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[54] **PRODUCTION OF PITCH SUBSTANTIALLY SOLUBLE IN QUINOLINE**

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[51] **Int. Cl.²** **C10C 1/16**

[58] **Field of Search** 208/22, 39, 42, 43, 44

[56] **References Cited**

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[57] **ABSTRACT**

A precursor for needle coke is produced by heat treatment under pressure of a heavy aromatic oil of coal tar origin. The oil is obtained from the distillation of coal tar and is preferably the distillate fraction boiling above 300°C. The precursor is a pitch of a DMFI content of 10 – 30% and substantially quinoline soluble. When processed to coke it yields a needle coke of a preferred orientation ratio above 80.

6 Claims, No Drawings

PRODUCTION OF PITCH SUBSTANTIALLY SOLUBLE IN QUINOLINE

The present invention relates to the production of pitch from coal tar. It relates more particularly to a process for producing pitch of a very low quinoline insoluble content from a coal tar source material.

Coal tar is an exceeding complex mixture of hydrocarbon compounds generally obtained as a by-product of the distillation of coal in coke ovens, e.g., during the manufacture of metallurgical coke. A number of useful commercial products can be derived from the tar by distillation and then, if desired, by further processing of the distillation products. As oil fractions of progressively higher boiling point range are removed from the tar, the viscosity of the residual material increases until finally what is left in the still is a pitch — a material which is substantially solid at ordinary temperatures but softens and flows when heated. Commercial pitches are often classified according to their Softening Point (S.P.) which is the temperature at which the pitch softens sufficiently to undergo a specified deformation under standardized conditions. Another important characteristic of a pitch is its solubility in certain selected solvents, quinoline and dimethyl-formamide or benzene being among such solvents most frequently used. Thus, pitches will often be characterized by the percentage of their content that is insoluble in quinoline (QI) or in dimethyl-formamide (DMFI) or in benzene (BI).

The major product of the commercial distillation of coal tar is, at present, pitch. An important use of pitch is that of a binder in the manufacture of carbon electrodes of the type used, e.g., in the aluminum industry; hence such pitches, formed directly by distillation of coal tar, are often referred to as binder pitch. The properties of such pitches are fairly closely controlled in accordance with specifications to correspond to performance requirements. It is desirable, of course, to make economic use of the distillate as well. The distillate oils are usually taken off in fractions. The light fractions, such as tar acid oil and naphthalene oil have been used as a source of chemicals such as phenols, cresols, naphthalene and the like; however, the economic importance of these oils as a chemical raw material has been declining steadily. The heavier fractions include wash oil and heavy creosote oil or anthracene oil, and have been traditionally used for the preparation of wood preservative compositions, but their importance too, has greatly declined as they are being replaced by synthetic organic preservatives or inorganic formulations. There is often no better use for these fractions than the relatively uneconomic use as fuel.

We have now found that the heavy oils distilled from the tar in the manufacture of electrode binder pitch can be converted by an appropriate heat treatment into a pitch of a very low quinoline insoluble content, such pitch being particularly useful for the manufacture of needle coke.

The present invention, accordingly, provides for distilling a coal tar material to produce a pitch and distillate oil, separating from the distillate oil a heavy creosote fraction of a boiling point above about 300°C and subjecting said creosote oil fraction to heat treatment at a temperature between 400°C and 470°C, under pressure, to produce a second pitch having a DMFI content between 10 and 30% and a QI content not exceeding 2%.

The coal tar material used in this invention is the usual heavy, viscous liquid obtained from the destructive distillation of coal in coke ovens. Tar is now produced essentially as a by-product of the manufacture of metallurgical coke. It is generally rich in aromatic compounds which polymerize readily at elevated temperatures; it usually also contains a certain amount of solid carbonaceous particles. These solid particles result from the cracking accompanying the formation of tar at the high temperatures at which the manufacture of coke is generally carried out. These solids are dispersed in the tar and, upon distillation, remain as a constituent of the pitch. In the analysis of the tar or pitch, these solids constitute the quinoline insoluble material (QI). The presence of even substantial amounts of QI is quite acceptable in binder pitch but may be undesirable in pitches for other use and will be tolerated in only very small quantities in pitches intended for use in the making of needle coke.

In accordance with the invention the coal tar is distilled and thus separated into fractions which are removed from the still and recondensed. The distillation is generally carried out at atmospheric or subatmospheric pressures in a suitable still and may be carried out continuously, for example in a pipe still, or in batch operation, as in a pot still. The main product of the distillation being the residual pitch, the distillation is generally carried to the point where a pitch of the desired Softening Point is obtained. The desired S.P. will depend on the intended use of the pitch, e.g., electrode binder pitch will have a S.P. above 90°C, preferably between 100°C and 120°C, core pitch used in foundry work will have a S.P. 130°C – 150°C, while the S.P. of an impregnating pitch, used for the impregnation of fibrous material for use in the building industry, would be about 70°C – 80°C. In the majority of pitches so formed the DMFI content will be about 10 – 30% and the QI content will be about 2 – 15%.

Of the oils removed from the tar by distillation only the heavy fraction will be suitable for use in making pitch according to the present invention. This heavy fraction includes the heavy creosote oil or anthracene oil and may even include a portion of the wash oil; it generally consists of the fraction at least about 90% of which boils at about 300°C or higher, and is sometimes referred to herein as the fraction of a B.P. above 300°C. These oils consist to a very large extent of aromatic hydrocarbons, such as anthracene derivatives or the like, and upon heat treatment in controlled conditions, polymerize to a pitch which is substantially completely soluble in quinoline.

As indicated, the heavy oil is now subjected to heat treatment under controlled conditions. The heat treatment may be carried in a closed vessel under autogenous pressure or in a continuous type apparatus where, e.g. the feed material is introduced into, and circulated through, a heating coil passing through a heat exchanger and pitch is removed continuously or intermittently from the apparatus. The conditions of treatment are important for the quality of the pitch and also determine in large measure the quality of the coke that will eventually be made from the pitch. The grade of coke that is desirably produced by subsequent treatment of the pitch of this invention is often referred to as needle coke. This is a coke having a striated appearance and a needle-like structure, with an X-ray diffrac-

tion pattern showing an orderly crystal orientation particularly developed in one direction. When such coke is graphitized, the graphite is characterized by a very low co-efficient of thermal expansion, hence such coke is particularly useful for the making of graphite electrodes for electric arc furnaces, e.g. for use in steelmaking and the like. The ordering of molecules and spherule formation that ultimately leads to the anistropic structure of the coke begins quite early in the pitch formation stage and is influenced by the conditions of the heat treatment to which the oil is subjected. These conditions, therefore, must be controlled. If the treatment is too severe, coking will occur simultaneously with the development of pitch and QI material will appear in the pitch: the appearance of such materials at this stage in any appreciable amount will generally hinder the formation of the orderly anisotropic structure. On the other hand, the polymerization of the oil to pitch necessarily involves the formation of a certain amount of DMFI material, and in fact a certain minimum DMFI content is necessary to secure from the pitch, upon subsequent treatment, an acceptable yield of coke. Thus the conditions of pitch formation will be controlled to produce a pitch having a DMFI content between 10 and 30%, and a QI content as close to 0 as practicable and in any case not greater than 2%. The formation of DMFI material in higher amounts than those stated usually goes together with the formation of QI components and is, therefore, undesirable, while a lower DMFI content of the pitch generally results in relatively low yields of coke upon subsequent coking of the pitch.

It is preferred to carry out the heat treatment of the oil at a temperature between 400°C and 470°C, preferably between 420°C and 460°C, at super-atmospheric pressure, and for a time between 1 and 24 hours. The time and temperature are coordinated, shorter times generally being used with higher temperatures within the range and the pressure can be maintained within a wide range, from about 10 to about 500 psig. Since the DMFI content of the treated material increases with the length of treatment, the rate of increase being greater the higher the temperature, the pitch formation is conveniently controlled by setting or adjusting the temperature and time of treatment, within the ranges as hereinabove stated, so as to obtain a pitch of a DMFI content between 10% and 30%. In these conditions, a pitch substantially completely soluble in quinoline is obtained in high yields relative to the oil starting material, and upon further processing anisotropic graphitizable coke is obtained in green yields of between 30 to 55% based on the oil starting material.

The pitch so produced has many applications, e.g., as a material for the manufacture of carbon anodes for the aluminum industry, or as an impregnating pitch, or as a raw material for carbon fibres, but a preferred use is for the making of needle coke. The preparation of coke from pitch is known, the methods entailing essentially a graduated controlled heating of the pitch, prolonged heat soaking, and finally a calcining of the coke so formed at a temperature of about 1200°–1300°C. The coke formed from the pitch of this invention, as above indicated, has a crystalline structure of a pronounced anistropic character, as reflected in its X-ray diffraction pattern, the crystal development along the vertical *c* direction (stacking direction) being much greater than along the horizontal *a* direction. The ratio of the size of the crystallite in the *c* direction to the size along the *a* direction is the so-called preferred orientation ratio (P.O.R.). The higher the ratio, the more anistropic the structure and the better the quality of the coke: a P.O.R. value above 80 is considered very satisfactory. Pitches prepared in accordance with the invention yielded on coking anistropic cokes of a P.O.R. value generally in excess of 80, and in a great number of cases — in excess of 120. By contrast, pitches prepared from the same oil at temperatures exceeding 470°C contained substantial quantities of QI material and on coking yielded coke of a P.O.R. as low as 30 – 40.

The following examples are illustrative of the invention without in any way limiting the same.

EXAMPLE I

A crude coal tar of specific gravity 1.2, obtained from a by-product oven, was passed through a heat exchanger to a dehydration tower. There the water and other low-boiling constituents were flashed off. The dried tar was sent through a direct fired heat exchanger to raise its temperature to about 750°F. From the heat exchanger the tar entered onto a plate in a fractionating column where fractionating took place: the oil vapours passed upwards to a condenser, and the pitch product collected at the bottom. The yield of pitch was about 60% (based on dehydrated tar) and its properties were: S.P. 100°C; QI about 10%; DMFI 22%. The oil was collected in four fractions: a tar acid fraction 95% of which boiled below 215°C, a napthalene oil fraction 95% of which boiled between 215° and 230°C, a wash oil fraction 95% of which boiled between 230° and 300°C and a heavy creosote fraction 95% of which boiled above 300°C. The heavy creosote fraction constituted about 20% off the initial tar and about 50% of the total distillate oil.

A number of samples of the heavy creosote oil, 40 grams each, were heated in a sealed reactor under autogenous pressure at a temperature and for a time as shown in Table I below. The reactor consisted of a tubular container one inch in diameter and 9 inches long, sealed at one end and covered at the other with a cap fitted with a pressure gauge and a relief valve. The container was fully immersed in a steel block, 4 inches in diameter, heavily insulated and heated by three cartridge heaters distributed 120° apart. Temperature was measured by a thermocouple. A high yield of pitch was obtained from the treatment. The pitch was removed and tested. A number of the pitches so obtained were further processed to coke, the coke was analyzed for its diffraction pattern and the respective preferred orientation ratios (P.O.R.) were measured. These conditions of treatment of the oil samples and the properties of the pitch obtained from such treatment are shown in Table I:

TABLE I

No.	Treatment Time Hrs.	Temp. °C.	Press psig	Yield % (on oil)	Pitch Properties MF-I %	Q-I %	Coking Value (%)
B 28	18	420°	100	90	25.0	1.0	49.3
B 81	6	435°	150	90	10.1	0	30.2
B 166	4	445°	250	95	11.2	0	32.1
B 167	4	452°	280	97	15.8	0.5	38.0
B 168	4	455°	300	94	20.0	0.8	43.8
B 170	4	464°	425	92	20.4	0.8	48.0

The P.O.R. values of these coke samples were of the order of 135 – 145.

EXAMPLE II

The heavy creosote oil fraction obtained from the initial distillation of tar in Example I was subjected to heat treatment in a pilot apparatus consisting essentially of a reactor (holding tank) and a recirculating coil. The reactor was provided with an inlet for the feed oil and an outlet for the pitch product and was further fitted with a gas remover, with suitable instrumentation for measuring temperature and pressure, and with the necessary safety devices. The reactor was insulated to mimimize heat losses. The recirculating coil was immersed in a salt bath maintained at a temperature 20°–40°C higher than the temperature of treatment so as to compensate for heat losses and maintain the temperature of the oil circulating therethrough at the temperature of treatment. Some of the gases formed were removed during the treatment, so that the pressure within the apparatus was maintained substantially constant. Each run was carried out with 4 gallons of oil and the treatment was carried out batchwise. By maintaining stable conditions a uniform product was obtained throughout each run. The conditions of treatment and the properties of the pitch obtained are shown in Table II:

TABLE II

No.	Treatment Time Hrs.	Temp. °C	Press. psig	Yield % (on oil)	Pitch Properties DMF-I %	Q-I %	Coking Value (%)
P 140	17	420°	20	73.5	17.0	0.6	39.4
P 100	9.5	425°	30	77	14.7	0.4	35.0
P 7304	8	430°	20	75	12.7	0.2	34.0
P 110	8.5	430°	30	83	17.1	0.6	38.5

The P.O.R. value of the samples tested was about 125.

What we claim is:

1. A process for producing pitch from a coal tar material comprising: distilling said coal tar material under atmospheric or reduced pressure to produce a pitch and distillate oil,

separating from said distillate oil a heavy creosote oil fraction having at least 90% of its constituents boiling above 300°C,

subjecting said creosote oil fraction to heat treatment at temperatures 400° – 470°C under pressure 15 – 500 psig to produce a pitch, and

terminating said heat treatment when a pitch having a DMFI content between 10 and 30% and a QI content not greater than 2% is obtained.

2. The process of claim 1 wherein the time of treatment is between 1 and 24 hours.

3. The process of claim 1, wherein the heat treatment is carried out at a temperature between 420°C and 460°C.

4. The process of claim 1, wherein the said creosote oil fraction is subjected to heat treatment in a closed vessel under autogenous pressure.

5. The process of claim 1, wherein said creosote oil fraction is passed continuously through a heating zone under pressure to effect the heat treatment thereof and said pitch having a DMFI content between 10% and 30% and a QI content not greater than 2% is continuously withdrawn.

6. A pitch when produced according to the method as defined in claim 1.

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