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CARBONIZING PROCESS

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This invention relates to a process for increasing the yield of carbon and graphite from selected aromatic compounds which normally do not produce appreciable quantities of carbon when coked at atmospheric pressure.

It is known that most lower molecular weight, polynuclear, aromatic compounds give little or no carbon when coked under non-oxidizing conditions at atmospheric pressure and temperatures above about 450° C.

This has been considered unfortunate from the standpoint that these compounds are easily purified and could constitute a source of high grade carbon and graphite for applications wherein high purity material is necessary.

The main object of this invention, then, is to provide means for increasing the yield of carbon and graphite from selected aromatic compounds.

This object has been attained in accord with the invention which comprises mixing from 1 to 30 parts by weight of iodine with 100 parts by weight of aromatic compound followed by coking of the mixture to form carbon.

The present invention is applicable to those aromatic compounds having a structure containing two to four fused rings and which are able to share electrons with iodine to form a complex therewith. Such compounds include anthracene, acenaphthene, acridine, 2–3 benzodiphenylene oxide, carbazole, chrysene, fluoranthene, indene, phenanthrene, pyrene, quinoline, 1,2-benzanthracene, triphenylene, 3,4-benzphenanthrene and alkyl derivatives of such compounds, such as methyl anthracene, ethyl anthracene, dimethyl anthracene and mixtures thereof. The process of the invention is also applicable to petroleum oils which are known to contain mixtures of alkylated derivatives of aromatic compounds having the indicated fused ring structure. The additive of the invention will also increase the yield of carbon from hydrocarbons which give some carbon on coking, such as acenaphthylene and naphthacene. The coke prepared by the present process may contain small amounts of iodine.

Coking may be done on any scale in a manner similar to that illustrated in the following experiments. The compound is weighed out into a glass beaker or other suitable non-reactive container. The iodine is weighed out and added to the compound with thorough mixing. The glass beaker with its contents is placed inside a metal beaker. The beaker in turn is placed inside a protective double metal sagger which is packed with steel wool, charcoal, and sand to prevent oxidation of the sample. The temperature is increased slowly to a temperature somewhat below final coking temperature, held there for several hours, increased to final coking temperature and held there for a few hours. The preferred heating schedule used during coking is from about 10 to about 60° C. rise per hour to 390° C., a ten-hour hold period at 390° C., then a 60° C. rise per hour to 475° C. and a six-hour hold period at 475° C., followed by cooling and collection of the product.

Although the preferred range of amount of iodine is from about 10 to about 20 parts per hundred parts of organic compound, a broad range of 1–30 p.p.h. may be employed as desired. Experiments with as little as 1, 2

and 5 parts per hundred of iodine showed improvement in the coking yields of the compounds. Larger amounts were considerably more effective.

The results of the addition of 10 or 20 parts per hundred (p.p.h.) of iodine on the coking value at atmospheric pressure after heating to about 475° C. of a number of aromatic hydrocarbons and compounds are shown in Table I. It should be noted that in most cases those compounds which ordinarily yield little or no coke became reasonably productive of coke with the addition of iodine. In addition, there has occurred an increase in the yield of coke from those compounds which originally gave some coke. The data presented, then, proves that iodine will bring about the formation of coke in most cases where little or none was formed previously and will give an increased yield where coke was formed previously.

It has been observed that when larger samples are employed, the coke yields are somewhat higher presumably because of greater surface area contact between the aromatic hydrocarbon and the iodine, with a resultant better utilization of the additive. This effect may be observed with a certain compound, chrysene, as follows:

Chrysene sample weight, gm.:	With coking value after heating to 450–475° C. with 10 p.p.h. iodine
10	15.2
45	19.6
200	33.5

The degree of iodine retention was determined for coke produced from the following sources:

Compound	Amount of Iodine Employed, p.p.h.	Iodine Content (Wt. Percent) of Coke After Heating to—	
		500° C.	1,000° C.
Anthracene	5	1.7	1.1
Do	10	1.1	1.0
Pyrene	10	0.4	
Acridine	20		4.8

While the degree of iodine retention varies with the compound, it is usually in the range of about 0.4 to about 5.0 percent.

The effect of iodine on the quality of graphite obtained from cokes prepared in the presence of iodine is shown in Table II. For this determination, raw cokes, obtained from the indicated compounds at 450° to 500° C. were calcined to 1000° C., then crushed and sized to make a coke flour which was hot-mixed with coal tar pitch and formed into rods by extrusion. These rods were baked to 1000° C. and were then graphitized at 3000° C. The properties listed in Table II result from measurements made on the thus-prepared rods.

For purpose of comparison a range of physical properties displayed by 3000° C. graphitized articles prepared from petroleum coke obtained from various material and refinery sources also is shown in Table II. It can be seen that physical properties obtained with the addition of iodine to the aromatic hydrocarbons generally compare quite favorably with properties obtained with petroleum coke articles. Other ways of increasing the yield of carbon or coke from these same compounds exist, but these require the use of superatmospheric pressures, or of a dehydrogenating agent, such as sulfur. Pressure does not adversely affect coke quality, but sulfur generally does.

Certain petroleum oils are known to contain varying

amounts of alkylated derivatives of aromatic compounds having fused ring structures. Such oils were also subjected to the process of the invention.

The same data as above-presented in connection with single compounds, appears in Table III for petroleum oils to which iodine had been added prior to coking. Examination of this data shows improvement in the coking value of the oil when iodine is added thereto. This improvement is not as marked as in the case of the single compounds, possibly because of dilution effects and other interfering factors.

Iodine appears to bring about this increased yield of carbon by forming a complex with the compound. This complex is stable enough to tie down the compound and prevent its loss by distillation or sublimation, yet reactive enough to cause the molecules to react with each other and polymerize to form a more highly carbonaceous structure. Iodine does not seem to function as a dehydrogenation agent, as does sulfur. Iodine reacts with highly unsaturated, conjugated olefinic or aromatic compounds as shown by the results in Table I below. The ability of the compound to share its electrons with iodine to form a complex seems to be a necessary prerequisite for having initial complexing action and subsequent carbon formation.

TABLE I

Effect of Adding Iodine on the Coking Value of Aromatic Compounds After Heating at 475° C.

[10 gram samples used unless otherwise indicated]

Compound	Coking Value, Percent by Weight		
	Without Iodine	With 10 p.p.h. Iodine	With 20 p.p.h. Iodine
Acenaphthene	0.2	11.8	27.2
Acenaphthylene	40.1	46.8	52.2
Acridine	8.7	----------	96.4
Anthracene	0.3	25.6	62.9
2,3-Benzodiphenylene Oxide	0.1	----------	5.0
Carbazole	0.3	----------	14.7
Chrysene	0.2	[1] 33.6	[1] 34.1
Fluoranthene	0.1	2.6	9.7
Indene	1.4	[1] 39.6	41.3
Naphthacene	42.8	----------	[1] 85.6
Phenanthrene	0.3	6.3	[1] 20.4
Pyrene	0.1	10.4	[1] 35.4
Quinoline	0.2	----------	14.1
Trans-stilbene	0.5	----------	6.2
Eicosane	0.0	0.1	0.3
Tetralin	0.1	0.3	0.5
Diphenyl	0.0	0.1	0.1
Naphthalene	0.1	0.1	0.1
Fluorene	0.0	1.8	2.6
Phenanthrene	0.3	6.3	12.8

[1] Indicates that samples weighing from 150 to 300 grams were used.

TABLE II

Results of Rod Method Evaluation of Various Cokes

Compound	Additive, p.p.h. I_2	Properties of Graphite		
		A.D. gm./cc.	Specific Resistance μ ohm-cm.	CTE[1]/° C. $\times 10^{-7}$
Acridine	20	1.43	1,800	34.6
Anthracene	20	1.53	930	8.0
Indene	20	1.67	995	32.8
Naphthacene	None	1.55	914	15.7
Do	20	1.40	1,240	25.3
Phenanthrene	20	1.62	965	27.0
Pyrene	10	1.57	884	12.9
Petroleum	None	1.44–1.62	760–1,195	4.0–31.0

[1] CTE = Coefficient of Thermal Expansion (measured over the range of 20° C. to 100° C.).

TABLE III

Effect of Iodine Additions on Yield and Quality of Coke From Various Types of Petroleum Charge Stocks

[150–300 g. sample size]

Type of Material	Iodine Additive p.p.h.	Percent Coke Yield at—		Percent Improvement in yield of coke (1,000° C.)	Properties of 3,000° C. Graphite		
		450° C.	1,000° C.		A.D. g./cm.[3]	Specific Resistance μ ohm-cm.	CTE $\times 10^{-7}$/° C.
Slurry Oil	None	8.8	8.0	(0)	1.54	869	4.9
Do	5	[1] 10.5 [2] (11.0)	[1] 9.8 [2] (10.2)	[1] (+22.5) [2] (+27.5)	1.55	755	6.
Do	10	[1] 12.7 [2] (14.0)	[1] 11.8 [2] (13.0)	[1] (+47.5) [2] (+62.5)	1.51	853	7.4
Desulfurized Heavy Catalytic Cycle Oil	None	2.4	2.2	(0)	1.52	978	7.2
Do	10	[1] 6.4 [2] (7.0)	[1] 5.9 [2] (6.5)	[1] (+168) [2] (+195)	1.48	955	7.5

[1] Based on oil + iodine.
[2] Based on oil only. Excludes iodine since the iodine does not form coke itself. This is the preferred method of calculation.

What is claimed is:

1. A process for increasing the yield of carbon from aromatic compounds comprising forming a mixture of 1 to 30 parts of iodine with 100 parts of an aromatic compound having a structure containing from two to four fused rings and capable of sharing electrons with iodine to form a complex therewith and coking said mixture under atmospheric pressure and collecting the thus-formed coke.

2. The process of claim 1, wherein said iodine is present in the range of 10 to 20 parts per one hundred parts of compound.

3. The process of claim 1, wherein said aromatic compound is selected from the group consisting of acenaphthene, anthracene, acridine, carbazole, chrysene, fluoranthene, indene, phenanthrene, pyrene, quinoline, acenaphthylene, naphthacene, benzodiphenylene oxide, 1,2-benzanthracene, triphenylene, 3,4-benz-phenanthrene, alkyl derivatives thereof, and mixtures of aforesaid compounds.

4. A process for increasing the yield of carbon from aromatic compounds comprising forming a mixture containing from 1 to 30 parts by weight of iodine to 100 parts by weight of an aromatic compound having a structure containing from two to four fused rings and capable of sharing electrons with iodine and heating said mixture in the absence of air first to a temperature below coking temperature at a rate of about 10 to about 60° per hour rise, holding said heated mixture at said temperature for several hours, and increasing said temperature to coking temperature until substantial coking of said compound has taken place.

5. A process for making graphite comprising forming a mixture containing aromatic compounds having from two to four fused rings and capable of sharing electrons with iodine and from about 1 to about 30 parts iodine per hundred parts of said aromatic compounds, coking said

mixture under atmospheric pressure, and graphitizing the thus-produced coke.

6. A process for increasing the yield of carbon from indene, which process comprises forming a mixture of 1 to 30 parts iodine with 100 parts indene, coking said mixture under atmospheric pressure, and collecting the thus-formed coke.

References Cited in the file of this patent

UNITED STATES PATENTS

1,984,164	Stock	Dec. 11, 1934
2,246,645	Virbain et al.	June 24, 1941
2,915,370	Mitchell	Dec. 1, 1959
2,960,554	Sandri et al.	Nov. 15, 1960