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METHOD OF INCREASING THE ANTHRACENE CONTENT OF CREOSOTE

Claude E. Bole, O'Hara Township, Allegheny County, and Gerald Gilbert, Pittsburgh, Pa., assignors to United States Steel Corporation, a corporation of New Jersey

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This invention relates to the recovery of anthracene and, more particularly, to a method of increasing the anthracene content of the creosote fraction of coal tar.

Anthracene is one of the commerically important coal-tar products. It is usually present to the extent of about 5% in the creosote fraction boiling between 315 and 355° C. The recovery of this particular product, however, involves considerable difficulty. Regardless of the exact method of recovery, the results would normally be considerably improved if the anthracene concentration were greater to start with. It is accordingly the object of our invention to provide a method of treating this creosote fraction to increase its anthracene content before separating the latter by any of the known methods.

We have discovered that the concentration of anthracene in creosote may be markedly increased by heating it to a moderate temperature for a period of several hours. The increase is greater if the creosote fraction is contacted with a dehydrogenating agent or a catalyst. Indeed, by use of the latter, an increase in anthracene content of 100% or better may be achieved. In more exact terms, we heat the fraction of coal tar boiling between 315 and 355° C. to a temperature of from 200 to 450° C. for a period of from one to eleven hours or even longer, preferably in the presence of a dehydrogenating agent such as sulfur, selenium or oxygen, or a catalyst such as palladium or platinum or the oxides of chromium, molybdenum or vanadium. These metallic oxides are conveniently supported on a carrier such as alumina.

A complete understanding of our invention may be obtained from the following typical examples of the practice thereof.

Example I

A coal tar fraction boiling over the range of 315 to 355° C. was found to contain 5.5 weight percent anthracene. Heating the fraction for eleven hours at reflux temperature (about 320° C.) increased the anthracene content to 8.6 weight percent.

Example II

A portion of the starting material used in Example I was heated with about 5 weight percent of sulfur for two hours at reflux temperature (about 320° C.). An additional 1.5 weight percent of sulfur was added to insure completeness or reaction, and the heating was continued for another hour. The anthracene content was increased from 5.5 weight percent to 11.0 weight percent by the treatment.

Example III

A portion of the starting material used in Example I was heated at reflux temperature (about 320° C.) for six hours in contact with a catalyst containing 5 weight percent palladium on asbestos. The anthracene content

was increased from 5.5 to 11.7 weight percent by the treatment.

As shown by the examples, thermal treatment of the 315–355° C. fraction of coal tar according to the present invention increased the anthracene content of the fraction by as much as 113%. The invention, therefore, in addition to improving the potential production of anthracene from a coal tar, permits known processes for recovering anthracene to be operated more efficiently by making available a feed material containing greater concentrations of anthracene.

We believe that our treatment, which is primarily a dehydrogenation process, converts some of the anthracene-precursor compounds in the fraction to anthracene. The two most important precursors of the additional anthracene produced by the treatment are believed to be 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene, which are known to be present in the 315–355° C. fraction of coal tar.

In applying our process, the anthracene-containing fraction is taken directly from the tar still and maintained at reflux temperature for a period of from one to several hours, as necessary to significantly increase the anthracene content of the fraction. We have found that short thermal treatment periods of less than one hour significantly increase the anthracene content; however eleven or more hours are required to increase the anthracene content to a maximum value. Treating temperatures as low as 150° C. and as high as 450° C. can be used in the practice of our invention, however, temperatures between 280° and 380° C. are preferred. At lower temperatures the speed of the reaction is slow, and this is an important consideration in the economics of the process. At higher temperatures, thermal decomposition of anthracene and other valuable chemicals in the fraction occurs. Our thermal treating process can be carried out batchwise, continuously, or in the vapor phase. The exact operating conditions will be dependent on such economic considerations as the size of the plant or installation, the chemical nature of the fraction, and others.

It should be noted that the initial step in the process of isolation from coal tar should be one in which the hydroanthracenes are concentrated along with the anthracene. Thus, our process is more efficient when applied to a distilled anthracene-containing creosote fraction than to the crystals from the conventional process of crystallization of creosote since, in the latter, the anthracene precursors tend to concentrate in the mother liquor.

It will be evident from the foregoing that our invention provides a simple, inexpensive and effective method of upgrading creosote from the standpoint of anthracene content, thereby facilitating the separation of the latter and reducing the cost thereof.

While we have disclosed herein the preferred practice of our invention, we intend to cover as well any change or modification therein which may be made without departing from the spirit and scope of the invention.

We claim:

1. The method of increasing the concentration of anthracene in coal tar which comprises fractionally distilling coal tar, collecting the fraction boiling between 315 and 355° C. containing anthracene precursors including 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene, and holding said fraction at a temperature between 280

and 380° C. for from one to eleven hours, thereby dehydrogenating said precursors and converting them at least in part to anthracene.

2. A method as defined by claim 1, characterized by maintaining in contact with said fraction from 2 to 7 weight percent of a dehydrogenation agent selected from the group consisting of sulfur, selenium and oxygen.

3. A method as defined by claim 1, characterized by maintaining in contact with said fraction about 5 weight percent of a catalyst selected from the group consisting of palladium, platinum and the oxides of chromium, molybdenum and vanadium.

References Cited in the file of this patent

UNITED STATES PATENTS

2,007,212	Penniman	July 9, 1935
2,161,066	La Lande	June 6, 1939
2,438,148	Carson et al.	Mar. 23, 1948
2,475,977	Meier	July 12, 1949
2,795,538	Ratte et al.	June 11, 1957
2,838,346	Swaney	Mar. 25, 1958
2,868,713	Ratte et al.	Jan. 13, 1959

FOREIGN PATENTS

531,038	Canada	Oct. 2, 1956