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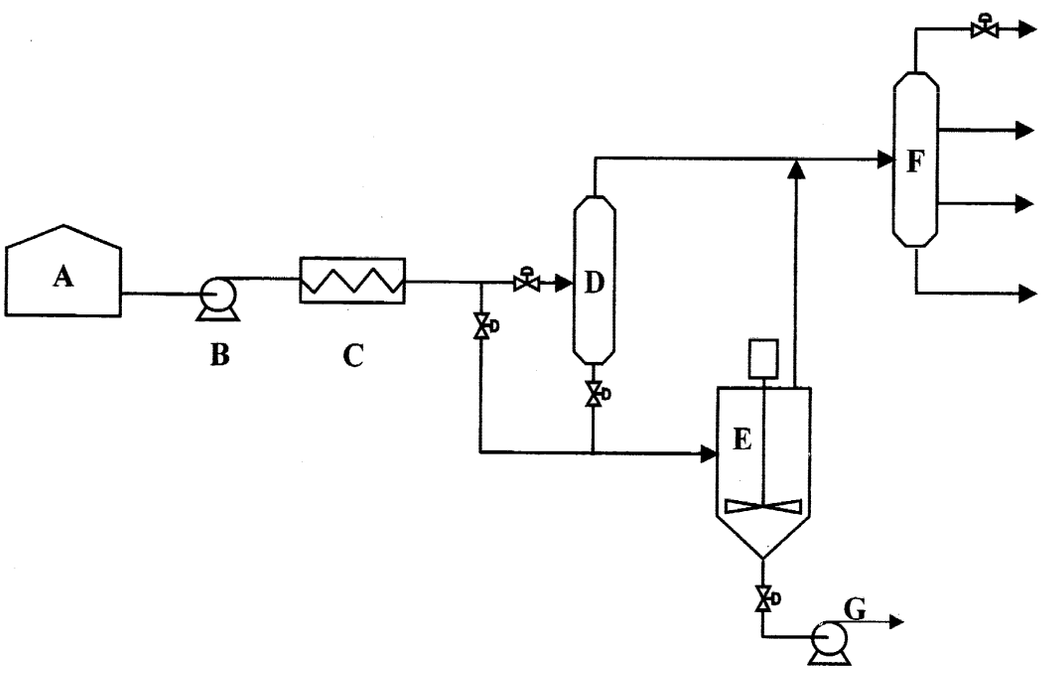
(54) Highly aromatic petroleum pitches, their preparation and use in the manufacture of electrodes

(57) A procedure for obtaining non-polluting petroleum pitches for their use in the manufacture of electrodes and other graphitic compositions. It comprises the subjecting of a petroleum fraction or residue to a heat treatment at temperatures lying between 350° and 470° C, preferably between 370° and 430° C, for a time less than 120 minutes, preferably less than 60 minutes and in an inert atmosphere at a pressure under 20 atmospheres, preferably under 10 atmospheres absolute.



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Description

[0001] The present invention relates to a procedure for producing petroleum pitches of the type termed commercially as " binding" or " impregnating" , to the pitch so obtained and to its use in the fabrication of anodes for the Aluminium industry, electrographites for steel production, and also the conforming, agglomeration and impregnation of carbon compounds and ceramic (refractory) materials, and in the production of general purpose carbon fibres.

[0002] The pitches that constitute the purpose of the present invention are produced from petroleum fractions and residues and have the advantage, when compared to those presently in use and obtained from the distillation of coal tar, of being much less toxic and less polluting in terms of poly-aromatic hydrocarbons (benzo(a)pyrene, crysene, dibenzo-anthracene, etc.).

[0003] The production of electrical carbons (anodes and electrographites), of carbon agglomerates, and of graphite, has the need to make use of materials that provoke mutual adherence of the grains and particles of the different types of carbon, coke or graphite employed in their production process. There is also a requirement for a material which, once the shaping process of the piece or electrode is over, through impregnation of its outside surface, seals the open pores and improves the end properties of the block. The first type of material is commercially known as *agglomerating pitch;* and *impregnating* in its second application.

[0004] The materials employed for binding or impregnating must fulfil different characteristics among which are:

- Once the carbon artefact is ready, the binding or impregnating agent must not reduce the density or conductivity of the whole;
- Result in strong bonding between particles, low post-carbonising porosity and high mechanical strength;
- Sufficient fusibility (softening point) and satisfactory viscosity to permit the correct mixing and compacting of the artefact;
- High degree of purity and absence of catalytic metals from the oxidation and gasification reactions;
- Low Sulphur and ash content;
- High coke yield and easy graphitization, if necessary.
- Very easy to extrude, meaning the production of a monofilament in a continuous and highly uniform manner.

[0005] All these properties are met by both commercial coal tar pitches and the petroleum pitches object of this invention. Nevertheless, the petroleum pitches obtained according to the procedure claimed herein have the exceptional virtue of being environmentally clean: they produce practically no polluting gaseous emissions, like carcinogenic polyaromatics of the benzo(a)pyrene, crysene, dibenzoanthracene, etc. types.

[0006] Nor are they present in a meaningful amount in the solid artefact. When comparing the contents in these carcinogenic polyaromatic hydrocarbons of coal tar pitches and those of petroleum produced according to the process of the invention, the latter offer a reduction of up to 95%, both in emissions and by weight of carcinogenic polyaromatics in the solid pitch.

[0007] The objective of this invention is to define the process and operating conditions in order that through the heat treatment of petroleum fractions or residues selected for this purpose, they evolve; and by combining cracking, dehydrogenation and polymerisation reactions it is possible to obtain a petroleum pitch with suitable properties to be used for binding or impregnating in the production of anodes for the production of Aluminium, electrographites for producing steel, in the manufacture of whatever composition or conglomerate of a carbonaceous nature and in the production of carbon fibres.

[0008] As a result of his research, the applicant has discovered how to obtain a highly aromatic pitch, with variable anisotropy contents in the range 0 - 70%, according to the wish of the producer; and insoluble in Toluene and Quinoline within the range 0 - 50% and 0 - 30% by weight, respectively, again according to the wish of the producer, by controlling the variables of this new process.

[0009] In addition to permitting pitches to be obtained with coke yields (40 - 70%) and softening points (60 - 250° C) suitable for their subsequent use (mainly anodes, electrographites and carbon compounds),this petroleum pitch is environmentally " cleaner" than that of coal tar. In the solid pitch, the equivalent content in benzo(a)pyrene, is below 4000 ppm; the emission of PAHs in gases being less than 6 mg/m^3. In both cases these contents imply a reduction of 85-95% in comparison with those encountered in coal tar pitches.

[0010] These new petroleum pitches can replace those currently in use by manufacturers of electrodes, electrographites and carbon compositions without any requirement to alter any stage in their productive system since they adapt to the latter and satisfy the specifications set by the user in each case.

[0011] Consequently and in accordance with a first aspect, the present invention provides a procedure for obtaining non-polluting petroleum pitches, of the binding or impregnating type, said procedure comprising the subjecting of a petroleum fraction or residue to a heat treatment at temperatures lying between 350° and 470° C, preferably between 370° and 430° C, for a time less than 120 minutes, preferably less than 60 minutes and under a pressure under 20

atmospheres absolute, preferably under 10 atmospheres absolute.

[0012] The input material for producing petroleum pitches according to the invention includes industrial petroleum residues, such as atmospheric petroleum residues, residues obtained under reduced pressure conditions, or heavy petroleum oils coming from thermal or catalytic cracking of petroleum-derived products.

[0013] The more reactive the feed is or the higher the process temperature, the faster does the system evolve, and it is difficult to control, the material at the end being transformed into a solid product totally insoluble in quinoline and termed coke. This material lacks the binding and impregnating properties of petroleum pitch.

[0014] On the other hand, if the temperature or reactivity of the feed are not sufficiently high, the process is more easily controllable and the formation of coke can be avoided.

[0015] The feed selected, as may be seen from the process schematic attached, is held in a tank (A) at between 100° and 150° C, is extracted by pump (B) and heated in an oven (C) up to a minimum temperature of 300° C without undergoing any change in chemical composition. Next it is transferred to a flash distillation column (D) in order to remove the light distillates and then to a stirred reaction chamber (E), or else directly without passing through the distillation column (D), to the said stirred reaction chamber. In both cases the distillates are sent to a fractioning column (F) in order to be used later. In the reaction chamber (E) the product is treated thermally with the provision of external heat in order maintain the temperature constant. This temperature shall be maintained between 350° and 470° C, preferably between 370° and 430° C, for a dwelling time less than 120 minutes, preferably less than 60 minutes and under a pressure under 20 atmospheres absolute, and preferably under 10 atmospheres absolute.

[0016] During this stage different dehydrogenation, cracking and polymerisation reactions occur within the material, producing a high amount of distillates ranging between 40 and 90%. The removal of these distillates from the reaction mass results in an increased density and viscosity of the medium, making highly its outflow from the reactor. By controlling the variables of pressure and temperature, it is possible to manage that the pitch produced in the reactor can flow through the outlet (200-350° C) or an extruder (G) in order to transfer it to a storage tank where it shall be kept liquid at the corresponding temperature or else to a conveyor belt system in an inert atmosphere where the pitch produced solidifies.

[0017] The product so obtained proves to be a highly aromatic pitch, with anisotropy contents variable in the range 0-70% (measured as a mesophase percentage observed in a polarised light optical microscope over a total of 5000 points), at the will of the producer, and insoluble in Toluene and Quinoline within the range 0-50% and 0-30% respectively, also at the will of the producer, through the control of the variables in this new process. These new petroleum pitches can replace those currently being used by manufacturers of electrodes, electrographites and carbon compositions with no need to alter any stage of their productive system since they adapt to the latter and satisfy the specifications set by the user in each case. Likewise they can be used as agglomerating agent in refractory products and a base material for producing general purpose carbon fibre.

[0018] The product obtained, as can be gathered from the details of this description, in addition to having softening points (60-250° C) adaptable to its subsequent use, is environmentally " clean" . In the solid pitch, the equivalent benzo (a)pyrene content is below 4000 ppm; their PAH emission in gases being less than 5 mg/m^3. In both cases, these contents imply a reduction of 85-95% in comparison with those found in coal tar pitches presently in use.

[0019] According to a second aspect, the present invention provides a highly aromatic petroleum pitch, which has the following properties:

- anisotropy content of 0-70%;
- content of matter insoluble in Toluene and Quinoline of 0-50% and 0-30%, respectively;
- coke yield of between 40 and 70% when carbonised at 1000° C;
- softening point between 60° and 250° C;
- PAH content measured as equivalent benzo(a)pyrene less than 4000 ppm;
- PAH emission in gases less than 5 mg/m^3.

[0020] Finally, and according to a third aspect, the present invention provides for the use of highly aromatic petroleum pitches which have the properties aforementioned and obtained by the procedure described above, in the manufacture of anodes, in particular anodes for the aluminium industry, electrographites for steel production, as well as in the conforming, agglomerating and impregnating of carbon compositions and graphitic materials and in the fabrication of carbon fibres.

[0021] Herebelow examples are given by way of illustration but not restrictively, of the procedure of the present invention.

Example 1

[0022] A decanted oil obtained by catalytic cracking in a fluid bed of a light petroleum residue, with an asphaltenes

content less than 0.8%, and density of between 1.02 and 1.03 g/cm^3, is subjected to heat treatment at 460° C for 30 minutes in an inert atmosphere and under a pressure of 4 atmospheres absolute. Afterwards it is cooled down to 210° C during five minutes, the pressure being maintained constant, and is extracted from the plant becoming solid at the outlet. The resulting product is 32.5% by weight of the total decanted oil. The resulting product, termed petroleum pitch, has the following properties:

TABLE I

Matter insoluble in Toluene(% by weight)	31.2
Matter insoluble in Quinoline(% by weight)	13.1
Viscosity at 177° C (cP)	1210
Viscosity at 240° C (cP)	280
Ring and Ball (°C)	118
Sulphur (% by weight)	2.2
Fixed carbon yield (% by weight)	57

[0023] Moreover, this petroleum pitch is environmentally " cleaner" than that of coal tar since its content in PAHs measured as equivalent benzo(a)pyrene is 3600 ppm with a PAH emission in gases of 6 mg/m^3. In both cases these contents imply a reduction of 85-95% in comparison with the figures corresponding coal tar pitches presently in use.

[0024] This petroleum pitch can replace those in use by manufacturers of electrodes, electrographites and carbon compositions without any requirement to alter any stage in their productive system since they adapt to the latter and satisfy the specifications set by the user in each case.

Example 2

[0025] A petroleum residue coming from an ethylene producing operation starting with Naphtha, with an asphaltenes content of 9%, density of 1.07 g/cm^3 at 15° C and Sulphur content less than 0.5%, is subjected to a pre-heating treatment at 300° C for 8 minutes in an inert atmosphere and at atmospheric pressure, later reaching 410° C for 30 minutes in an inert atmosphere and at a pressure of 4atmospheres absolute. Afterwards it is cooled down to 210° C during five minutes, the pressure being maintained constant, and is extracted from the plant becoming solid also in an inert atmosphere at the outlet. The resulting product is 34.2% by weight of the total residue fed to the plant.

[0026] The resulting product, termed petroleum pitch, has the properties indicated in Table II, column A:

TABLE II

Example	2	3
Column	A	B
Matter insoluble in Toluene(% by weight)	27.6	22.01
Matter insoluble in Quinoline(% by weight)	<0.1	<0.1
Viscosity at 177° C (cP)	7500	474
Viscosity at 204° C (cP)	1150	119
Ring and Ball (°C)	149	100
Sulphur (% by weight)	<0.1	<0.1
Carbon yield (% by weight)	59	51
Commercial equivalent	" binding "	" impregnating "

[0027] This petroleum pitch is environmentally " cleaner" than those of coal tar for its low Sulphur content (less than 0.1% by weight) and the low PAH concentration (measured as equivalent benzo(a)pyrene) present in it (3290 ppm)

and its low PAH emission in gases of (5 mg/m^3), but in addition it can replace the pitches presently in use by manufacturers of electrodes, electrographites and carbon compositions without any requirement to alter any stage in their productive system since they adapt to the latter and satisfy the specifications set by the user in each case, with the advantage of having, with respect to coal tar pitches, 85-95% less PAHs expressed as equivalent benzo(a)pyrene.

Example 3

[0028] A petroleum residue coming from an ethylene producing operation starting with Naphtha, with an asphaltenes content of 9%, density of 1.07 g/cm^3 at 15° C and Sulphur content less than 0.5%, is subjected to a pre-heating treatment at 300° C for 8 minutes in an inert atmosphere and at atmospheric pressure, later reaching 420° C for 40 minutes in an inert atmosphere and at a pressure of 11 atmospheres absolute. Afterwards it is cooled down to 210° C during five minutes, the pressure being maintained constant, and is extracted from the plant becoming solid also in an inert atmosphere at the outlet. The resulting product is 36.8% by weight of the total residue fed to the plant.

[0029] The resulting product, termed petroleum pitch, has the properties indicated in Table II, column B.

[0030] This petroleum pitch is " cleaner" than those of coal tar for its low Sulphur content (less than 0.1% by weight) and the low equivalent benzo(a)pyrene concentration present in the pitch (1820 ppm) and PAH emission in gases (4 mg/m^3), but in addition it proves to be a product which can replace the pitches presently in use by manufacturers of electrodes, electrographites and carbon compositions without any requirement to alter any stage in their productive system since they adapt to the latter and satisfy the specifications set by the user in each case, with the advantage of having, with respect to coal tar pitches, 85-95% less PAHs expressed as equivalent benzo(a)pyrene.

[0031] In Table III attached hereto are to be found details of PAH and equivalent benzo(a)pyrene analyses of two commercially available pitches and the pitches of example 2 and example 3.

Table III.

Comparison of PAH (ppm) and Benzo(a)pyrene (ppm) contents in petroleum and commercially available carbon pitches								
	Commercially available binding carbon pitch		Commercially available impregnating carbon pitch		Petroleum pitch A (Example 2)		Petroleum pitch B (Example 3)	
	PAHs	Equivalent B(a)P	PAHs	Equivalent B(a)P	PAHs	Equivalent B(a)P	PAHs	Equivalent B(a)P
Fluorene	534		1250		1117		80	
Phenantrene	3714		5878		9095		533	
Anthracene	2611		1792		1770		180	
Fluoranthene	23524	800	12988	442	1907	65	311	11
Pyrene	15553		9774		3473		770	
Benzo(a) anthracene	17267	570	9149	302	1530	50	449	15
Crysene	22248	5784	11415	2968	1678	436	588	153
Benzo(b) fluoranthene	15199	1520	18079	1808	560	56	350	25
Benzo(k) fluoranthene	15955	160	14173	142	722	7	353	4
Benzo(e) pyrene	7889	394	8793	440	667	33	398	20
Benzo(a) pyrene	16048	16048	15571	15571	1513	1513	838	838
Perylene	4176		3245		214		100	
Indeno (1,2,3,c,d) pyrene	18434	1843	33948	3395	1318	132	814	81
Dibenzo(a,b) anthracen e	2595	3632	4510	6314	360	504	240	336
	7486	7486	13815	13815	493	493	338	338

Table III. (continued)

Comparison of PAH (ppm) and Benzo(a)pyrene (ppm) contents in petroleum and commercially available carbon pitches								
	Commercially available binding carbon pitch		Commercially available impregnating carbon pitch		Petroleum pitch A (Example 2)		Petroleum pitch B (Example 3)	
	PAHs	Equivalent B(a)P	PAHs	Equivalent B(a)P	PAHs	Equivalent B(a)P	PAHs	Equivalent B(a)P
Benzo(g,h,i) perylene	2232		4307		204		166	
Dibenzo (1,2,4,5) pyrene								
	180463	38238	168689	45196	26622	3290	6409	1820
Total (ppm)	18.0		16.9		2.7		0.6	
% by weight								

Example 4

[0032] A residue coming from an ethylene producing operation starting with Naphtha, with an asphaltenes content of 9%, density of 1.07 g/cm^3 at 15° C and Sulphur content less than 0.5%, is subjected to a pre-heating treatment at 300° C for 5 minutes in an inert atmosphere and at atmospheric pressure, later reaching 400° C for 30 minutes in an inert atmosphere and at a pressure of 1.1 atmospheres absolute. Afterwards it is cooled down to 210° C during five minutes, the pressure being maintained constant, and is extracted from the plant becoming solid also in an inert atmosphere at the outlet. The resulting product is 30.4% by weight of the total residue fed to the plant.

TABLE IV

Matter insoluble in Toluene(% by weight)	30.0
Matter insoluble in Quinoline(% by weight)	1.0
Viscosity at 177° C (cP)	9000
Viscosity at 240° C (cP)	850
Ring and Ball (°C)	190
Sulphur (% by weight)	0.1
Fixed carbon yield (% by weight)	64

[0033] This petroleum pitch is " cleaner" than those of coal tar for its low Sulphur content (less than 0.1% by weight) and the low concentration of PAHs measured as equivalent benzo(a)pyrene present in the pitch (2250 ppm) and PAH emissions in gases (4 mg/m^3). This pitch has an important facility for extrusion, producing mono-filaments in a continuous and highly uniform manner.

[0034] According to another aspect of the invention, in order to alter determined properties of the pitches, for example the wettability, a coal tar can be added to the petroleum residue or fraction before subjecting the latter to the heat treatment, said coal tar being in amounts lying between 10 and 90% by weight and preferably between 30 and 70%.

Claims

1. A procedure for obtaining non-polluting petroleum pitches, of the binding or impregnating type, characterised in that said procedure comprise the subjecting of a petroleum fraction or residue to a heat treatment at temperatures lying between 350° and 470° C, preferably between 370° and 430° C, for a time less than 120 minutes, preferably less than 60 minutes and under a pressure of under 20 atmospheres absolute, preferably under 10 atmospheres absolute.

2. A procedure, in accordance with claim 1, characterised in that the initial petroleum fraction or residue is heated previously to a temperature of between 100 and 150° C

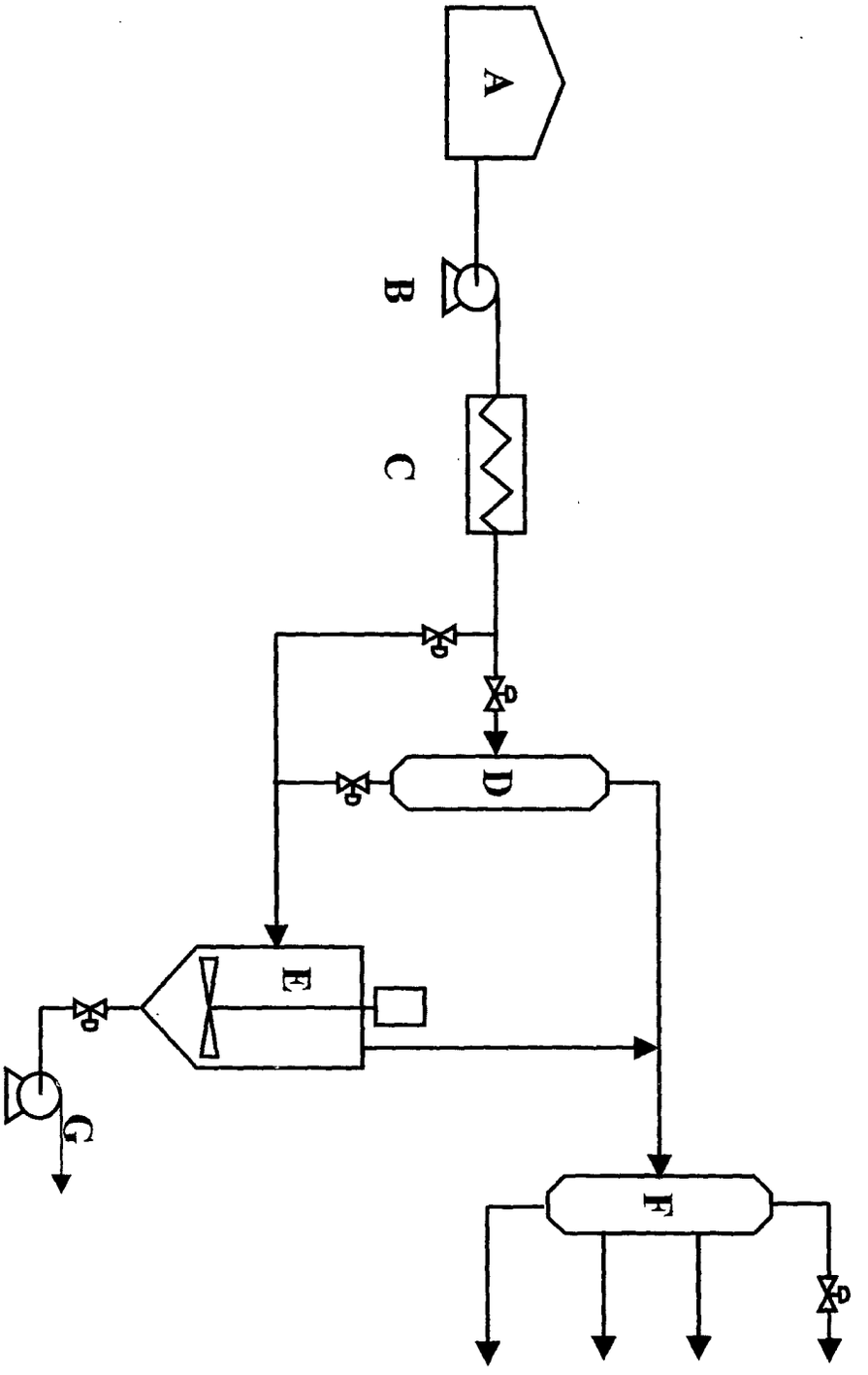
3. A procedure, in accordance with claims 1 and 2, characterised in that as starting material use is made of industrial petroleum residues, such as atmospheric petroleum residues, residues obtained under reduced pressure conditions, or heavy petroleum oils coming from thermal or catalytic cracking of petroleum-derived products.

4. A highly aromatic petroleum pitch, which has the following properties:

- anisotropy content of 0-70%;
- content of matter insoluble in Toluene and Quinoline of 0-50% and 0-30%, respectively;
- coke yield of between 40 and 70% when carbonised at 1000° C;
- softening point between 60° and 250° C;
- PAH content measured as equivalent benzo(a)pyrene 85-95% less than carbon pitches presently used;
- PAH emission in gases much less than carbon pitches presently used.

5. The use of highly aromatic petroleum pitches which have the aforementioned properties and obtained by the procedure described above, in the manufacture of electrodes, in particular anodes for the aluminium industry, electrographites for steel production, in the conforming, agglomerating and impregnating of carbon compositions and graphitic materials and in the fabrication of carbon fibres.

6. Procedure in accordance with the previous claims, characterised in that a coal tar can be added to the petroleum residue or fraction before subjecting the latter to the heat treatment, said coal tar being in amounts lying between 10 and 90% by weight and preferably between 30 and 70%.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