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PREPARATION OF HIGH PURITY COKE AND GRAPHITE

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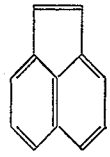
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This invention has reference to the preparation of high purity coke and graphite from certain purified polynuclear aromatic hydrocarbons.

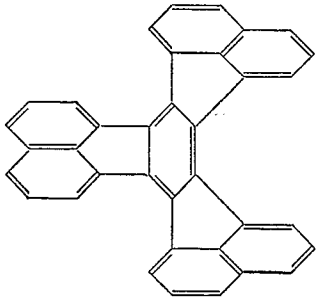
Nuclear applications require an extremely pure grade of graphite for various uses in reactors. In searching for new sources of pure graphite, it has already been proposed to employ organic starting materials because of the ease with which such materials can be purified prior to carbonization and graphitization. One prior proposal has required special coking catalysts to increase the coking value of materials such as naphthalene, anthracence and phenanthrene. In another, superatmospheric pressure coking techniques have been necessary. As a result of such specialized operational requirements, however, the concept of using purified polynuclear aromatics as a source of high purity graphite has not gained industrial acceptance.

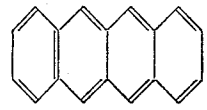
The main object of the present invention is to provide an efficient process for making high purity graphite from certain polynuclear aromatic hydrocarbons, which process does not require catalysis or high pressure conditions.

It now has been found in the practice of the invention that acenaphthylene



decacyclene and naphthacene





yield appreciable quantities of coke at atmospheric pressure. As is known, decacyclene is related to acenaphthylene, since three molecules of the latter can be joined to form one of the former.

In the practice of the invention the compound to be coked is placed in a suitable refractory vessel, which is inserted in a metallic double sagger, and placed in a coking oven. The vessel is provided with a protective atmosphere of nitrogen, helium or argon. In the preferred practice of the invention, heating is effected as follows. The temperature is first increased at a rate of about 60° C. per hour to 390° C., held at 390° C. for about 10 hours, increased to 450° C., and held there for 5 to 6 hours, and cooled. To calcine the raw coke thus obtained, the material is placed in a metal or ceramic beaker, enclosed in the double sagger, and heated under ambient pressure at a rate of increasing temperature of about 60° C. per hour to 1000° C., and held at this temperature for about one hour or until all the volatile materials had

been driven off. Graphitization of the coke can be effected by any known manner.

Variations in heating periods and temperatures employed in preparing the coke may be made within the scope of the invention. For example, the rate of heating may be varied between 10° and 100° C. per hour with a preferred rate being about 60° C. The first hold temperature may be varied between 350° and 400° C., and the hold period in this temperature range may vary from one to fifteen hours. The final hold temperature may vary between 450° to 500° C., and the hold period between one and ten hours. Calcination of the raw coke may be done at 800° to 1000° C. employing the same 10° to 100° C. per hour heating rate up to that temperature.

The appended tables show experimental data highlighting features of the instant invention.

Table I compares the coking values at 450° C. of various polynuclear aromatic hydrocarbons and acenaphthylene. The superiority of acenaphthylene in this respect is clearly demonstrated. Many polynuclear aromatic compounds have been investigated, but none have been observed to give such high yields of high quality coke at atmospheric pressure as acenaphthylene. In addition to giving a good yield of coke, acenaphthylene also gives an excellent grade of graphite when graphitized by conventional methods. Table II compares the excellent properties of graphite rods prepared from acenaphthylene and from other sources including pressure-coked anthracene, pressure coked phenanthrene, and commercially available petroleum fractions. The rods were prepared by taking 1000° C. calcined coke (prepared as previously described) from these sources, grinding, sizing, and mixing the coke with coal tar pitch and extruding this mix into rods. The rods were baked to 1000° C. on a 60° C. per hour schedule, and subsequently graphitized to 3000° C. in a graphite tube furnace. The superior quality of the acenaphthylene-based graphite, particularly the low electrical resistance and coefficient of thermal expansion, are apparent from the data in Table II. Coefficients of thermal expansion (CTE) of the order of 6×10^{-7} inch/inch/° C., are preferred, and resistances of the order to 300 micro ohm inches or less are considered good in this art.

Of the many polynuclear aromatic hydrocarbons which have been investigated, three others besides acenaphthylene show appreciable yields of coke at atmospheric pressure. These are naphthacene (2,3-benzanthracene), α-truxene and decacyclene. However, the data in Table III show that these materials, with the exception of decacyclene, yield poor quality graphite in comparison with acenaphthylene, and, therefore, do not detract from the unique behavior of acenaphthylene. It is not too surprising from a comparison of the related structures of acenaphthylene and decacyclene, that decacyclene yields a good graphite, although it is not quite as good in respect to resistance and CTE as that from acenaphthylene.

TABLE I

Comparison of 450° C. Coking Values of Polynuclear Aromatic Hydrocarbons

Hydrocarbon:	450° C. coking value, percent
Acenaphthylene	40.1
Decacyclene	92.0
Naphthalene	0.0
Acenaphthene	0.2
Fluoranthene	0.1
Anthracene	0.3
Phenanthrene	0.3
1,2-benzanthracene	1.0
Chrysene	0.2
Pyrene	0.1

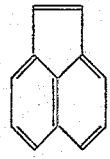
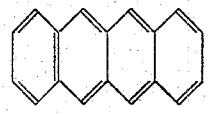
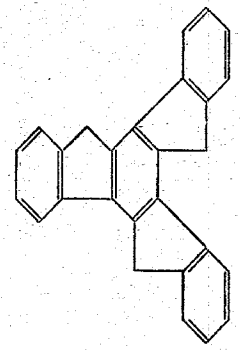
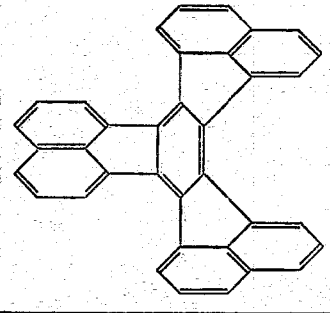
TABLE II

Properties of Graphite Rods From Acenaphthylene Coke and Other Sources

Coke Source	Type of Coking	1,000° C. Coke Yield, Percent	A.D., gm./cc.	Resistance, μOhm In.	CTE, in./in./° C. × 10^{-7}
Acenaphthylene	Atmospheric	38.0	1.50	283	3.6
Anthracene	Pressure	59.9–77.3	1.43–1.51	290–340	4.2
Phenanthrene	do	22.0–77.0	1.51–1.53	380–400	10.7–12.6
Petroleum Decant Oils	Atmospheric	3.0–19.0	1.40–1.52	320–424	4.0–6.6
Petroleum Thermally Cracked Oils	do	10.4–38.8	1.51–1.52	320–395	4.0–7.1
Petroleum Virgin Residuals	do	10.0–20.2	1.44	314–470	16.9–30.6
Petroleum Vacuum Tower Bottoms	do	13.3–21.8	1.54–1.62	328–436	15.3–21.3
Petroleum Duo Sol Extract	do	24.4–28.0	1.55	327–399	17.0–17.7

TABLE III

Comparison of Graphite Properties From Various Atmospheric Coked Polynuclear Aromatic Hydrocarbons

Hydrocarbon	Type of Structure	1,000° C. Coke Yield, Percent	Properties of Graphite Rods		
			A.D. gm./cc.	Resistance, μOhm In.	CTE, in./in./° C. × 10^{-7}
Acenaphthylene		38.0	1.50	283	3.6
Naphthacene		48.5	1.54	352	15.7
α-Truxene		47.5	1.30	1,301	31.5
Decacyclene		85.8	1.58	324	8.9

This application is in part a continuation of my previous application, Serial No. 825,895, filed July 9, 1959, now abandoned.

What is claimed is:

1. A process for making high purity graphitizable coke comprising placing in a heating vessel a starting material selected from the group consisting of acenaphthylene, naphthacene and decacyclene, coking said material by heating the same at a rate of between about 10° C. and about 100° C. rise per hour in an inert atmosphere under ambient pressure to a temperature between about 350° and 400° C., maintaining said material at said temperature for about ten hours, increasing said temperature to between about 450° C., and 500° C., maintaining said tem-

perature for about 1 to about 10 hours, and then cooling the thus-formed coke.

2. The process of claim 1 wherein said temperature is initially raised to about 390° C. at a rate of about 60° C. per hour.

3. The process of claim 1 wherein the thus-formed coke is calcined by heating to about 800° to about 1000° C. at a rate of between 10° to about 100° C. rise per hour.

4. A process for making high purity graphitizable coke comprising placing in a refractory vessel inserted in a metallic double sagger a starting material selected from the group consisting of acenaphthylene, naphthacene and decacyclene, coking said material by heating the same under a protective atmosphere under ambient pressure and at a rate of increase of about 60° C. per hour to a temperature of about 390° C., maintaining said material

at said temperature for about 10 hours, increasing said temperature to about 450° C., maintaining said temperature for about 5 to 6 hours, cooling the thus-formed coke, and calcining said coke by heating the same to about 1000° C. at a rate of about 60° C. rise per hour.

5. In a process for making coke by the pyrolysis of polynuclear aromatic hydrocarbons, the improvement consisting in selecting said hydrocarbons from the group consisting of naphthacene, decacyclene and acenaphthylene.

References Cited in the file of this patent

UNITED STATES PATENTS

2,670,322	Krebs et al.	Feb. 23, 1954
2,764,539	Horvitz	Sept. 25, 1956