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MANUFACTURE OR RECOVERY OF POLY-
NUCLEAR CARBON COMPOUNDS

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The present invention relates to improvements in the manufacture or recovery of polynuclear carbon compounds.

Polynuclear compounds, in particular those having comparatively large molecules, as for example anthracene, pyrene, picene, chrysene, fluorene and carbazole, have hitherto mainly been obtained from mineral coal tar by fractional distillation and more or less troublesome working up of the fractions so obtained. Recently processes have also been proposed with the aid of which it is possible in a simple manner to obtain polynuclear compounds of the said kind and also some hitherto unknown substances from destructive hydrogenation products, in particular from their fractions of higher boiling point. It is not yet possible, however, to obtain any desired polynuclear compound because it is not known, or not sufficiently known, under what conditions the polynuclear compounds occur or are formed.

We have now found that valuable polynuclear compounds, in particular mono- or di-methylpyrene or 1.12-benzoperylene or coronene (hexabenzobenzene), can be obtained in a simple manner by freeing the product leaving the reaction vessel, in the destructive hydrogenation of mineral coal, in a liquid or pulpy state and consisting of oils of high boiling point and solid constituents (which product is hereinafter referred to for the sake of brevity as "mineral coal destructive hydrogenation sludge") from a part of its oil by mechanical means, distilling the residue and separating the polynuclear compounds from the resulting distillate, if desired after the removal of any paraffin waxes present.

The mechanical splitting up of the sludge may be effected for example by filtration, if necessary after dilution with for example comparatively mobile hydrocarbon oils. The splitting up is, however, advantageously effected by centrifuging. In this way there is obtained on the one hand an oil free from solid constituents which may be used for example for making fresh coal into a paste for destructive hydrogenation, and on the other hand a residue which consists mainly of ashes and residual coal and oily constituents of high molecular weight and which also contains paraffin wax.

This residue is then subjected to a distillation, preferably to a decomposing distillation, whereby the temperature is advantageously selected as high as possible so that all constituents capable of being distilled are separated

from the solid constituents of the residue. If the distillation be carried out by bringing the residue from a comparatively low temperature, as for example from room temperature, up to the high temperatures necessary for the distillation, the oily distillate also contains the paraffin waxes present in the residue. In this case it is preferable to free the distillate oil from paraffin wax before its further working up, for example by mixing it with suitable selective solvents, as for example methyl formate, chlorinated hydrocarbons or liquefied hydrocarbons of the methane series which are normally gaseous at room temperature, and then cooling the resulting solution. There is then always the danger that together with the paraffin wax there may be precipitated a certain amount of the desired polynuclear compounds which can then no longer be separated in an economical manner from the precipitated paraffin wax. The distillation of the residue is therefore preferably carried out by bringing it into a vessel heated at least to about 500° C. The residue is immediately strongly overheated by the hot walls of the vessel so that the paraffin wax is split. Paraffin waxes are then no longer present in the distillate but only its cleavage products which do not interfere with the separation of the polynuclear compounds. Moreover in the said kind of distillation, a dehydrogenation may simultaneously take place by which such polynuclear compounds, as are present in the form of their hydro derivatives, are converted into the corresponding non-hydrogenated substances.

It has also been found that it is very advantageous to add small amounts of oxygen or gases containing or supplying oxygen to the material to be distilled during the decomposing distillation, especially at high temperatures, as for example above the boiling point of pyrene. In this manner the heating is promoted by oxidation or combustion processes on the one hand and on the other hand, when using air, the vapors containing coronene are more readily led away from the distillation vessel by the residual nitrogen. By interposing a sublimation chamber, it is thus possible to recover the vapors of the coronene mainly by sublimation, while the vapors of the resinous and oily constituents distil over with only a little coronene and can be recovered in the liquid state in receivers. In this manner the difficultly isolatable coronene (hexabenzobenzene) is obtained as a crude sublimate in the form of crystals which are completely pure after a single crystallization.

Air is especially suitable for carrying out the process according to this invention, but other gas mixtures containing oxygen or pure oxygen or even steam may also be used.

5 The distillate obtained can then be split up into fractions, if this has not already been effected during the distillation, advantageously into fractions of narrow boiling point range, as for example boiling within every 2° to 5° C. This splitting up is preferably effected in vacuo. In certain fractions of narrow boiling point range, which fractions are of large amount, there occur pure readily separable aromatic compounds, while in the fractions arising from the usual mineral coal tar distillation high molecular mixtures are frequently obtained from which the pure substances can only be recovered in a troublesome manner. For example from the comparatively low boiling fractions, carbazole and hydrogenated pyrene are obtained. Among the following fractions there are those which contain pyrene in a pure form. The mean boiling point in which the pyrene fractions occur depends on the vacuum employed. For example with the vacuum of the Röntgen tube the boiling point of such fractions lies at from 150° to 190° C. while at 2 millimetres (mercury gauge) it is from 190° to 220° C. The recovery of higher condensed rings is effected from the following fractions, which are preferably obtained under still higher vacua. From these fractions there are then first obtained pyrene derivatives containing one or more methyl groups, as for example 4-methylpyrene having a melting point of 143° C. and dimethylpyrene. In the further distillation there occurs a strong overheating of the contents of the still which is accompanied by a formation of gas and which may proceed very violently if too much energy be supplied. When the formation of gas has ceased, fractions of narrow boiling point are prepared from which almost pure 1.12-benzoperylene and coronene are recovered. The intermediate fractions contain mixtures of the two substances which may be readily separated by fractional chystallization from xylene.

The resulting polynuclear compounds may be purified in a simple manner and if necessary separated from each other. For example the methyl derivatives of pyrene can be purified by treatment with solvent mixtures, as for example mixtures of xylene and alcohol. 1.12-benzoperylene and coronene may be separated from each other by fractional crystallization from xylene.

55 1.12-benzoperylene forms pale yellowish green crystals which melt at from 271° to 273° C. The solutions of this compound in organic solvents have a blue fluorescence. The compound dissolves in concentrated sulphuric acid giving an emerald green colouration. The picrate of the benzoperylene is violet to dark brown and melts at from 268° to 270° C.

60 Coronene forms pale yellow compact needles which melt at from 430° to 432° C. (corrected). Its solutions in organic solvents have a blue fluorescence; it forms a dark red picrate.

If value is only placed on the recovery of especially highly condensed cyclic compounds, the removal or decomposition of the paraffin waxes is not necessary.

70 The following examples will further illustrate how this invention may be carried out in practice, but the invention is not restricted to these examples.

Example 1

A sludge consisting of 70 per cent of oil and 30 per cent of solid constituents obtained by the destructive hydrogenation of mineral coal is centrifuged, if necessary after the addition of a heavy oil and/or middle oil obtained in the process, whereby a residue containing 55 per cent of solid constituents is obtained. The centrifuged oil is used for making fresh coal into a paste. The centrifuge residue is continuously introduced into an externally heated rotary tubular furnace provided with balls the wall temperature of which is from 500° to 550° C. Within this furnace there occurs the decomposition of the paraffin waxes contained in the residue to form oils of low molecular weight so that the effluent oil vapors are free from paraffin wax. The vapors are then condensed. The oil is then distilled under a pressure of 10 millimetres (mercury gauge) until a first running oil, which is practically free from valuable aromatic compounds has been obtained in an amount of from 25 to 30 per cent. The distillation is then continued in such manner that fractions each having a boiling range of from 2° to 3° C. are collected. In the fractions occurring in an amount of from 30 to 35 per cent there are contained carbazole, hydrogenated pyrenes, in several fractions pure pyrene, in the following fractions monomethylated pyrenes, such as 4-methylpyrene, and in the further fractions dimethylpyrene. By further distillation there is then obtained a resin fraction in an amount of from 5 to 10 per cent. By further distillation a decomposition takes place and an oil fraction is obtained in an amount of from 5 to 10 per cent which is also collected in fractions each having a boiling point range of from 2° to 3° C. 1.12-benzoperylene and coronene are obtained from these fractions.

The first-mentioned aromatic compounds up to and including dimethylpyrene are obtained in a pure form from the fractions by crystallization, centrifuging of the crystals and subsequent washing with a mixture of benzene and alcohol. The substances of higher molecular weight, such as 1.12-benzoperylene and coronene, must, however, be crystallised from xylene.

The centrifuge residue may also be heated gradually and thereby distilled, whereby an oil containing paraffin wax is obtained. To this is added twice its volume of methyl formate and the whole is cooled to zero C. so that the paraffin wax is precipitated. The latter is then separated from the oil solution by filtration. The oil is then freed from solvent and further worked up in the same manner as described above.

Example 2

100 parts of a heavy oil obtained by decomposing distillation according to Example 1 from which the fractions which contain pyrene and its homologues have already been removed, are distilled under a pressure of 15 millimetres (mercury gauge).

65 The first fraction, boiling up to about 340° C. and amounting to about 40 parts, consists of resins which contain no isolatable cyclic compounds. There then follow 15 parts of fractions from which benzoperylene can be recovered, up to a temperature of 440° C. in the sump at 15 millimetres pressure (mercury gauge).

75 During the further distillation, air is introduced into the distilling vessel, whereby the temperature rises more rapidly than previously up to about 500° C. or more. The effluent vapors con-

5 taining coronene are led through a sublimation chamber and then into a drain pipe. The coronene is deposited in the sublimation chamber in the form of very long crystal needles. After a single crystallization they have a melting point of 432° C. (corrected) and are therefore pure.

What we claim is:

10 1. The process of producing polynuclear compounds which comprises mechanically freeing a product, obtained in the destructive hydrogenation of mineral coal in a liquid to pulpy state and consisting of oils of high boiling point and solid constituents, from part of its oil, subjecting the remainder to distillation the temperature during said distillation being at least 500° C. after lower boiling fractions, if such are present, have been distilled off, and separating polynuclear compounds from the resulting distillate.

20 2. The process of producing polynuclear compounds which comprises mechanically freeing a product, obtained in the destructive hydrogenation of mineral coal in a liquid to pulpy state and consisting of oils of high boiling point and solid constituents, from part of its oil, subjecting the remainder to distillation the temperature during said distillation being at least 500° C. after lower boiling fractions, if such are present, have been distilled off, freeing the distillate from paraffin wax, and separating polynuclear compounds from the resulting product.

30 3. The process of producing polynuclear compounds which comprises mechanically freeing a product, obtained in the destructive hydrogenation of mineral coal in a liquid to pulpy state and consisting of oils of high boiling point and solid constituents, from part of its oil, subjecting the

remainder to a decomposing distillation the temperature during said distillation being at least 500° C. after lower boiling fractions, if such are present, have been distilled off, and separating polynuclear compounds from the resulting distillate. 5

4. The process of producing polynuclear compounds which comprises mechanically freeing a product, obtained in the destructive hydrogenation of mineral coal in a liquid to pulpy state and consisting of oils of high boiling point and solid constituents, from part of its oil, subjecting the remainder to a decomposing distillation the temperature during said distillation being at least 500° C. after lower boiling fractions, if such are present, have been distilled off in the presence of a gas comprising oxygen, and separating polynuclear compounds from the resulting distillate. 10 15

5. The process of producing polynuclear compounds which comprises freeing a product, obtained in the destructive hydrogenation of mineral coal in a liquid to pulpy state and consisting of oils of high boiling point and solid constituents from part of its oil by centrifuging, subjecting the remainder to distillation, fractionally distilling the distillate so obtained, isolating pyrenes from a high boiling fraction and isolating a substance selected from the class consisting of 1.12-benzoperylene and hexabenzobenzene from a still higher boiling fraction. 20 25 30

6. The process as defined in claim 5 wherein the fractional distillation is carried out in vacuo.

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