Fig. 1.

- % Anthracene in Product
- % Recovery of Anthracene

Fig. 2.

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The present invention relates to anthracene and particularly to an improved process of recovering anthracene of substantially high purity from coal tar crudes known to the trade as "anthracene salts." The presence of impurities in crude anthracene having characteristics similar to those of anthracene has rendered the production of reasonably pure anthracene expensive and difficult. The coal tar crudes, i.e., anthracene salts, from which anthracene is recovered is of variable composition and ranges from 25-45% anthracene, 6-20% carbazole, and the balance phenanthrene, with some fluorene, acridine, hydroacridine, acenaphthene, diphenyl methyl anthracene, pyrene, chrysene, rotene, floranthene, chrysogen, high boiling paraffins, such as eicosene, docosene, and the like. Other impurities are sometimes also present in small amounts. The relative proportions of the different impurities vary somewhat with the nature of the coal from which the crude anthracene is produced. Crude anthracene presscake, which may contain from less than 20 to 60% of anthracene, is usually purified by various methods of fractional solubility, or by causing some of the major impurities to react with chemicals which can then be easily separated. The processes at present in use for the most part use solvents, such as pyridine, tetrachloroethylene, water, hydroacridine, 4-hydroxy-4-methyl-2-pentanone, carbon tetrachloride, solvent naphtha, creosote oil, petroleum hydrocarbons and the like, and by these methods the crude anthracene may be purified, leaving mainly carbazole and phenanthrene as impurities. The processes are very costly, and troublesome, and in the case of pyridine the odor is extremely unpleasant.

One method which has been used consists of grinding crude anthracene in a ball or pebble mill with a sufficient quantity of solvent, such as benzol, crude coal tar solvent, carbon tetrachloride and the like to dissolve high boiling paraffins and phenanthrene but which do not appreciably dissolve the anthracene and carbazole. The grinding is continued for a period of time until the crude anthracene has become very finely pulverized or sub-divided. In order to dissolve substantially all the high boiling paraffins, it is essential that two or more grinding treatments with solvent be employed. This operation alone is time consuming and requires a minimum of 4 to 6 hours. At the conclusion of the grinding operations and solvent action, the contents of the mill are discharged and filtered. The remaining residue is washed several times with the same solvent or solvents and dried. The removal of carbazole from the ground and paraffin refined anthracene is accomplished by solvent extraction with either acetone or pyridine. The best possible yield of anthracene obtainable according to this procedure is about 72% of 85-88% purity. Another method consists of extracting the crude anthracene by the action of sulfur dioxide, aqueous ammonia containing at least 75% ammonia in solution, methyl and ethyl ethers, acetone and the like. Regardless of the extracting medium employed, the extraction must be repeated for at least 13 to 26 times at specified volumes of solvent until the anthracene is purified to the desired extent. After the anthracene has been treated with the solvent to remove the desired amount of impurities, the solvent remaining in contact with the anthracene must be removed by either heating the anthracene to a sufficient temperature to evaporate the solvent; or by treatment with steam which is blown through or over the anthracene to expel the solvent. When steam is employed, the mixture of steam and solvent, for example, acetone, must be cooled to condense the water-acetone mixture.

The recovery of anhydrous acetone for recycling into the extraction system poses a serious problem. It is well known that the production of relatively anhydrous acetone is a difficult process to achieve economically because a "pinch" occurs in the acetone rich portion of the vapor-liquid equilibrium phase diagram of the acetone-water system. Large amounts of heat are required to remove the water and the relatively high reflux ratios required to produce a recovered solvent containing low water concentrations result in the use of large sized distillation columns, excessive amounts of cooling water, etc.

All of the foregoing processes are expensive, slow, inefficient, and require a great deal of time, labor and equipment. Accordingly, it is an object of the present invention to overcome these shortcomings and to provide a less expensive and more efficient method of recovering high purity anthracene from coal tar crudes involving solvent leaching followed by distillation.

In accordance with the present invention, the improved method involves two purification steps. The first is leaching of the solid anthracene salts with a solvent at a temperature ranging from 15 to 30° C., preferably at or near room temperature, to remove substantially all phenanthrene, fluorene, and carbazole. The solid product, after adhering solvent has been removed by heating at a temperature ranging from 55° to 295° C., contains 85-90% anthracene. The second step is a fractional distillation of the leached crude in a conventional manner which produces a product having a purity of 95-98% anthracene or better and which is suitable for production of high purity anthraquinones by oxidation of the anthracene in the conventional manner.

The solvent employed is one which has high solubility for the impurities, i.e., phenanthrene, fluorene, carbazole, etc., and low solubility for anthracene. As examples of such solvents, the following may be mentioned:

**Alcohols**
- methanol
- ethanol
- propanol
- isopropanol
- n-butanol
- sec.-butanol

**Amides**
- formamide
- dimethyl formamide

**Amines**
- aniline
- monoethanolamine

**Miscellaneous nitrogen compounds**
- acetonitrile
- nitromethane

**Acids**
- acetic
3 Esters
methyleacetate
ethylacetate

Ketones
acetylacetone
acetonylacetone
acetyltrimethylene
cyclobutanone
cyclopentanone
cyclohexanone
cycloheptanone

Glycols
propylene glycol
triethylene glycol

Phenanthrene and fluorene are considerably more soluble in these solvents than are carbazole and anthracene. However, all of the foregoing solvents and mixtures thereof show a high ratio for the solubility of carbazole relative to anthracene. The foregoing solvents are readily recovered from the solid product and from the spent leaching solvent for reuse. They are thermally stable and have a boiling point below 250°C. Moreover, they are all liquids at room temperature. Of all the foregoing solvents, we prefer to employ acetone and methyl ethyl ketone because of their availability, cheapness, and ability to produce a leached solid having high anthracene content and because of their low boiling points which facilitate their recovery by distillation processes. In addition, the latter solvents can be used effectively in the presence of 5-20% of water for the recovery of anthracene from crude anthracene salts. This is extremely important because it results in significant economies in the recovery of these two solvents.

Another advantage of using water in the solvent, not only in acetone or methyl ethyl ketone, but in all the others listed above, is the increase of the recovery of anthracene. The increase in recovery rises as the percent of water in the solvent increases with a maximum recovery at 20% water content in the solvent. The actual recovery is 90% of 80-90% purity or 72% yield of anthracene. Subjecting the leached or solvent extracted product to distillation yields anthracene of 95-98% purity. The anthracene is of such high purity that upon oxidation, it yields anthraquinone of 99% purity in a yield of 92% of theory. The anthraquinone is used successfully to prepare 1-amino-anthraquinone of acceptable quality. This indicates that the anthracene is of such quality that it may be used in manufacture of anthraquinone-type dyestuffs.

In practicing the present invention, one part by weight of any crude anthracene salts containing from 24 to 45% anthracene is agitated in a vessel at a temperature of 20 to 35°C with 1.5, 2.0, 3.0, or 4.0 parts by weight, preferably 2.5 parts by weight, of any one of the foregoing solvents of technical grade or mixtures thereof for a period of time ranging from 1 to 3 hours. The slurry is filtered and the solid product dried by any conventional means. The leached crude product is a light green to light green-brown color and has a bright green fluorescence when viewed under ultraviolet light. During the leaching operation essentially all of the compounds which have lower boiling points than anthracene, along with most of the carbazole which has a higher boiling point than the anthracene, are removed. The leached product which is then stripped of the major components, i.e., phenanthrene, carbazole, and a number of lower boiling components, is readily susceptible to fractional distillation during which mostly the compounds having boiling points higher than that of anthracene, including substantially all of the carbazole and naphthacene, are completely removed. In general, however, to achieve purities of 98% of anthracene or better, the minimum number of theoretical plates required will be 10 to 50 and the minimum reflux ratio of 2 to 3. In order to achieve the production of at least 95-98% of pure anthracene, we prefer to employ a distillation column having approximately 50 theoretical plates at a pressure in the range of 100 to 600 mm. of mercury absolute and a pot temperature in the range of 265° to 360°C and a head temperature of 230° to 330°C. Any conventional distillation column having the required number of plates may be employed. The distillation step removes all traces of the green fluorescence which is attributable to the presence of naphthacene. The resulting distilled product is white to light yellow in color and fluoresces to blue when viewed under ultraviolet light.

The leaching or solvent extraction may be carried out as a single stage process, a multi-stage process, or continuously. The multi-stage or continuous process may be concurrent with regard to the relative direction of flow of solid and solvent. The multi-stage operation may be carried out in a single unit or in multiple units, all modifications being based chiefly on the economics of the overall process. A higher purity and improved recovery of anthracene is obtained by the use of counter-current multi-stage type of equipment. Equipment of this type is illustrated by G. G. Brown in his text “Unit Operations” published by John Wiley & Sons, 1950, and the schematic flow diagrams together with a description illustrated by Perry on pages 1216-1220 in his “Chemical Engineers Handbook,” second edition.

The foregoing two-stage process is much more effective than a two-stage process involving solvent extraction and sublimation as the second step. In the latter process, all the impurities in the leached crude, particularly carbazole, tend to sublime along with the anthracene to a degree sufficient to seriously impair the purity of the final product.

The two-stage process in accordance with the present invention is very critical as established by the following facts:

(1) Solvent extraction without distillation of crude anthracene does not lead to a higher purity product and improved recovery.
(2) Distillation alone of crude anthracene does not lead to purified anthracene of suitable purity for dye-stuff manufacture.

To obtain a product of high purity and improved recovery it is essential that our two steps be carried out in the order prescribed. If the process is carried out in the reverse manner, i.e., distillation followed by solvent extraction, sufficiently pure anthracene is not obtained for the manufacture of dyestuffs.

The two graphs constituting the accompanying drawing illustrate the relationship of the purity of anthracene to the percent of water in the extracting solvents. Figures 1 and 2 show this relationship with acetone and methyl ethyl ketone, respectively.

By reference to Figure 1, it will be observed that while anhydrous acetone may at first appear to be desirable, a water content of 4.5% in the acetone can be readily tolerated without appreciably lowering the purity of the anthracene product while at the same time the anthracene recovery is improved. In addition, as pointed out above, this is highly desirable since in the recovery of acetone and methyl ethyl ketone, it is difficult to remove the last traces of water during distillation.

Figure 2 shows that as much as 10% of water in methyl ethyl ketone can be tolerated without appreciably lowering the purity of the anthracene product, while at the same time, the anthracene recovery is improved.

From the foregoing description, it becomes manifest that depending upon the solvent, i.e., anhydrous or containing water, it is possible to obtain about 80% recovery of anthracene with about 90% purity or 72% yield of
anthracene as well as about 90% recovery with 80% purity or 72% yield of anthracene. By subjecting the leached product to the distillation step, the two-step process produces a final product of 95-98% purity.

The following examples describe in detail the methods for accomplishing the above objects, but it is to be understood that they are inserted merely for the purpose of illustration and are not to be construed as limiting the scope of the invention.

EXAMPLE I

5,000 grams of crude anthracene salts containing 42% anthracene were agitated at 30° C. with 12,500 grams of technical grade acetone for 2 hours. The slurry was filtered and the solid product dried. The solid product weighed 2,021 grams and was found to contain 85% anthracene as analyzed by the maleic anhydride adduct method.

1,650 grams of the above leached crude were distilled at 200 mm. pressure of mercury absolute in a distillation column having approximately 50 theoretical plates with a pot temperature of 280° C. and a head temperature of 270° C. The distillate included 1,234 grams of a material having a white color and containing 95.4% anthracene.

EXAMPLE II

Example I was repeated with the exception that 12,500 grams of technical grade acetone were replaced by an equivalent amount of technical grade of methyl ethyl ketone containing 10% of water. After distillation, the distillate included 1,259 grams of a material having a white color and containing 97% anthracene.

EXAMPLE III

Example I was again repeated with the exception that 12,500 grams of technical grade acetone were replaced by an equivalent amount of technical grade acetone containing 4 to 5% of water. After distillation, 1,286 grams of a material having a white color and containing 98% of anthracene was obtained.

We claim:

1. The process of purifying crude anthracene salts containing 24 to 45% anthracene which consists of extracting the impurities therefrom with a solvent selected from the group consisting of liquid alkanols, liquid ketones, and liquid glycols having 1 to 4, 3 to 7, and 2 to 6 carbon atoms, respectively, the said solvent containing from about 5 to about 10% water, at a temperature ranging from 20 to 35° C., filtering and drying the extracted crude, and then subjecting it to a fractional distillation in a multistage column at a selected pressure of 100 to 600 mm. of mercury at a selected pot temperature of 265° to 305° C. and a selected head temperature of 250 to 330° C., which selected temperatures are above the boiling point of the anthracene at the selected pressure.

2. The process according to claim 1, wherein the solvent is acetone.

3. The process according to claim 1, wherein the solvent is acetone containing about 5% of water.

4. The process according to claim 1, wherein the solvent is methyl ethyl ketone.

5. The process according to claim 1, wherein the solvent is methyl ethyl ketone containing about 10% of water.

6. The process according to claim 1, wherein the solvent is diethylene glycol.

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