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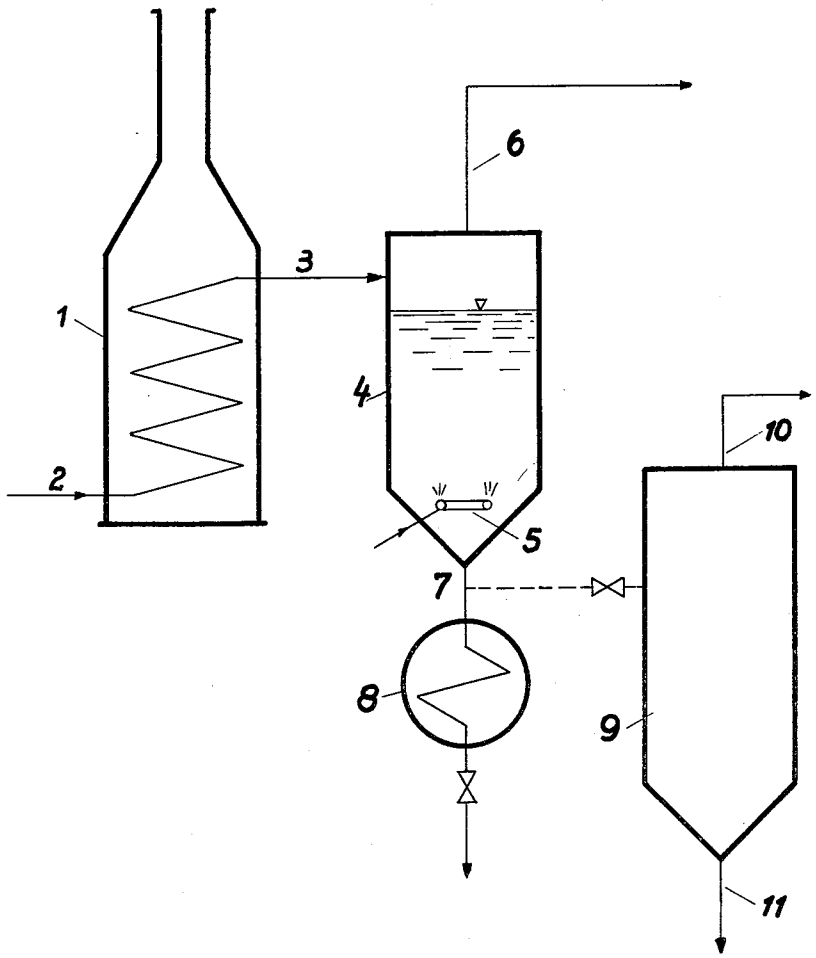

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PROCESS FOR THE TREATMENT OF COAL TARS AND COAL TAR PRODUCTS

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This invention relates to a process for the preparation of coal tar pitches and it has particular relation to a process of this type for the preparation of pitches containing about 55%, and more, of coke residue.

It has been known that by heating coal tars and coal tar pitches in an autoclave for several hours to high temperatures, e.g. about 430° C., products are obtained, which contain about 55% of free carbon. It has also been suggested to separate undissolved components from coal tar by filtration and to convert the filtrate by heating it to high temperatures, into pitch containing 15–50% of components which are insoluble in benzene. Furthermore, it has been known to heat tars or pitches in a tube furnace to high temperatures, e.g. a discharge temperature of about 445° C. and to distill off volatile ingredients from the heated material by flash evaporation into a chamber which is under a very low pressure, in order to increase the softening point. Hard pitches having varying softening points, e.g. up to 155° C., are thus obtained. The production of such high-melting hard pitches by mere heating to still higher temperatures in a tube furnace was considered impracticable in view of the danger of coke formation. Finally, it has been known to produce hard pitches of high softening point by a specific distillation process, in which inert gases were kept in circulation in the system.

It has now been found that coal tars and coal tar pitches can be converted in technically and economically advantageous manner into hard pitches, by heating the starting material in a tube furnace to a discharge temperature in the range of 450–475° C. and allowing the discharged material to further react at this temperature under pressure in a container before the pressure is released in conventional manner and, if desired, the material is subjected to flash-evaporation.

In comparison with oxidizing treatments and other prior art processes, the method of the present invention has significant advantages. By using this method, the polymerizable hydrocarbons can be almost completely converted into hard pitch products and the amount of distillate formed upon release of the pressure, is very low. This, in turn, results in the further advantage that the ash content of the produced hard pitch only slightly exceeds the ash content of the starting material and the pitch prepared according to this invention is particularly suitable and valuable for the production of high grade electrode coke. Moreover, the method of the invention can be carried out in an extremely strongly shortened period of time, in comparison with prior processes.

If starting materials of low ash content, e.g. so-called briquetting pitch of low ash content, are available, the method of the present invention can be combined with the known process of blowing with air or other oxygen-containing gases, whereby the period of stay of the highly heated material in the pressure container, can be still further reduced. In this combination treatment, in which decomposition at very high temperatures takes place simultaneously with oxidation of increased reaction velocity, the velocity of oxidation is the highest if the oxygen-containing gases, e.g. air, are introduced into the material heated to above 400° C. prior to the entrance of said material into the pressure vessel and oxidation is the most complete if said gases are introduced into said material after its entrance into the pressure vessel.

The gases formed by thermal decomposition of the treated tar products and the residue of the oxygen-containing gases are discharged under pressure from the upper part of the pressure vessel.

According to an embodiment of the invention, the pressure of the material in the pressure vessel is released and the material is subjected to flash evaporation, if at a reduced period of stay of the material in the pressure vessel and at incomplete decomposition, nevertheless the production of hard pitch is contemplated. In proceeding according to this modification, volatile ingredients can be removed from the material treated if necessary, so that the final coke residue of the hard pitch is adjusted only by the flash evaporation. However, in this embodiment of the invention it is necessary that—like in the combination with the oxidizing treatment—in spite of the increase of the initial ash-content by concentration—the ash content of the hard pitch does not exceed the maximum value admissible in the production of pitch coke.

In carrying out the present invention, blowing with air, or oxidation, can be also carried out prior to, or simultaneously with, the flash evaporation of pitch or the like. This combined procedure is preferred if the amount of distillate during flash evaporation has to be kept low.

In carrying out the invention, the waste heat of the product can be utilized in various ways. For example, the sensible heat of the hard pitch and/or the condensation heat of products obtained in flash evaporation, can be utilized for preheating the material to be treated according to the invention.

The following examples describe some specific embodiments of and best ways for carrying out the invention, to which the invention is not limited.

Example 1

Through a tube furnace having a heating surface of about 75 m.^{2}, continuously 10 tons briquetting pitch having an initial coke residue of 25–30% and an initial temperature of 350° C., are passed per hour and thereby heated to 475° C., under a pressure of 3 atmospheres. The heat consumption amounts thereby to 750,000 kilogram calories per hour. At a diameter of 50/60 millimeters of the heating tube and a tube length of about 400 meters, the period of stay of the material treated in the tube furnace, amounts to about 5 minutes. Subsequently, the briquetting pitch heated to 450–475° C. is introduced into a thermally insulated decomposition vessel of at least about 30 m.^{3}, which is well thermally insulated and is under the pressure of the tube furnace. This vessel has a conically shaped lower part, from which the hard pitch having a softening point at about 150° C. and a coke residue of about 55%, is continuously discharged after a stay of about 3 hours. The pressure in the decomposition vessel is controlled by the discharge of decomposition gases at the head of the decomposition vessel.

Example 2

Through a tube furnace having a heating surface of about 75 m.^{2}, 10 tons of briquetting pitch poor in ash, of an initial coke residue of 25–30%, and of an initial temperature of 350° C., are continuously passed under a pressure of 3 atmospheres, and heated to about 475° C., with a heat consumption of about 750,000 kilogram

calories per hour. This pitch heated to about 475° C. is introduced into a thermally insulated pressure vessel of about 20 m.^{3}, the volume of which permits a stay of about 2 hours of the material in the vessel. From this pressure vessel the hard pitch which has now a coke residue of about 49%, is subjected to flash evaporation to normal pressure in such a manner that about 10% of the charged briquetting pitch, are received as volatile components in a connected condenser as a distillate of pitch, whereby the coke residue of the hard pitch is increased to about 55% by this flash evaporation.

Due to the use of the pressure vessel connected to the discharge of the tube furnace, the gaseous ingredients formed by decomposition can be continuously drawn off and passed on to further processing in a simple manner.

The temperatures used in carrying out the present invention can be increased, e.g. to 500° C. and higher, for example 525° C. If it is contemplated to obtain at such high temperatures end products which still have the character of pitch and can be liquefied, or at least rendered plastic, by heating, it is necessary to considerably shorten the period of stay of the heated pitch or the like in the zone of thermal aftertreatment. For example, in using as starting material a briquetting pitch having an initial coking residue of about 25–30%, a hard pitch having a coking residue of 55% can be obtained by adjusting the temperature of the pitch at the discharge opening of the tube furnace to about 500° C. and permitting the pitch discharged from the tube furnace to stay in the zone of thermal aftertreatment for about 15 minutes. If the temperature in the tube furnace is increased still further, for example to 525° C. at the discharge of the tube furnace, the period of stay in the zone of thermal aftertreatment can be shortened to 4–5 minutes. A pitch having a coking residue of about 80% can be obtained at a temperature of 525° C. at the discharge of the tube furnace and a period of stay of about one hour in the zone of thermal aftertreatment.

The period of stay in the zone of thermal aftertreatment can be also shortened (*a*) by subjecting the starting material, e.g. pitch, to be treated according to the invention, to an oxidizing treatment at 200–300° C. with solid liquid, or gaseous oxygen carriers, prior to the treatment according to the present invention, or (*b*) by combining such oxidizing treatment with the treatment in the tube furnace and/or in the pressure vessel. This can be done, for example, by heating the pitch or the like essentially to a temperature above 450° C. and adding to it, prior to or after its introduction into the pressure vessel, predetermined amounts of oxygen-containing gases, e.g. air. By the use of such oxidizing treatment the decomposition and polymerization of the starting material can be essentially accelerated.

End products of the above described type having high coking residues can be also obtained by using as starting material tars or mixtures of tar oils with pitches. It is preferred to remove by distillation from the tar oils the relatively easily volatile ingredients prior to their treatment according to the invention.

In this manner for example tar oils from low-temperature carbonization, or generator tars, or tars obtained by the conventional high temperature carbonization of coal, as well as pitches and waste oils of all kinds, can be converted into hard pitches of most varied composition which can be utilized for various uses such as briquetting, binding agents, adhesive masses, starting materials in the production of electrodes, for structural purposes, road building and the like, depending on the extent of conversion by the process of the invention. Pitches yielding particularly high coking residues, e.g. 70–90%, can be shaped and then converted into molded products containing carbon in high concentration, by conventional processes.

Example 3

According to the method of Example 1 tar oil, boiling between 350°–480° C., is used, instead of briquetting pitch. The tar oil is heated to 490° C. in the tube furnace and then treated in the pressure vessel during 1 hour and 50 minutes under 10 atm. and about 490° C. The coking residue of the resulting pitch is 38%, corresponding to DIN DVM 3725, with a softening point of 63° C.; yield of pitch 94–95%.

If the pitch is treated in the pressure vessel 3 hours and 25 minutes under the same conditions, the resulting hard pitch has a coking residue of 55–57%, and a softening point of 115°; the yield is also 95%.

Example 4

According to the method of Example 1 a low-temperature coal tar boiling above 280° C. is heated to 450° C. and then treated in the pressure vessel under 10 atm. at the same temperature during 1 hour.

The resulting pitch with a coke residue of 38% has a softening point of 74° C.; the yield is 90%.

Example 5

According to Example 1 there is treated a mixture of 75% of briquetting pitch (coking residue 31%, softening point 76° C.) and 25% of a tar oil boiling between 320° and 400° C. is treated under 10 atm. and 470° C. during 1 hour and 45 minutes. The obtained pitch with a coke residue of 49% has a softening point of 74° C.; the yield is about 91%.

The coking residue of the pitches obtained by Examples 4 and 5 is increased to more than 55% by extending the thermal after treatment in the pressure vessel.

Example 6

In the above Example 1, the briquetting pitch is treated in the tube furnace at an increased temperature, so that the temperature amounts to about 500° C. at the discharge from the tube furnace. The material discharged from the tube furnace is introduced into the decomposition vessel and subjected there to a stay of about 15 minutes, whereby a pitch yielding a coking residue of about 55% is obtained.

If in this example the discharge temperature in the tube furnace is increased to about 525° C., the period of stay in the decomposition vessel can be reduced to 4–5 minutes. Under otherwise equal conditions, but at a period of stay of about 1 hour in the decomposition vessel, a pitch yielding a coking residue of about 80% is obtained.

Instead of coal tar and/or instead of briquetting pitch, or in mixture with the same other tars, e.g. low temperature carbonization tars or generator tars and other pitches, e.g. pitches obtained from said other tars, and hydrocarbon oils, e.g. oils obtained from tars, can be used in this example.

The briquetting pitches used as starting material in the above Examples 1 and 2, have a softening temperature of, for example, 70 to 80° C., and the ash content of these pitches amounts to 0.1–0.2%. The pressure in the tube furnace may amount to 3–4 atmospheres, and the pressure in the decomposition vessel may amount to 3–4 atmospheres for the treatment of briquetting pitch. As to the thermal treatment of tars and tar oils a pressure of about 10 atmospheres is necessary. As mentioned above, blowing with air of the material treated according to this invention, can be carried out in the pressure or decomposition vessel, or prior to the introduction into the decomposition vessel, e.g. in the tube furnace. Furthermore, instead of oxygen-containing gases, solid or liquid oxidizing agents can be used in the oxidizing treatment of pitch or the like. As examples of such solid and liquid oxidizing agents, lignite, lignin and oxygen containing organic compounds which set free their oxygen under the conditions described above are mentioned. The flash evaporation used in the above Example 2 is carried out in conventional manner. It will be understood by those skilled in the art that these and other modifications can

be made without departing from the scope of the invention, as defined in the appended claims.

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

The content of the coke residue is determined by the method of the German Standard DIN DVM 3725; this method is quite similar to the standardized method described in the book: Abraham, Asphalts and Allied Substances, 5th edition, pages 1132–34.

The appended drawing diagrammatically illustrates a device or arrangement for carrying out the process of this invention.

In the drawing, reference symbol **1** denotes the tube furnace. The pitch, or the like, is fed through tube **2** into and discharged through **3** from the tube furnace, which is heated to the desired temperature by conventional heating means not shown in the drawing. **4** denotes the pressure or decomposition vessel, **5** the coil for the introduction of air, or the like, **6** the opening for the discharge of vapors and gases and **7** the opening for the discharge of the material treated. **8** denotes a pitch cooler, **9** means a flash evaporation chamber, where the gases and vapors are discharged by the outlet **10** and the pitch by **11**.

Oxygen-containing gases can be introduced into and discharged from the pitch, or the like, also in the tube furnace **1** or in the conduit **3** before the entrance in the vessel **4**, through conduits not shown in the drawing.

The products obtained according to this invention are particularly suitable for the production of pitch coke adapted to be used in the manufacture of electrodes.

What is claimed is:

1. A process for the treatment of coal tars, distillation products of coal tars, and mixtures of these starting materials, consisting of passing through a tube furnace under heating and under a pressure of 3–10 atmospheres said

starting materials to a discharge temperature in the range of 450°–525° C. discharging the material substantially without loss of heat and pressure into a thermally insulated decomposition vessel, in which said material undergoes further treatment under a pressure in the range of 3 to 10 atmospheres, without supply of heat to said vessel, and is then discharged as pitch containing at least 55% of coke residue.

2. A process as claimed in claim 1, in which the starting material is subjected to an oxidizing treatment at 200°–300° C. in order to effect its partial decomposition and polymerization prior to its introduction into the tube furnace.

3. A process as claimed in claim 1, in which the starting material is additionally treated with an oxidizing agent during its heating in the tube furnace.

4. A process as claimed in claim 1, in which the starting material is additionally treated with an oxidizing agent during its stay in the thermally insulated decomposition vessel.

5. A process as claimed in claim 1, in which the material discharged from the thermally insulated decomposition vessel, is subjected to flash evaporation.

6. A process as claimed in claim 1, in which the starting material is a coal tar pitch yielding 25–30% coke upon destructive distillation.

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