

## UNITED STATES PATENT OFFICE

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PROCESS FOR THE PRODUCTION OF POLY-  
NUCLEAR CARBON COMPOUNDS

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The present application for patent is a division of our copending application Ser. No. 751,251, filed November 2, 1934.

The invention described and generically claimed in the said application relates to the production or recovery of unitary polynuclear carbon compounds of high molecular weight, not only such as contain at least four rings in the molecule, but also such as contain less than four rings. The said compounds may belong to the isocyclic or to the heterocyclic group. As examples of such compounds may be mentioned alkyl-naphthalenes, naphthofluorenes, triphenylene, anthracene, alkyl-anthracenes, acenaphthene, retene, pyrene, chrysene, picene, fluorene, fluoranthene, truxene, naphthanthracene, naphthacene, decacyclene, diphenylene sulphide, diphenylene oxide, brasane, carbazole, phenyl-naphthylcarbazole, acridine and other ring systems, in part still higher condensed ring systems, as well as their homologues and hydrides which in pure form are valuable as initial materials for organic syntheses.

It has been disclosed in the said application Ser. No. 751,251 that carbon compounds of high molecular weight of the said kind can be prepared in a simple and inexpensive manner and in large amounts, by a process which in its most important forms utilizes the known destructive hydrogenation of bituminous crude substances as, for example, of mineral coals, brown coals, peats, woods, lignin, oil shale, mineral oils, tars, distillation products, extraction products and residues thereof. Whenever in this specification we simply speak of "destructive hydrogenation," we wish this expression to be understood in a broad sense, including not only a treatment with hydrogenating gases under conditions resulting in a more or less drastic breaking down of the molecules of the initial materials, but also under conditions under which mainly a hydrogenation takes place or under which only some of the constituents of the initial materials are considerably attacked or degraded, others being left unaltered or substantially unaltered.

We have found, contrary to expectation, that the destructive hydrogenation products of high boiling point of bituminous crude materials contain very considerable amounts of high molecular cyclic carbon compounds and that these may be recovered therefrom very readily and simply, for example by the methods which have hitherto been employed for recovering compounds of the said kind from mineral coal high temperature tar.

We further investigated into the possibilities of recovering the valuable compounds from the said products and also the conditions which during the destructive hydrogenation lead to the production or chemical change of such compounds, and as a result thereof we have found out several methods by which the recovery of the unitary organic compounds from the products of the destructive hydrogenation can be effected with particular advantage. These methods which will be described in detail below, prove valuable not only for the recovery of compounds with 4 or more nuclei, but also of compounds with less than 4 nuclei and both from the initial materials specifically mentioned in the foregoing as well as from products of the destructive hydrogenation of high temperature tars.

For the recovery of the polynuclear compounds it has proved advantageous in many cases to employ as one step in the process a dehydrogenation. Such dehydrogenation step may be adapted to the particular circumstances of each case, for example by suitably selecting the conditions of working or by carrying it out in stages, as will be described in detail below, and may be combined with other methods of working, as for example precipitation of asphaltic substances or subsequent hydrogenation of the recovered polynuclear compounds in order to produce hydrogenated polynuclear compounds.

Another method of working which is somewhat related to the dehydrogenation consists in distilling the destructive hydrogenation products with an addition of metals or of condensing or polymerizing agents. Also this method of working is preferably used in conjunction with other treatments, as for example removal of asphaltic substances or dehydrogenation.

A removal of paraffin waxes from the destructive hydrogenation products also proves valuable in many cases.

But not only asphalts and asphaltic substances or paraffin waxes may tend to hinder the separation of the valuable polynuclear compounds, but also pitch forming substances, which are mostly olefines of high molecular weight tending to form asphalts under the influence of oxygen and/or heat, so that their removal may be advantageous, especially when compounds of very high molecular weight are to be recovered.

It will be understood from the foregoing that the methods of recovering the valuable polynuclear compounds may be varied to a large extent to suit the requirements of each particular case. However, the nature of the products re-

covered may also be influenced in other ways, as for example by suitably modifying the conditions of the destructive hydrogenation or by subjecting the crude destructive hydrogenation products to a hydrogenation treatment under special conditions or to an isomerization or other treatment modifying the nature of the polynuclear compounds.

The process according to the present invention consists in subjecting the aforesaid bituminous crude materials to destructive hydrogenation, the cyclic carbon compounds containing four or more rings being separated by suitable methods from the high boiling fractions of the reaction products.

Before describing in detail the several methods which we have developed for the recovery of the polynuclear compounds, the modes of carrying through the destructive hydrogenation and the other treatments which are made use of as separate steps in the said methods, as for example the dehydrogenation and others, will be explained.

#### *The destructive hydrogenation*

The destructive hydrogenation of the bituminous substances may be carried out according to known methods in different ways as shown for instance in U. S. Patent 1,890,434. Of course, the conditions to be employed during the destructive hydrogenation may be adapted to the requirements of each particular case in any suitable manner.

For example, in the working up of mineral coal, the latter may be finely ground and advantageously freed from the gangue and the basic constituents, which may be effected by treatment with acid-reacting agents, as for example hydrochloric acid. The catalysts are advantageously added dissolved in water or organic solvents. They may also be incorporated with the initial materials in a solid form, if desired applied to carriers. The coal thus pretreated is then made into a paste with oil and subjected to the destructive hydrogenation. By suitable selection of the temperature, as for example from 380 to 500° C. preferably from 444° to 471° C., a pressure of 200 atmospheres or more and the throughput, as for example 0.5 kilogram of coal per liter of reaction space per hour, the reaction can readily be so carried out that the resulting product consists mainly of constituents of high boiling point.

When it is desired to obtain destructive hydrogenation products which are particularly rich in hydrogen, not too high temperatures, in most cases not more than 470° C. and the highest possible partial pressure of hydrogen, preferably more than 150 atmospheres, should be employed. The constituents of high boiling point of such destructive hydrogenation products as are obtained while splitting to benzine, may also be used for the process.

The destructive hydrogenation products may, if necessary, be freed from phenols by treatment with alkalies and from pyridine bases by treatment with acids.

When it is desired to prepare or recover polynuclear compounds containing side chains in the molecule, mineral coal destructive hydrogenation products may be used and procedure may be as follows:

The mineral coal is finely ground and advantageously freed from the gangue and the basic constituents of the ash as previously suggested. The coal is then mixed with finely ground

catalytic substance or impregnated with a solution of the latter. The amount of catalyst is preferably from 0.05 to 5 per cent. The coal thus pretreated is then made into a paste with oil preferably derived from the same coal, and subjected to destructive hydrogenation. The addition of catalyst may also be made after the coal is made into a paste; catalyst may also be added in batches in different phases of the process. Furthermore different catalysts may be employed. Thus for example a coal which has been provided with a molybdenum or tin compound may have added thereto after heating up a halogen or sulphur compound, as for example carbon tetrachloride or carbon disulphide. The reaction temperature is advantageously between 400° and 440° C. The amount to be passed through the reaction chamber per hour is preferably between 0.05 and 0.3 kilogram of coal paste (consisting of 1 part of coal and 1 part of oil) per liter of reaction space. The coal paste heated to the reaction temperature is led through the reaction chamber and the resulting product is led into a separator in which a level of liquid is maintained. The temperature in this vessel is kept at only about 5° and 30° C. below the reaction temperature so that all heavy oil freshly formed from the coal passes in the vapor phase together with the hydrogen into an adjacent vessel. The product distilling over into the latter consists of from 30 to 50 per cent of constituents boiling up to 325° C. and from 70 to 50 per cent of heavy oil which latter is free from asphalt and soil constituents.

In some cases it is even possible by a chemical pretreatment of the initial materials to obtain particular results during the destructive hydrogenation. For example, by first treating mineral coal or graphite with oxidizing agents, as for example nitric acid, potassium chlorate, chlorine or oxygen, the molecules are rendered more readily attackable and can then be split up into comparatively large and uniform molecules. By sulphonating the material under conversion either before or between the several stages of the treatment and converting the sulphonation products into the alkali metal salts it is possible directly to produce hydroxyl compounds during the destructive hydrogenation. By acting with ammonia on materials containing oxygen or halogen or sulphonic acid groups in the presence of such catalysts as the double compound of zinc chloride and ammonia, amino compounds may be produced. An addition of for example phenols or hydrocarbons rich in hydrogen or halogenated hydrocarbons often favours the formation of valuable compounds of high molecular weight.

#### *The dehydrogenation and related methods*

The usefulness of a dehydrogenation and related methods is due to the fact that in the destructive hydrogenation the cyclic compounds to be recovered are often converted into the corresponding hydro compounds, the boiling points of which usually are about from 20° to 90° C. or more lower than those of the non-hydrogenated compounds originally present in the initial materials; for example anthracene boils at about 360° C. while perhydroanthracene (tetradecahydroanthracene) boils at about 275° C. and chrysene boils at about 448° C. while perhydrochrysene boils at about 360° C. Furthermore the constituents of the initial materials which before the treatment are non-distillable and readily coked,

as for example asphaltic substances of tars or humic substances of coals, are at the same time considerably degraded by the destructive hydrogenation so that in some cases, depending on the reaction conditions, they even yield an additional amount of valuable polynuclear compounds. By the lowering of the boiling point and by the removal of the asphaltic substances, the ring compounds of high molecular weight are distillable without decomposition. Other compounds, as for example those containing oxygen, nitrogen or sulphur, may be split up during the hydrogenation and this facilitates the separation of the remaining compounds.

By the dehydrogenation, the hydro compounds are reconverted or converted into the corresponding less hydrogenated, as for example purely aromatic, compounds, which have by nature a high melting point and pronounced crystallizing power and which are readily split up by fractional crystallization into the desired pure substances. The yield of cyclic compounds may be still further increased in some cases by carrying out the dehydrogenation under such strong conditions that side chains present on the aromatic nucleus are split off.

The dehydrogenation may be effected in any suitable manner. However, several methods have been found to be of particular value, and these will now be described in detail.

One such method consists in heating the materials to be treated to temperatures of from 400° to 700°, especially from 400° to 600° C., preferably while employing catalysts. If it is desired to split off any side chains present, the destructive hydrogenation product is preferably heated to temperatures of from 500° to 1000°, advantageously from 550° to 700° C.

As catalysts may be mentioned silver or metals of the 2nd to 8th groups of the periodic system, as for example magnesium, zinc, aluminum, silicon, titanium, tin, lead, vanadium, chromium, molybdenum, tungsten, uranium, manganese, iron, nickel, cobalt, or rare earth metals, preferably in the form of their compounds, as for example oxides, sulphides, phosphates or halides, or mixtures of such substances. These catalysts may be applied to carriers, as for example active carbon, activated brown coal small coke which has preferably been de-ashed or neutralized with acid, active silica, magnesia or bleaching earths. The dehydrogenation may be carried out in the presence of hydrogen under a total pressure for example of from 5 to 200 atmospheres or more. It is advantageous to employ a partial pressure of hydrogen of less than 50 atmospheres, when the total pressure is 200 atmospheres. Other gases or vapors, as for example water vapor, nitrogen, carbon monoxide or methane, or gas mixtures, as for example water gas, may also be present. Especially valuable results are often obtained by working in the presence of carbon dioxide. For dehydrogenations in the presence of hydrogen, the oxides or sulphides of metals from the 5th and 6th groups of the periodic system, if desired in admixture with other metal compounds, are especially valuable as catalysts.

When it is desired to increase the yield of cyclic hydrocarbons by splitting off side chains which may be present, the dehydrogenation may be carried out first at comparatively elevated temperature, as for example from 350° to 550° C., advantageously in the presence of catalysts, as for example those mentioned above, no split-

ting off or only an incomplete splitting off of the side chains thus occurring, the resulting products or fractions of the same being then treated with such substances as for example aluminum chloride, boron fluoride, iron chloride, or titanium chloride, if desired with an addition of hydrochloric acid, at temperatures of from 50° to 300° C., advantageously from 80° to 200° C., whereby a splitting off of the side chains from the cyclic nuclei takes place. This may also be effected by treating the dehydrogenated product with potassium permanganate, chromic acid or other oxidizing agents at temperatures of from 80° to 150° C.

The splitting off of the side chains by means of the said action of chlorides or by oxidation may, however, be carried out before the dehydrogenation proper, which in this case may be carried out under milder, non-splitting conditions, especially at comparatively low temperatures and with a short time of contact with the catalyst.

In many cases it is advisable to carry out the dehydrogenation of the destructive hydrogenation products of the bituminous substances in stages. According to this modification the dehydrogenation is carried out under such conditions that only comparatively readily dehydrogenatable compounds are dehydrogenated at first; the dehydrogenated compounds may then be separated as such, as for example by crystallization. The remaining oil is then dehydrogenated under stronger conditions, the more difficultly dehydrogenatable compounds thus being converted into crystallizable form. If necessary the oily fraction remaining may be subjected to dehydrogenation under still stronger conditions in one or more further stages.

In the catalytic dehydrogenation trouble may be experienced by reason of local overheating or of substances being deposited on the surface of the catalysts and the consequent alteration in the activity of the catalyst, whereby an unavoidable decrease in the yield takes place.

We have found that this disadvantage is avoided by carrying out the dehydrogenation of the products obtained by destructive hydrogenation in the liquid phase in the presence of finely divided catalysts which are led through the reaction zone together with the products to be treated. For this purpose a small amount, for example from 0.1 to 5 per cent or more, of a finely divided catalyst is added to the hydrogenation product. Suitable catalysts for this purpose are those mentioned above. The initial materials to be dehydrogenated are mixed with the finely divided catalyst and either heated in a gas-heated system, as for example a pipe coil, and then led through an unheated or heated reaction chamber, or for example led through an apparatus heated to the reaction temperature. It is advantageous to add the catalyst only during or after the preheating, and it may also be added in fractions to the material to be treated at several places in the apparatus. The catalyst is separated from the reaction products for example by centrifuging, filtration or distillation and may then be added to fresh hydrogenation products to be dehydrogenated, if desired after complete or partial regeneration.

We have found that complete dehydrogenation can be carried out in a simple manner and the desired compounds obtained in good yields by working with a pressure which should generally not exceed 200 millimeters, pressures of from 2 to 70 millimeters (mercury gauge) being employed

for example. The temperature for the dehydrogenation according to this method is usually between 100° and 700°, advantageously between 300° and 700° C. Suitable catalysts are metals of the 3rd to the 8th groups of the periodic system or their compounds for example molybdenum, tungsten, chromium, uranium, rhenium, manganese and vanadium or their oxides, sulphides and phosphates. It is advantageous to carry out the dehydrogenation in the presence of hydrogen which should, however, not have too high a partial pressure, for example a partial pressure of from 5 to 30 millimeters at a total pressure of 50 to 100 millimeters.

Another method consists in working in the presence of finely divided metals or their compounds in an amount of .01 to 5%, and of acid substances, in particular acids or substances forming the same under the reaction conditions in a lesser amount. It is specially advantageous to employ as catalysts for this purpose metals of the 2nd group, the 4th group, the 7th group and the iron group, as for example zinc, magnesium, titanium, silicon, lead, manganese, iron and tin, the latter advantageously in the form of its compounds. The following are also suitable: aluminum, copper, sodium, potassium and calcium, and also chromium, vanadium, molybdenum and tungsten, the latter chiefly in the form of their oxides and sulphides. The catalysts may also be applied to carriers, in which case they need not necessarily be employed in a finely divided state. Suitable carriers are those mentioned above. It is preferable, however, that in any case the catalyst should be in a finely divided state.

The acid substances are the halogens, as for example chlorine, bromine or iodine, or their compounds with hydrogen, carbon or ammonia, as for example carbon tetrachloride, or readily decomposable metal compounds of these halogens. Other acids, as for example sulphuric acid, nitric acid, phosphoric acid, sulphurous acid or sulphonic acids or carboxylic acids, as for example formic acid or acetic acid, may also be employed. The metal or compound acting as catalyst may be added to the initial material before or during the heating up. The acid substances may be added at elevated temperature, for example at between 50° and 200° C., and at a time when the initial material already contains the metal or metal compound. It has, however, been found to be more advantageous to add the acid substance before the commencement of the heating or during about the first half of the temperature range through which the product is heated in order to attain the reaction temperature. In this case the metal or metal compound may be added simultaneously or, preferably, at a higher temperature, as for example during the second half of the heating period or after the heating.

It has been found to be most advantageous to carry out the process in the liquid phase and continuously so that the catalyst remains for but a short time in the reaction chamber, and suffers no injurious change in its activity; in this manner, moreover, the formation of polymerization products and the splitting of the initial materials by local overheating are avoided. It may however also be carried out in the gaseous phase by passing the vapors over the finely divided catalysts, while adding the acid substances prior to the entrance into the catalyst chamber. It is advantageous to maintain a high partial pressure of the initial materials. It is preferable to work at temperatures of from 400° to 600° C., the speed

of flow and the time during which the substances are present in the reaction chamber being such that practically no splitting off of carbon chains from the initial material takes place but only a splitting off of hydrogen. The reaction may be carried out at atmospheric, reduced or, preferably, increased pressures, as for example at from 10 to 50 atmospheres or more.

Dehydrogenation, if desired while splitting off side chains from cyclic compounds, can also be effected by exposing the initial materials, if desired in the presence of solvents, to the action of silent electric discharges under such conditions as to temperature and duration that the formation of polymerization products is substantially avoided. For this purpose the initial materials are subjected in the usual Siemens' ozone tubes or in apparatus of a similar kind to treatment with silent electric discharges, produced with high tension electric currents, having a tension of at least 50 to 200 volts and preferably above 1000 volts, preferably of high frequency. The frequency should be at least 16 periods and preferably range above 1000 periods per second. When employing initial materials of high boiling point, i. e. above 350° C., it is sometimes advantageous to carry out the reaction in the presence of preferably inert, solvents, as for example illuminating oil or paraffin wax, which are preferably added only in the course of the reaction. As a general rule no discoloration of the foam formed on the liquid under treatment should take place, since this indicated the beginning of a polymerization. The conditions should be such in all cases that the products undergo no appreciable increase in viscosity, i. e. the reaction should be interrupted when merely the dehydrogenation and/or the splitting off of side chains has taken place. The reaction usually proceeds at a temperature of from 20° to 90° C. which should be the higher, the higher the viscosity of the initial material. The duration of the treatment is from about two to ten hours. The treatment may also be carried out in the presence of substances having a catalytic action, for example those mentioned above.

The dehydrogenation may also be carried out in other ways as for example by leading the material to be treated over copper at 350° C. while adding a measured amount of air or oxygen, or by heating it for example at from 150° to 300° C. with sulphur. Agents combining with hydrogen, as for example selenium, tellurium, nitrogen oxides or dilute nitric acid, may also be employed. The dehydrogenation may also be effected by treatment with halogen directly or by halogenation and splitting off hydrogen halides, if desired while adding catalysts. These latter methods have the advantage that they may be carried out at comparatively low temperatures and that the reaction materials are only within the reaction chamber for a short period of time.

A method of treatment which is somewhat related to dehydrogenation in that a splitting off of hydrogen may take place therein, is the distillation of the destructive hydrogenation products with an addition of metals or of condensing or polymerizing agents. For this purpose, the oils are distilled at atmospheric, increased or preferably under reduced pressure. Suitable metals are those from the 1st and 2nd groups of the periodic system and of these the alkaline earth metals and especially the alkali metals are to be recommended. The employment of metals of the 8th group of the periodic system, as for

example iron, is not advisable as a rule. Sodium, potassium, lithium, calcium and zinc may be mentioned as suitable metals. Aluminum chloride, zinc chloride, titanium chloride, ferric chloride, stannous chloride, or boron fluoride, if desired in admixture with substances retarding the reaction, as for example zinc oxide, may be employed for example as the condensing or polymerizing agents, which should be of the type promoting the Friedel-Crafts reaction. The metals or other agents are usually employed in rather small amounts, as for example from 0.1 to 10 per cent of the weight of the oils. The oils may also be treated prior to distillation with a small amount, as for example from 1 to 5 per cent, of a condensing agent at ordinary or elevated temperature, as for example up to 150° C. In this case it is not necessary to add metals or condensing or polymerizing agents during the distillation.

#### *The isomerization*

The isomerization of initial materials containing cyclic constituents belonging at least in part to the hydroaromatic series serves for effecting a molecular rearrangement thereof. In this treatment the cyclic constituents of the initial material which contain 5-membered rings and side chains attached thereto may be converted into compounds with 6-membered rings. Simultaneously a conversion of 6-membered rings into 5-membered rings with side chains may take place. In most cases both types of conversion take place simultaneously so that an equilibrium is finally attained. It is also possible to convert compounds containing at the same time 5-membered rings and 6-membered rings into other compounds in which the 6-membered rings have been converted into 5-membered rings. When the initial materials do not contain hydroaromatic constituents or contain only an insufficient amount thereof, the initial materials may be subjected to a hydrogenation prior to being subjected to the process in accordance with this modification of the present invention. During such hydrogenation, hydroaromatic compounds may also be formed from constituents of a heterocyclic nature, as for example from carbazole, in which case such ring members as nitrogen, oxygen or sulphur are usually split off so that hydroaromatic hydrocarbons are obtained.

In order to effect the isomerization especially such catalysts are used as promote the Friedel-Crafts reaction, as for example aluminum chloride, ferric chloride, titanium chloride or zinc chloride which are preferably used in the form of salts containing water of crystallization. Use may also be made as catalysts of boron fluoride or of metal oxides or sulphides, especially those of the metals of the 5th and 6th groups of the periodic system. The isomerization is effected by heating the initial materials, or more suitably fractions thereof boiling within a narrow range of temperatures or even fractions having a definite boiling point, to elevated temperatures between 50° and 500° C., in the presence of these catalysts, if desired in the presence of gases as for example hydrogen, water vapor, or oxides of carbon. The temperatures used for the isomerization will usually range between about 50° and about 500° C. and should preferably amount to at least about 100° or 120° up to 300° C. The time of the treatment should usually range between 30 minutes and 4 hours, preferably between 1 and 2 hours.

For example, by treating carbazole with hydrogen under atmospheric or elevated pressure in the presence of an oxide or sulphide of a metal of the 6th group of the periodic system, dicyclohexyl is obtained which by the isomerization, for example by heating to about 450° C. in the presence of the oxides or sulphides of tungsten or molybdenum is converted into dimethyldicyclopentyl. By the subsequent dehydrogenation this compound is converted into dimethyldicyclopentadiene. Similarly anthracene may be converted by hydrogenation in glacial acetic acid in the presence of a nickel catalyst into 9,10-dihydroanthracene which in the liquid phase at temperatures of about 350° C. in the presence of molybdenum sulphide and of hydrogen under a pressure of 200 atmospheres is simultaneously isomerized and hydrogenated to form methylfluorene-perhydride. By dehydrogenating this product in the presence of hydrogen under a pressure of 50 atmospheres and at a temperature of about 470° C. in the presence of a mixed catalyst from nickel sulphide and tungsten sulphide a product is obtained which is mainly composed of methylfluorene.

#### *The separation of the polynuclear compounds*

For the separation of the single polynuclear compounds from the products containing the same, use may be made for example of cooling, precipitation, crystallization, dissolution or distillation, each of which treatments may be a fractional one, or several of these methods may be used in combination. In some cases it may be advantageous to refine the crude distillates for removing resinous constituents, as for example by treatment with concentrated sulphuric acid or with caustic alkali solution or with hydrogen under moderate conditions in the presence of refining agents, for which purpose agents having adsorbent properties may be used. The substances of high molecular weight in part often crystallize directly after this first rough separation. The further separation may be carried out by the usual methods, as for example by further distillation or crystallization, the latter being carried out if desired with the addition of precipitants or solvents, or by chemical methods, as for example fusion with caustic potash, sodium amide or alkali metals, or sulphonation.

For example, phenanthrene may be recovered from a fraction passing over between 325° and 345° C., anthracene from the fraction boiling between 300° and 400° C., fluorene from the fraction boiling between 295° and 320° C., or pyrene and chrysene, which may be separated from each other by means of carbon disulphide, from the fraction boiling above 390° C. The precipitated compounds may be separated from the oil by centrifuging or filtering at moderately elevated, ordinary or reduced temperatures, if desired while employing a diluent as for example benzene, pyridine, glacial acetic acid or dioxane. By crystallization from a suitable solvent or by dissolution and precipitation, the substances may be obtained in a state of great purity. Furthermore several of the said substances may be separated from fractions having a comparatively wide boiling point range, the single substances being separated from each other by fractional crystallization or treatment with different solvents or by dissolution and precipitation in stages with the same or different precipitants. When the compounds to be recovered do not crystallize at ordinary or reduced temperatures,

the unitary substances may be recovered by fractional distillation, preferably in vacuo.

The oily fraction remaining after the separation of the crystallizable compounds may be subjected again to dehydrogenation either alone or together with fresh destructive hydrogenation products or fractions thereof, further amounts of crystallizable products often being obtained from the fractions of high boiling point of the resulting products.

It is also possible to separate from the hydrogenation products of high boiling point the crystallizable, partially hydrogenated polynuclear compounds and to subject only the latter to the dehydrogenation.

In order to isolate unitary substances which have not been deposited by cooling of the distillates, the oil freed from crystals may be treated with picric acid. The picrates thus formed may then be separated from the oil by filtration or centrifuging. Cyclic compounds may be isolated from the fractions of the distillate consisting of viscous constituents of high boiling point and also from the distillation residue by treatment with selective solvents, as for example by extraction with one or more solvents, if desired in stages. Suitable solvents are for example illuminating oil, carbon disulphide, alcohol, benzene or xylene.

In the following we shall now give a detailed description of the methods in which use is made of one or several of the steps or operations specifically described in the foregoing.

When the destructive hydrogenation products are distilled with metals or with condensing or polymerizing agents, as described above it is preferable to free the destructive hydrogenation products or their fractions wholly or partly from asphalts and asphaltic substances and preferably from substances not having a neutral reaction and also advantageously from any paraffin wax present. The oils thus freed from asphaltic substances may be further treated with adsorption agents, such as bleaching earths or active carbon, preferably in the presence of solvents which are incapable of dissolving resinous substances in an adsorbed condition, as for example alcohol, ketones or mixtures of alcohol and benzene. The oils thus purified, when they contain paraffin wax, are advantageously cooled to low temperatures in the presence of a diluent. The paraffin wax deposited is separated from the oil solution. The latter is then freed from solvent, the bases then being preferably removed by treatment with acids, as for example sulphuric acid, and the phenols by washing with alkaline liquors, as for example caustic soda solution. If the subsequent distillation is to be carried out in the presence of metals, it has proved advantageous to remove at least the said constituents. If, however, the distillation is to be carried out with condensing or polymerizing agents, the removal of the acid and basic substances is not necessary, though advantageous. When the resulting distillate is cooled, large amounts of crystallizable substances separate.

It is frequently advantageous to subject the pretreated destructive hydrogenation products to a dehydrogenation before or after the distillation with an addition of metals or condensing agents. This may be effected in the manner fully explained above. When the distillation is effected prior to the dehydrogenation, it may be advantageous to carry out a further distillation in the presence of metals or condensing agents after the dehydrogenation. The procedure may also

be, however, that the distillation is carried out under such conditions of temperature that a dehydrogenation of the destructive hydrogenation product is effected at the same time. From the oils freed from the crystallized compounds it is frequently possible to isolate still further amounts of such compounds by subjecting the oils to a dehydrogenation and, if desired, again to a distillation in the manner already described.

A specific method which is valuable especially for the treatment of initial materials containing cyclic constituents belonging at least in part to the hydroaromatic series consists in first heating such initial materials to effect isomerization, as explained in detail above, the resulting products then being subjected to dehydrogenation which in some cases may be accompanied by the splitting off of side chains from the molecules.

It has been found to be advantageous in producing components with side chains to adjust the throughput of coal in the destructive hydrogenation step that while the throughput is within the limits specified above, the amount of constituents boiling above 325° C. in the destructive hydrogenation product corresponds to the amount of unitary substances to be separated. In this manner there is always present a sufficient amount of oil for making fresh coal into a paste. Alternatively, the fraction of heavy oil may be increased by increasing the throughput, the dehydrogenated oil, after removal of the polynuclear compounds, being worked up in another reaction vessel into benzene and middle oil by catalytic destructive hydrogenation.

When it is desired to obtain wholly or partly hydrogenated cyclic compounds of high molecular weight these can be obtained in a simple manner from destructive hydrogenation products of bituminous substances by dehydrogenating the initial materials or their fractions of high boiling point, separating from the resulting reaction product unitary cyclic compounds or mixtures of only a few of such compounds by physical or chemical methods and subjecting the products thus obtained to a hydrogenation to form the desired wholly or partly hydrogenated compounds. In order to obtain a specially good yield of the desired hydrogenated cyclic compounds, it is advantageous to carry out the destructive hydrogenation of the bituminous substances so that at the most only a slight splitting of the initial material but the greatest possible addition of hydrogen to the aromatic compounds present in the initial materials or formed during the reaction take place, in the manner more specifically described above. Any solid constituents contained in the destructive hydrogenation products or their fractions of high boiling point and preferably also the asphaltic substances are separated therefrom before the further treatment. The fractions of high boiling point of the destructive hydrogenation products, which contain the cyclic compounds mainly in the form of their hydro derivatives, are then subjected to dehydrogenation, preferably after they have been split up into fractions having narrow boiling point ranges. The resulting dehydrogenation products contain the cyclic compounds of high molecular weight in a readily crystallizable form. The non-hydrogenated substances thus obtained are then subjected to hydrogenation to form the desired hydro derivatives without any appreciable degradation thereof to lower molecular weight compounds. For example temperatures of from 100° to 300° C. with hydrogen under a pressure of

from 50 to 500 atmospheres or more may be employed in the presence of one of the known hydrogenation catalysts, such as those mentioned above. Thus when employing a nickel catalyst, phenanthrene may be converted into tetrahydrophenanthrene under a pressure of 90 atmospheres at 260° C. and tetrahydrophenanthrene may be converted into octahydrophenanthrene under a pressure of 87 atmospheres at 175° C.

It will be readily understood from the foregoing that it is not necessary according to the present invention to use the destructive hydrogenation exclusively for the production of valuable polynuclear compounds. It is often very advisable to combine the process in accordance with the present invention with the usual destructive hydrogenation for the production of oils for motor fuels, impregnating, lubricating and similar purposes. This may be done by employing for the recovery of the valuable polynuclear compounds only those fractions of the crude destructive hydrogenation products which are particularly suitable for this purpose, the other fractions being worked up in the usual manner for the production of benzines, lubricating oils and so on. Of course, only such destructive hydrogenation products or fractions thereof are suitable for the purposes of the present invention as contain cyclic constituents and as have a boiling point of at least 150°, preferably at least 250° or 280° C.

We shall now further explain our invention by giving a number of specific examples, but we wish it to be understood that our invention is in no way limited to these examples. When in the examples we speak simply of parts, these are always meant to be parts by weight.

#### Example 1

100 parts of mineral coal having a carbon content of 82 per cent, which have been pretreated with dilute sulphuric acid for the purpose of neutralizing the alkaline ashy constituents, are triturated to a paste with 40 parts of topped mineral coal tar and 5 parts of a pulverized iron-molybdenum catalyst. The paste, together with 0.7 cubic meter of hydrogen per kilogram of paste, is pumped continuously through three high-pressure vessels arranged one behind another of which the two first are kept at 200 atmospheres and a temperature of 460° C. while the third is kept at 100 atmospheres and a temperature of 510° C.

An adding on of hydrogen and the degradation of the coal substance into distillable oils takes place in the first two vessels, while in addition to a splitting of C—C linkages the dehydrogenation of mainly the oil fractions of high boiling point takes place in the third. The distillable oils are recovered from the reaction product by steam distillation under reduced pressure. From the fraction which boils between 170° and 270° C. at 50 millimeters (mercury gauge) pyrene and carbazole separate after dilution with 10 per cent of ligroin and allowing to stand for three days at zero C; the pyrene and carbazole may be separated by filtration and crystallization from an equal amount of pyridine.

The remaining oil, after removal of the ligroin, is dehydrogenated again at 550° C. under a pressure of 20 atmospheres of hydrogen and then fractionally distilled. Crystals separate from the distillate from which pure anthracene is obtained by crystallization from benzene and pyridine.

#### Example 2

An oil boiling above 325° C. obtained by the catalytic destructive hydrogenation of mineral coal is heated with hydrogen in a pipe coil up to 500° C. under a total pressure of 120 atmospheres; to the initial material thus heated are added 2 per cent of a catalyst which consists of brown coal low temperature coke which has been treated with hydrochloric acid and washed and impregnated with a solution of ammonium molybdate so that it contains 2 per cent of its weight of molybdic acid, the mixture then being led continuously through the reaction chamber maintained at the same conditions of temperature and pressure. The resulting product is cooled, the pressure released, the catalyst centrifuged off and the remainder carefully fractionally distilled. The fraction boiling up to 200° C. contains a high percentage of aromatic hydrocarbons, as for example toluene and xylene. From the fraction boiling between 200° and 275° C. about 15 per cent of crude naphthalene are obtained on standing (the corresponding fraction of the initial material containing less than 0.5 per cent). The fraction boiling between 275° and 380° C. yields on standing about 25 per cent of crude anthracene (the initial material containing less than 1 per cent). The crude anthracene is split up by crystallization from alcohol into pure anthracene, phenanthrene, acenaphthene and methylated naphthalenes. The oil freed from crude anthracene yields, by fusion with caustic potash, about 15 per cent of fluorene (the initial material containing less than 1 per cent). The residue boiling above 300° C. is distilled to coke, about 20 per cent of coke remaining. From the distillate about 35 per cent of pyrene are obtained by extraction with carbon disulphide while about 5 per cent of chrysene is dissolved out from the remaining oil by glacial acetic acid. The remaining oil fractions freed from solid aromatic hydrocarbons may be dehydrogenated again.

#### Example 3

An oil obtained by destructive hydrogenation of mineral coal at 460° C. under a pressure of 250 atmospheres in the presence of a catalyst containing molybdenum is distilled at a pressure of 15 millimeters (mercury gauge) and the fraction boiling from 180° to 325° C. is isolated. This fraction contains 2 per cent of crystallizable substances which are separated by dilution with a mixture of ether and alcohol and cooling to 50° below zero C.

The remainder of the said fraction together with 0.15 per cent of carbon tetrachloride is heated to 510° C. under a pressure of 50 atmospheres. After the whole has reached the reaction temperature, 0.4 per cent of iron powder is added. The mixture is then allowed to remain at the reaction temperature for ten minutes. The reaction product obtained contains 14 per cent of crystallizable cyclic compounds, mainly crude pyrene, and about 12 per cent of constituents boiling above 325° C. in vacuo.

#### Example 4

Crude naphthalene is passed together with hydrogen under a pressure of 200 atmospheres and at a temperature of about 350° C. over a catalyst consisting of molybdenum oxide, magnesia and zinc oxide. The thionaphthene present in the initial material is destroyed and tetrahydronaphthalene free from naphthalene is obtained. This

product is boiled for 5 hours under a reflux condenser with aluminum chloride containing water of crystallization, whereby it is converted into methylhydrindene. This product is then passed  
 5 at about 300° C. together with hydrogen over a nickel catalyst precipitated on diatomaceous earth, whereby methylindene is formed.

*Example 5*

10 Finely ground mineral coal is impregnated with an amount of hydrochloric acid sufficient to neutralize the alkalinity of its ash and then with ammonium molybdate. The coal thus pre-treated is then mixed in the ratio of 1:1 with a heavy  
 15 oil obtained from the same coal by destructive hydrogenation. The resulting paste is treated at 475° C. with hydrogen under a pressure of 200 atmospheres. The ash and coal constituents are separated from the reaction product by centrifuging and the fractions of low boiling point distilled  
 20 off. The distillation residue is stirred with 50 per cent of benzine and the asphalt which flocculates separated.

The oil free from asphalt is then split up into  
 25 fractions and the latter are led in an atmosphere of hydrogen at a pressure of 40 millimeters (mercury gauge) over molybdenum sulphide at 550° C., whereby dehydrogenation takes place. Acenaphthene, anthracene, pyrene, and chrysene may  
 30 be separated from the dehydrogenation product. The acenaphthene is introduced into an autoclave together with 8 per cent of nickel which has been obtained by the reduction of nickel nitrate. With a temperature of 270° C. and an  
 35 initial pressure of hydrogen of 95 atmospheres, tetrahydroacenaphthene is obtained.

Similarly hexahydropyrene is obtained from  
 40 pyrene at 300° C. under an initial pressure of hydrogen of 80 atmospheres. The hexahydropyrene may be converted into decahydropyrene at 210° C. under an initial pressure of hydrogen of 90 atmospheres.

What we claim is:

1. The process of producing polynuclear carbon  
 45 compounds which comprises subjecting a bituminous material to a temperature of about 200 to 700° C. and a pressure of at least 20 atmospheres in the presence of hydrogen to effect at least a  
 50 substantial hydrogenation of said bituminous material and the formation of substantial and recoverable amounts of said polynuclear carbon compounds and cyclic carbon compounds of the hydroaromatic series, subjecting a fraction of the  
 55 resulting material which contains said polynuclear compounds and said cyclic compounds in substantial amounts to the action of an isomerization catalyst while heating to effect an isomerization of said polynuclear and cyclic compounds and recovering the resulting isomerization  
 60 products.

2. The process as defined in claim 1, wherein the isomerization is effected at a temperature of 50 to 500° C. and in the presence of a catalyst of the Friedel-Crafts type.

3. The process as defined in claim 1, wherein  
 5 the isomerization is effected at a temperature of 50 to 500° C. in the presence of a catalyst selected from the class consisting of the oxides and sulfides of metals of the fifth and sixth group of the  
 10 periodic system.

4. The process of producing polynuclear carbon  
 15 compounds which comprises subjecting a bituminous material to a temperature of about 200 to 700° C. and a pressure of at least 20 atmospheres, in the presence of hydrogen to effect at least a  
 20 substantial hydrogenation of said bituminous material and the formation of substantial and recoverable amounts of said polynuclear carbon compounds and their hydro-derivatives, subjecting a fraction of the resulting products which  
 25 contains said polynuclear compounds and their hydro-derivatives in substantial amounts to the action of a catalyst of the Friedel-Crafts type, while heating to 50 to 500° C. to effect isomerization, subjecting the resulting product to the action of a dehydrogenation catalyst, while heating to effect dehydrogenation, and recovering the desired polynuclear compounds.

5. The process as defined in claim 4, wherein  
 30 the catalyst is selected from the class consisting of oxides and sulfides of metals of the fifth and sixth group of the periodic system.

6. The process as defined in claim 1, wherein  
 35 a dehydrogenation is interpolated between the isomerization and the recovery of the desired polynuclear carbon compounds.

7. The process as defined in claim 1, wherein  
 40 non-hydrogenated polynuclear carbon compounds are recovered and wherein these are subjected to hydrogenation.

8. The process as defined in claim 1, wherein  
 45 a dehydrogenation with a finely divided dehydrogenation catalyst is interpolated between the isomerization and recovery of the desired polynuclear carbon compounds.

9. The process as defined in claim 1, wherein  
 50 a dehydrogenation is interpolated between the isomerization and recovery of the polynuclear carbon compounds and wherein the polynuclear carbon compounds are hydrogenated.

10. The process as defined in claim 4, wherein  
 55 the dehydrogenation is effected at a temperature between 400 and 1000° C.

11. The process as defined in claim 4, wherein  
 60 the polynuclear compounds are subjected to catalytic hydrogenation.

MATHIAS PIER.  
 KARL SCHOENEMANN. 60



## CERTIFICATE OF CORRECTION.

Patent No. 2,216,131.

October 1, 1940.

MATHIAS PIER, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 26, for "and" read --to--; page 5, second column, line 63, for "actic" read --acetic--; page 6, first column, line 52, for "in" read --is--; page 7, first column, line 5, for the syllable "terahydro-" read --tetrahydro- --; line 59, for the word "places" read --place--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 8th day of July, A. D. 1941.

(Seal)

Henry Van Arsdale,  
Acting Commissioner of Patents.