLE 2

Anthracene oil obtained from a residual oil in the manner described in Example 1 and having an anthracene content of 2.4% anthracene is concentrated in a column described in Example 1 to an anthracene content of 7.7%. 580 parts by weight of this anthracene oil of 7.7% anthracene content are centrifuged at 20° C., whereby 200 parts by weight of centrifuged material having an anthracene content of 20.7% are obtained. This centrifuged material is recrystallized from acetophenone, in two steps, using for the first crystallization step the mother liquor of the second step. The 200 parts by weight are dissolved in 350 parts by weight of mother liquor of the second crystallization at 100° C., allowed to cool and centrifuged at 20° C. 75.4 parts by weight of moist (66.8 parts by weight of dry) centrifuged material having an anthracene content of 60.8% based on the dry centrifuged material. The 75.4 parts by weight moist centrifuged material are dissolved in 350 parts by weight of the acetophenone obtained in the first crystallization step obtained at 125° C., allowed to cool down and centrifuged at 20° C. After washing with 16 parts by weight xylene and drying, 35 parts by weight of anthracene having a content of 98.9% are obtained (UV-by spectroscopy).

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The yield of anthracene amounts of 83%, based on the anthracene present in the centrifuged material of 20.7% and 77%, based on the anthracene present in the anthracene oil of 7.7%.

Comparative Experiment A

50 parts by weight of the anthracene oil fraction of 13.5%, described in the above Example 1, are dissolved in 60 parts by weight cyclohexanone at 125° C., the solution is allowed to cool down and the crystallized material is centrifuged at 20° C. The crude centrifuged material is washed with 20 parts by weight of cyclohexanone and dried. 4.38 parts by weight of anthracene having an anthracene content of 94.3% (according to Montecatini) are thus obtained. The anthracene yield amounts to 61%, based on the anthracene present in the anthracene fraction.

Comparative Experiment B

50 parts by weight of anthracene fraction of 13.5% of Example 1 are dissolved in 40 parts by weight of cyclohexanone at 125° C., the solution is allowed to cool down and the crystals formed are centrifuged at 20° C. The crude centrifuged material is washed with 10 parts by weight of cyclohexanone and dried. 4.84 parts by weight of anthracene with an anthracene content of 92% (according to Montecatini) are thus obtained. The anthracene yield amounts to 65% based on the anthracene present in the anthracene fraction.

Determination of the pure anthracene according to Montecatini is described in the following prior art: Postowsky and Chmielewskii, Chem. J. Ser. B., J. appl. Chem. 10, 759 (1937) and W. Schmidt, Brennstoff-Chemie 33, 176 (1952).

An apparatus adapted to carry out the process of the present invention is shown in the appended drawing.

In the drawing 1 denotes a compressor by which the starting material, e.g. a residual oil rich in aromatic ingredients is introduced into a tube furnace 2 under pressure and heated—e.g. with a time of stay of 45 minutes—to a final temperature of 380° C. Subsequently, it is allowed to expand into a distillation column 3, which is operated under 100 torr at the sump of the column 3. At

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a lower side current of column 3 anthracene oil is drawn off. 4 denotes a redistillation column having 30 calculated trays, operated at a return reflux ratio of 7:1 and at a pressure of 20 torr at the head of the column. 5 denotes a condenser, 6 is a container for treatment with the solvent; 7 a storage container for the solvent and 8 denotes a centrifuge.

The parts and percent are by weight, if not otherwise stated.

What is claimed is:

1. A process for obtaining anthracene from oils selected from the group consisting of oils rich in aromatics and residues from pyrolysis of gasoline to ethylene and acetylene, said starting materials containing 0.1 to 1.0% anthracene, by distillation to 1 to 4% and subsequently by redistillation up to 10–25% by weight of anthracene, and converting the resulting anthracene fraction, by dissolution and recrystallization from an aryl-alkyl-ketone, into an anthracene of the desired purity.

2. A process as claimed in claim 1, in which concentration of the starting material containing 0.1–1.0% anthracene, is carried out by said distillation, and by dissolution and recrystallization from an aryl-alkyl-ketone.

3. A process as claimed in claim 1, in which the starting material is an oil rich in aromatics, in mixture with aliphatic components.

4. A process as claimed in claim 1, in which the first step consists of the process in subjecting the starting material to a brief treatment at increased temperature and under superatmospheric pressure.

5. A process as claimed in claim 4, in which the starting material is heated to 380° C. under 4–10 atmospheres for about 45 minutes.

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