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COKING A MIXTURE OF A HYDROCARBON AND QUINONE

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The invention relates to a process for making carbon from a hydrocarbonaceous material which normally produces only a small quantity of carbon, if any at all, when coked under ordinary conditions.

Most lower molecular weight, polynuclear, aromatic compounds give little or no carbon when coked under non-oxidizing conditions at atmospheric pressure and temperatures up to 450° C. and above. This is unfortunate since these compounds are easily purified and can constitute a source of high grade carbon and graphite for applications in which a carbon product of high purity is necessary.

The main object of the invention, therefore, is to provide a process for making carbon from a hydrocarbonaceous material which normally has a low coking value.

Another object is to provide means for increasing the yield of carbon from a hydrocarbonaceous material normally of low coking value.

Broadly, the above objects are achieved by a process which comprises mixing at least one quinone with a hydrocarbonaceous material and coking the mixture. The addition of the quinone to the hydrocarbonaceous material improves the coking value of the latter, and improved yields of carbon are obtained in the coking process. As used herein, the term "coking value" refers to the quantity of carbon which can be obtained from a given material by coking to 450° C. in an atmosphere inert to carbon, and is expressed as percent by weight of the given material. The term "hydrocarbonaceous material" refers to those materials which contain carbon and hydrogen, examples of which are petroleum residues, coal tars, pitches, aromatic hydrocarbons, substituted aromatic hydrocarbons, heterocyclic compounds, mixtures thereof, and the like. In general, the hydrocarbonaceous material will contain at least 50 percent carbon by weight.

Any compound considered as a quinone may be used in accordance with the invention to improve the coking value of the hydrocarbonaceous material. Preferred quinones include p-benzoquinone, tetrachloro-p-benzoquinone, 1,4 - naphthoquinone, 2,6 - dichloro-p-benzoquinone, 2-chloroanthraquinone, 2,3-dichloro-1,4-naphthoquinone, and anthraquinone. Other quinones which may be used in accordance with the invention include o-benzoquinone, 2,6-dimethyl-p-benzoquinone, 2,3,5,6-tetramethyl-p-benzoquinone, 1,2-naphthoquinone, 2,6-naphthoquinone, β-anthraquinone-sulfonic acid, α-nitroanthraquinone, α-aminoanthraquinone, β-aminoanthraquinone, 2,3-dimethyl-1,4-naphthoquinone, tetranitro-p-benzoquinone, 1,2 - dihydroxy-anthraquinone, acenaphthenequinone, phenanthraquinone, and tetrabromo-p-benzoquinone.

The activity of the quinones in the process of the invention arises from their ability to react with the hydrocarbonaceous material by accepting labile or reactive hydrogens from the hydrocarbonaceous material, forming complexes with polynuclear aromatic compounds, undergoing direct addition to aromatic ring systems, or a combination of these mechanisms. Although substituents on the quinone affect its reactivity, they merely affect the degree of reactivity, and do not render the quinone inoperative as long as the structure of a quinone remains. In fact, halo and nitro substituents enhance the reactivity of the quinone. Hydrocarbon and substituted hydrocarbon substituents are beneficial, since these groups possess a coking value, and thereby increase the total coking value of the mixture in contrast with the halo and nitro substituents. For example, the coking value of 1,4-naphthoquinone is 80.5 percent whereas the coking value of p-benzoquinone is 2.0 percent and the coking value of tetrachloro-p-benzoquinone is 3.0 percent. The fact that the quinones possess a coking value by themselves is an important advantage when comparing them as complexing additives for coking against other materials, such as sulfur or iodine, which have no coking value. Another advantage is that the quinones which contain only carbon, hydrogen, and oxygen do not add impurities, such as sulfur, iodine, and their derivatives, to the final carbon product.

In general, the quinone structure may be substituted with monovalent substituents such as halo, nitro, nitroso, alkyl, alkenyl, alkynyl, aryl, alkoxy, carboxy, cycloaliphatic hydrocarbons, amino, hydroxy, and the like, and with one or more benzo groups and the substituted derivatives thereof containing one or more of the above monovalent substituents.

Although the quinones improve the coking value of almost all hydrocarbonaceous compounds, including aromatic hydrocarbons of a very high molecular weight which normally have a high coking value, they are particularly useful with hydrocarbonaceous materials normally of low coking value. The only time that the quinones have no measurable effect is when the hydrocarbonaceous material is of such low molecular weight as to volatilize prior to reacting with quinone or when the aromatic ring structure is too stable to react with the quinone. According to present test results, benzene, naphthalene, and phenanthrene do not show an increase in coking value by addition of a quinone. Further work on these particular materials, however, may show a contrary result by the proper selection of process conditions. It will be apparent that the process of the invention should be conducted in the absence of materials which interfere with the reactivity of the quinone with the hydrocarbonaceous material, or preferentially react with the quinone, an example of which is sulfuric acid.

In general, the quinone addition is particularly effective with aromatic hydrocarbons containing from 3 to 9 fused rings inclusive, aromatic-alicyclic hydrocarbons containing aliphatic hydrogens and from 3 to 9 fused rings inclusive, and heterocyclic compounds, saturated and/or unsaturated, containing from 3 to 9 fused rings inclusive. Alkyl groups of 1 to 20 carbons, alkenyl groups of 1 to 20 carbons, and aryl groups of a single ring and containing up to 20 carbons, such as phenyl tolyl, xylyl, and dodecylphenyl, and may be mentioned as groups which may be present on the fused rings, but other groups may also be present. Furthermore, in counting the number of fused rings in the compounds, only the rings within a single fused group should be counted. For example, 9,9'-bifluorenyl, which contains two sets of three fused rings bonded together by a covalent bond, is considered as containing 3 fused rings. The aromatic-alicyclic hydrocarbon acenaphthene is also considered as containing three fused rings.

The preferred coking process comprises mixing the quinone with the hydrocarbonaceous material, and then coking the mixture by heating the mixture to final coking temperature in an atmosphere inert to carbon. The mixture is preferably heated slowly, a rate of temperature increase up to about 100° C. per hour, for example, until final coking temperature is reached, which is usually between about 400° C. and about 600° C. or higher for raw coke. Preferably, the heating schedule also includes a hold period at about 350° C. to about 400° C. of about 1 to about 10 hours and another hold period at final coking temperature of about 1 to about 10 hours.

The hold periods may be omitted at low rates of temperature increase, for example, up to about 10° C. per hour. It will be apparent to those in the art that other heating schedules may be employed for the coking step.

The atmosphere during the coking step may be composed of materials unreactive or inert to carbon, such as rare gases, carbon monoxide, nitrogen, and mixtures thereof. A double-wall metal sagger or other suitable apparatus can be employed during the coking step to keep air and other harmful materials from the hydrocarbonaceous material and the carbon product.

Table I shows test results of the improvement in coking value for twenty-nine hydrocarbonaceous materials by the addition of a quinone to the materials before coking. The carbonizing process comprises first mixing intimately the hydrocarbonaceous material with p-benzoquinone in a 1 to 1 ratio by weight and then heating the mixture to 450° C. in a protective sagger and under a self-generated, inert atmosphere at a rate of 60° C. temperature rise per hour with a hold period of 10 hours at 390° C. and another hold period of 5 hours at 450° C. The coking value of the pure hydrocarbonaceous material and of the mixture of it and the quinone is listed as well as the increase in coking value of the mixture over that expected based on the sum of the individual coking values of the two components as if coked separately. The p-benzoquinone used in these tests had a coking value of 5.4 percent when coked separately.

TABLE I.—COKING VALUES OF HYDROCARBONACEOUS MATERIALS AND OF MIXTURES OF THESE MATERIALS WITH p-BENZOQUINONE

Hydrocarbonaceous Material	450° C. Coking Value of Hydrocarbonaceous Material, Percent	450° C. Coking Value of 1:1 Mixture of p-Benzoquinone with Hydrocarbonaceous Material, Percent	Increase in Coking Value of Mixture over that Expected, Percent
Trans-stilbene	0.0	5.9	3.2
Fluorene	0.0	42.5	39.8
1,2-benzfluorene	0.0	56.8	54.1
1,2,3,4-peridinaphthalene fluorene	59.4	40.9	8.5
9,9'-bifluorenyl	21.4	41.1	27.7
9,9'-bifluorylidene	58.6	33.3	2.1
Acenaphthene	0.0	44.1	41.4
Acenaphthylene	41.8	58.6	35.0
Anthracene	0.0	35.5	32.8
9,10-dihydroanthracene	0.0	34.3	31.6
9,10-dimethylanthracene	2.6	33.9	30.0
2-methylphenanthrene	0.0	3.9	1.2
Naphthacene	40.0	69.1	47.6
5,12-dihydronaphthacene	7.3	41.8	35.4
1,2-benzanthracene	0.0	25.7	23.0
7,12-dimethyl-1,2-benzanthracene	4.2	23.2	18.4
1,2,5,6-dibenzanthracene	1.0	20.2	17.3
Chrysene	0.0	12.6	9.9
Pyrene	0.0	5.7	3.0
1,2,6,7-tetrahydropyrene	0.0	3.7	1.0
4-methylpyrene	0.0	7.0	4.3
3,4-benzpyrene	0.0	13.8	11.1
1,2,4,5,8,9-tribenzpyrene	6.5	33.5	27.6
Perylene	0.0	43.7	39.0
1,12-benzperylene	1.1	6.3	3.1
Pentacene	49.8	60.7	33.1
1,2,8,9-dibenzpentacene	40.2	43.4	20.6
Coronene	0.5	18.2	15.1
Acridine	2.0	55.2	51.5

These results show that the quinone interacts with the hydrocarbonaceous material to yield a complex having a higher coking value than the sum of the coking values of the individual components. If one assumes that the coking value of the quinone is a constant even when mixed with the hydrocarbonaceous material, the coking value of 1,2-benzfluorene, as calculated from the data of Table I is increased from 0 percent to 108.2 percent by the addition of quinone. It is, therefore, obvious that a synergistic effect is obtained by mixing a quinone with the hydrocarbonaceous material, and also that the hydrocarbonaceous material improves the individual coking value of the quinone since an actual coking value above 100 percent for the hydrocarbonaceous material is impossible.

Test results which illustrate the beneficial effect of quinone addition on the coking value of various pitches are given in Table II. The pitches were coked by the same procedure employed for the compounds listed in Table I. The actual coking value of the mixture of pitch and quinone, the calculated coking value using the coking values of the individual components, and the calculated coking value of the pitch after correcting for the expected amount of coke from the quinone are shown.

The material designated as 240 Tar in Table II is a refined coal tar having a flow time at 90° C. of 240 seconds for a 100 milliliter sample when measured on an Engler viscosimeter (A.S.T.M. D–490 specification). 30 Medium Pitch is a coal tar pitch having a melting point of about 100° C. and a content of about 30 percent by weight insoluble in benzene. 175° Pitch is a coal tar pitch having a softening point of about 175° C.

TABLE II.—EFFECT OF QUINONE ADDITION ON COKING VALUES OF VARIOUS COAL TAR PITCHES

Material for Coking	Actual 450° C. Coking Value, Percent	Calculated 450° C. Coking Value, Percent	Calculated 450° C. Coking Value of Pitch after Quinone Correction, Percent
1,4-naphthoquinone	80.5	----------	----------
Anthraquinone	0.1	----------	----------
Chloranil (tetrachloro-p-benzoquinone	3.0	----------	----------
p-Benzoquinone	5.4	----------	----------
240 Tar	27.0	----------	----------
30 Medium Pitch	63.1	----------	----------
175° C. Pitch	81.1	----------	----------
25% Chloranil plus 75% 175° Pitch	77.8	61.5	102.5
25% Chloranil plus 75% 30 Medium Pitch	74.5	48.0	99.0
25% Chloranil plus 75% 240 Tar	57.9	21.0	76.4
25% 1,4-naphthoquinone plus 75% 175° Pitch	85.7	81.0	87.4
25% 1,4-naphthoquinone plus 75% 30 Medium Pitch	73.5	67.2	71.2
25% 1,4-naphthoquinone plus 75% 240 Tar	56.4	40.4	48.5
25% 9,10-Anthraquinone plus 75% 175° Pitch	66.0	50.8	89.0
25% 9,10-Anthraquinone plus 75% 30 Medium Pitch	53.9	47.1	72.3
25% 9,10-Anthraquinone plus 75% 240 Tar	37.5	20.3	50.1
25% p-Benzoquinone plus 75% 175° Pitch	79.5	62.2	103.1
25% p-Benzoquinone plus 75% 30 Medium Pitch	71.0	48.7	90.8
25% p-Benzoquinone plus 75% 240 Tar	51.7	21.6	68.1

These results indicate that the addition of a quinone to the pitch before coking improves the coking value of the pitch significantly. The coking value of 240 Tar, for example, is raised from 27.0 percent to 76.4 percent by the addition of chloranil (tetrachloro-p-benzoquinone). Similar results have been obtained by adding a quinone to materials derived from petroleum, such as thermal tars and vacuum jug bottoms.

The coke produced by the above-described process of the invention can be converted by conventional processes to a carbon or graphite suitable for commercial purposes. For example, amorphous carbon of electrode grade can be made by calcining the coke in an inert atmosphere to a temperature of about 800 to about 1400° C. at a rate of temperature increase of up to about 2000° C. per hour with a hold period at about 800 to about 1400° C. of about ½ to about 10 hours or more. This amorphous carbon can be graphitized directly in an atmosphere inert to carbon by heating to between about 2200° C. and about 3000° C., or made into rods or blocks with a suitable binder, such as coal tar pitch, and then baked

to between about 750° C. and about 1000° C. in an atmosphere inert to carbon followed by graphitization at temperatures between about 2200° C. and 3000° C.

It has been found that an extremely small amount of quinone, for example, about 0.1 percent by weight of the mixture with the hydrocarbonaceous material, will improve the coking value of the hydrocarbonaceous material. A larger amount, however, is more effective, and for this reason a minimum amount of about 1 percent is preferred. The upper limit for general purposes is about 75 percent although larger amounts of quinone in the mixture may be employed. The concentration of the quinone in the coking mixture does affect the properties of the final product, however, and the effect should be considered when making a coke for a specific use.

Table III, IV, V and VI show physical properties of a graphitized coke made in accordance with the invention. These results were obtained by mixing thermal tars or vacuum jug bottoms, derived from petroleum, with 1,4-naphthoquinone or p-benzoquinone in various concentrations and then coking each of the mixtures to 450° C. at a rate of temperature increase of 60° C. per hour with hold periods of 10 hours at 390° C. and 5 hours at 450° C. The cokes thus produced were calcined to 1000° C. at a rate of 60° C. per hour with a hold period of 5 hours at 1000° C.

The calcined coke was made into rods with 30 Medium Pitch as a binder in accordance with standard practice. These green rods were baked to 1000° C. at 60° C. per hour with a hold period of one hour and then graphitized at 3000° C. for ½ hour. The bulk density, specific resistance, and coefficient of thermal expansion were measured, and the results of the tests are shown in the tables which follow. Calculated coke yields at 1000° C. were computed from the individual coking values of the two components as if coked separately.

TABLE III.—EFFECT OF p-BENZOQUINONE ON COKE YIELD AND GRAPHITE QUALITY FROM THERMAL TAR

Composition, Percent by Weight		Coke Yield, Percent at—			Bulk Density of Rods, g./cc.		Properties of 3,000° C. Graphite		
Thermal Tar	p-Benzoquinone	450° C. (Obs.)	1,000° C. (Obs.)	1,000° C. (Calc.)	Green	Baked	Bulk Density, g./cc.	Specific Resistivity, micro-ohm-centimeter	Coefficient of Thermal Expansion, [2] ×10-7/° C.
100	0	28.3	25.3	25.3					
95.2	4.8	29.3	29.3	24.2			1.55	848	6.7
90.9	9.1	33.4	30.8	23.1	1.62	1.48	1.51	820	5.2
80	20	[1] 32.2	[1] 29.5	20.5	1.62	1.48	1.52	910	6.2
66.7	33.3	[1] 31.8	[1] 28.9	17.5	1.65	1.51	1.60	894	16.2
50	50	[1] 31.1	[1] 26.3	13.5	1.60	1.42	1.66	1,628	58.9
0	100	2.0	1.7	1.7	1.44	1.28	1.31	4,048	29.0

[1] Overflowed, yields low.
[2] Measured over temperature range of 30° C. to 100° C.

TABLE IV.—EFFECT OF p-BENZOQUINONE ON COKE YIELD AND GRAPHITE QUALITY FROM VACUUM JUG BOTTOMS

Composition, Percent by Weight		Coke Yield, Percent at—			Bulk Density of Rods, g./cc.		Properties of 3,000° C. Graphite		
Vacuum Jug Bottoms	p-Benzoquinone	450° C. (Obs.)	1,000° C. (Obs.)	1,000° C. (Calc.)	Green	Baked	Bulk Density, g./cc.	Specific Resistivity, micro-ohm-centimeter	Coefficient of Thermal Expansion, [1] ×10-7/° C.
100	0	13.9	12.9	12.9					
95.2	4.8	15.5	14.1	12.4			1.57	856	16.1
90.9	9.1	17.3	15.6	11.8	1.67	1.53	1.59	1,072	23.1
80	20	20.2	17.9	10.6	1.65	1.54	1.63	1,184	30.8
66.7	33.3	25.0	21.6	9.2	1.59	1.45	1.55	1,025	37.2
50	50	28.0	23.8	7.3	1.50	1.36	1.45	2,770	33.9
0	100	2.0	1.7	1.7	1.45	1.29	1.35	3,475	30.8

[1] Measured over temperature range of 30° C. to 100° C.

TABLE V.—EFFECT OF 1,4-NAPHTHOQUINONE ON COKE YIELD AND GRAPHITE QUALITY FROM THERMAL TAR

Composition, Percent by Weight		Coking Schedule, ° C./hr.	Coke Yield, Percent, at—			Properties of 3,000° C. Graphite		
Thermal Tar	1,4-naphthoquinone		450° C. (Obs.)	1,000° C. (Obs.)	1,000° C. (Calc.)	Bulk Density g./cc.	Specific Resistivity, micro-ohm-centimeter	Coefficient of Thermal Expansion, [1] ×10-7/° C.
100	0	60	28.3	25.3	25.3	1.55	848	6.7
95.2	4.8	60	30.4	28.7	27.3	1.65	683	6.3
90.9	9.1	60	34.3	32.2	29.0	1.65	663	4.7
80	20	60	43.5	40.9	33.5	1.56	808	6.2
65	35	60	38.6	35.7	41.2	1.66	958	21.2
50	50 (1st trial)	60	67.3	62.5	45.8	1.67	2,222	45.4
50	50 (second trial)	20	51.7	47.9	53.0	1.61	2,327	52.8
0	100 (first trial)	60	80.4	66.2	66.2	1.55	2,800	38.5
0	100 (second trial)	60	65.8	54.8	66.2	1.51	3,320	45.0
0	100 (third trial)	20	84.1	70.7	20.7	1.49	3,607	32.5

[1] Measured over temperature range of 30° C. to 100° C.

TABLE VI.—EFFECT OF 1,4-NAPHTHOQUINONE ON COKE YIELD AND GRAPHITE QUALITY FROM VACUUM JUG BOTTOMS

Composition, Percent by Weight		Coke Yield, Percent at—			Properties of 3,000° C. Graphite		
Vacuum Jug Bottom	1,4-naphthoquinone	450° C. (Obs.)	1,000° C. (Obs.)	1,000° C. (Calc.)	Bulk Density g./cc.	Specific Resistivity, micro-ohm-centimeter	Coefficient of Expansion [2], $\times 10^{-1/\circ}$ C.
100	0	13.9	12.9	12.9	1.57	856	16.1
95.2	4.8	16.7	15.2	15.5	1.58	830	13.7
90.9	9.1	19.8	18.3	17.7	1.57	855	13.4
80	20	27.5	25.6	23.6	1.60	790	16.9
50	50	[1] 45.1	41.8	39.6	1.67	838	23.6
0	100	80.4	66.2	66.2	1.55	2,800	38.5

[1] Overflow, yield probably somewhat low.
[2] Measured over temperature range of 30° C. to 100° C.

As the results in these tables indicate, small amounts of the quinone, for example, between about 5 percent and about 20 percent by weight in the coking mixture actually decrease the specific resistivity and the coefficient of thermal expansion of the graphite produced therefrom. For most uses, such as for electrodes, refractory bricks, and the like, this effect is desirable. At higher concentrations of quinone, the specific resistivity and coefficient of thermal expansion increase rather slowly until a relatively large change in these properties is encountered when the coking mixture contains above about 30 percent by weight quinone. Although the coke yield increases with an increase in quinone concentration, the advantage of the increased yield is offset by the higher resistivity and thermal expansion which obtain at concentrations above about 30 percent by weight quinone. For this reason quinone concentrations up to about 30 percent by weight are preferred for a coke to be used in making carbon or graphite for most purposes, such as electrodes and refractory bricks.

Coke produced from mixtures containing above about 30 percent by weight quinone, however, is also useful since a relative high resistivity and coefficient of thermal expansion are desirable for some specific applications. The addition of a quinone in high concentrations to the coking material appears to be a good technique for making isotropic graphite with equal thermal expansion in all directions. Such a graphite is sometimes preferred for refractory bricks, or as a substrate for oxidation resistant coatings. Further, an increase in strength generally occurs with an increase in quinone concentration.

Thus, it will be apparent to those in the art that the invention provides not only a method by which the coking values of hydrocarbonaceous materials can be increased, but also a method by which the properties of carbon and graphite produced therefrom can be modified.

What is claimed is:

1. In a process for making carbon by coking a hydrocarbonaceous material normally of low coking value and liquefiable below coking temperatures and reactive with a quinone, the improvement which comprises mixing a quinone with said hydrocarbonaceous material prior to coking in an amount sufficient to improve the coking value of said hydrocarbonaceous material, and then coking the mixture.

2. The improvement defined in claim 1 wherein said hydrocarbonaceous material reactive with a quinone is selected from the class consisting of aromatic hydrocarbons containing from 3 to 9 fused rings inclusive, aromatic-alicyclic hydrocarbons containing aliphatic hydrogens and from 3 to 9 fused rings inclusive, and heterocyclic compounds containing from 3 to 9 fused rings inclusive.

3. The improvement defined in claim 1 wherein said quinone is selected from the class consisting of p-benzoquinone, 1,4-naphthoquinone, tetrachloro-p-benzoquinone, 2,6-dichloro-p-benzoquinone, 2-chloroanthraquinone, 2,3-dichloro-1,4-naphthroquinone, and anthraquinone.

4. A process for making carbon from a hydrocarbonaceous material normally of low coking value and liquefiable below coking temperatures and reactive with a quinone, which process comprises forming a mixture prior to coking of said hydrocarbonaceous material and a quinone in an amount up to about 75 percent by weight of said mixture and sufficient to improve the coking value of said hydrocarbonaceous material, and then coking said mixture.

5. The process defined in claim 4 wherein said hydrocarbonaceous material reactive with a quinone is selected from the class consisting of aromatic hydrocarbons containing from 3 to 9 fused rings inclusive, aromatic-alicyclic hydrocarbons containing aliphatic hydrogens and from 3 to 9 fused rings inclusive, and heterocyclic compounds containing from 3 to 9 fused rings inclusive.

6. The process defined in claim 4 wherein said quinone is selected from the class consisting of p-benzoquinone, 1,4-naphthoquinone, tetrachloro-p-benzoquinone, 2,6-dichloro-p-benzoquinone, 2-chloroanthraquinone, 2,3-dichloro-1,4-naphthoquinone, and anthraquinone.

7. A process for making carbon from a hydrocarbonaceous material normally of low coking value and liquefiable below coking temperatures and reactive with a quinone, said carbon being suitable for making graphite having a relatively low specific resistivity and coefficient of thermal expansion, which process comprises forming a mixture prior to coking of said hydrocarbonaceous material and a quinone in an amount below about 30 percent by weight of said mixture, and then coking said mixture.

8. The process defined in claim 7 wherein said hydrocarbonaceous material reactive with a quinone is selected from the class consisting of aromatic hydrocarbons containing from 3 to 9 fused rings inclusive, aromatic-alicyclic hydrocarbons containing aliphatic hydrogens and from 3 to 9 fused rings inclusive, and heterocyclic compounds containing from 3 to 9 fused rings inclusive.

9. The process defined in claim 7 wherein said quinone is selected from the class consisting of p-benzoquinone, 1,4-naphthoquinone, tetrachloro-p-benzoquinone, 2,6-dichloro-p-benzoquinone, 2-chloroanthraquinone, 2,3-dichloro-1,4-naphthoquinone, and anthraquinone.

10. A process for making carbon from a hydrocarbonaceous material normally of low coking value and liquefiable below coking temperatures and reactive with a quinone, said carbon being suitable for making graphite having a relatively high specific resistivity and coefficient of thermal expansion, which process comprises forming a mixture prior to coking of said hydrocarbonaceous mate-

rial and a quinone in an amount above about 30 percent by weight of said mixture, and then coking said mixture.

11. The process defined in claim 10 wherein, said hydrocarbonaceous material reactive with a quinone is selected from the class consisting of aromatic hydrocarbons containing from 3 to 9 fused rings inclusive, aromatic-alicyclic hydrocarbons containing aliphatic hydrogens and from 3 to 9 fused rings inclusive, and heterocyclic compounds containing from 3 to 9 fused rings inclusive.

12. The process defined in claim 10 wherein said quinone is selected from the class consisting of p-benzoquinone, 1,4 - naphthoquinone, tetrachloro - p - benzoquinone, 2,6-dichloro - p - benzoquinone, 2-chloroanthraquinone, 2,3 - dichloro - 1,4 - naphthoquinone, and anthraquinone.

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DELBERT E. GANTZ, *Primary Examiner.*

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,347,776 Dated October 17, 1967

Inventor(s) Charles V. Mitchell et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Table VI, under Coefficient of Expansion, "X10^{-1}/°C" should read --X 10^{-7}/°C--.

Signed and sealed this 15th day of July 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
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