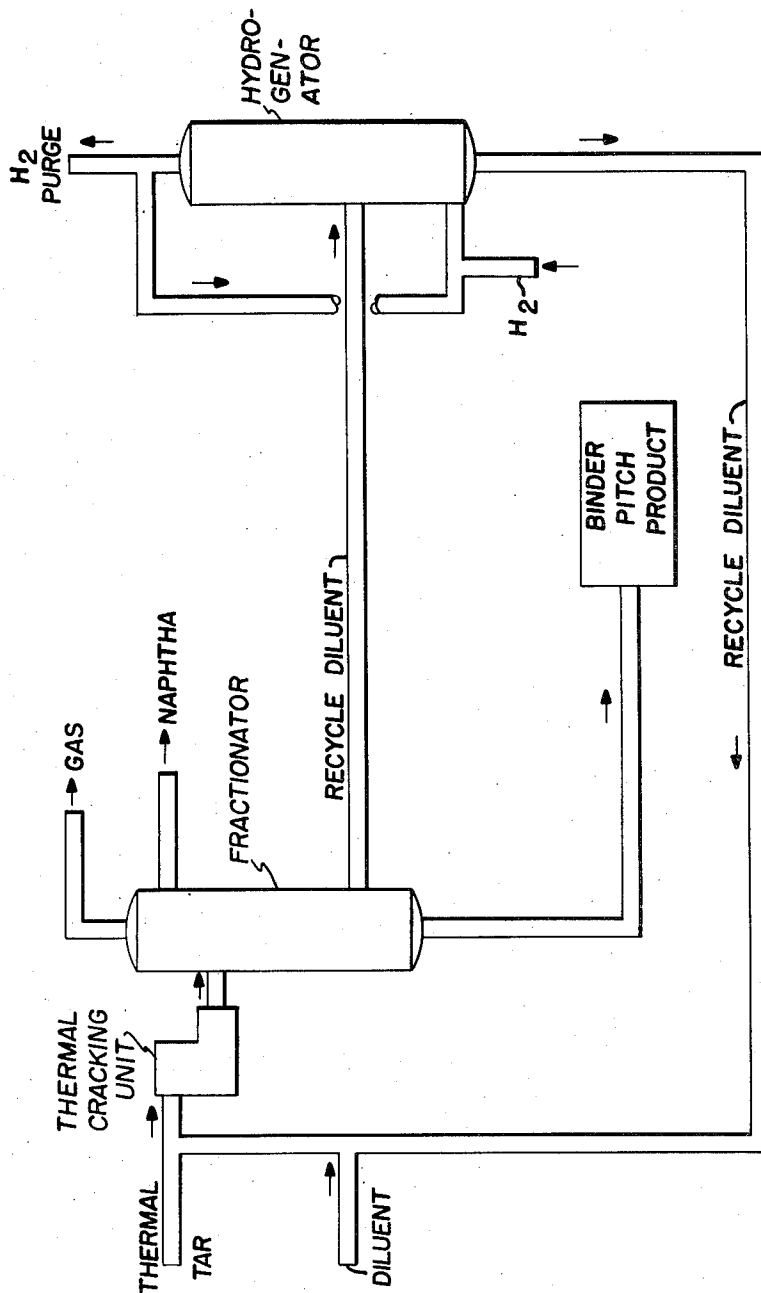


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PRODUCTION OF BINDERS FOR CARBON ELECTRODES
FROM PETROLEUM SOURCES
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PRODUCTION OF BINDERS FOR CARBON ELECTRODES FROM PETROLEUM SOURCES

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3 Claims. (Cl. 196—50)

This invention relates to the preparation of carbonaceous binders for use in the preparation of carbon and graphite electrodes. More particularly it relates to those binders for carbon particles prepared from cracked highly aromatic petroleum fractions.

In the manufacture of aluminum by electrolytic reduction of alumina in a suitable fused bath, the necessary carbon electrodes have usually been manufactured from so-called petroleum coke of relatively high purity.

This petroleum coke had been obtained largely from coking processes such as delayed coking which provide particles of relatively large diameter and densities. This supply of petroleum coke is being increased by the recently developed fluid coking process, e. g., see Serial No. 375,088, filed August 19, 1953.

The manufacture of the carbon electrodes requires the use of a carbonaceous binder usually referred to as a pitch binder, e. g., see U. S. Patent No. 2,683,107. The manner in which this binder is used is expanded upon later. More than 90% of the requirements for these binders are met by coal tar pitch. Only a small portion of the requirement is supplied by petroleum sources. It is desirable from the viewpoint of the latter industry to be able to make these binder materials as well as the coke charge for the electrodes.

The specifications of these binder materials are empiric in nature. A low H-C atomic ratio is required in order to minimize the development of porosity during the electrode baking operation. A high coking value is necessary. The coking value is a measure of the amount of coke residue produced by a pitch when decomposed by heating at 1200° F. for 4 hours. A softening point of 70°–120° C. is required. The pitches softening in the lower half of this range are designated as soft pitches, while those softening in the upper half are designated as hard pitches.

This invention provides an improved process for making these carbonaceous binders for carbon electrodes from petroleum sources. The process comprises thermally cracking in liquid phase a mixture of a cracked, highly aromatic, petroleum fraction and a highly aromatic petroleum fraction which has been partially hydrogenated so as to contain at least one and usually a plurality of condensed ring aromatic-naphthenic compounds. The term aromatic is to be understood to connote also condensed ring structures which on hydrogenation yield aromatic-naphthenes and their alkylated derivatives. The complete process is conducted to the point where the predominant bottoms product is the carbonaceous binder. The later is stripped at reduced pressures to obtain a product of the desired softening point.

It is surprising to find that conducting the thermal cracking in the presence of partially hydrogenated fractions gives the superior results obtained. These fractions containing naphthene type compounds are known to give up hydrogen during heating and their presence would have been thought to be inconsistent with the low concentration of hydrogen required in the carbonaceous binders.

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The feed utilized is a cracked, highly aromatic, petroleum fraction, i. e., one containing at least about 50 wt. percent aromatics. These feeds are obtained by the thermal cracking of catalytic cycle stocks, clarifier oils, steam cracking gas oils or naphthas and phenol extracts of these relatively aromatic distillates. Suitable feeds include both distillate and residual fractions boiling above about 650° F.

A particularly preferred feed is that petroleum fraction known as clarified oil thermal tar. The preparation of this thermal tar is well known and is no part of the invention but will be summarized herein. Fractionation of catalytic cracking products yields a relatively high boiling bottoms fraction containing catalyst. The catalyst is separated in a settler or clarifier and the effluent oil is known as clarified oil. This is a refractory and poor cracking stock. This clarified oil is thermally cracked by the conventional thermal cracking process at a temperature in the range of 850° to 950° F. and a pressure of 100 to 1000 p. s. i. g. The bottoms fraction separated from the thermal cracking products is the so-called thermal tar, a refractory stock. Such thermal tars are characterized by the following average values:

Carbon, wt. percent	About 90.0.
Hydrogen, wt. percent	About 8.5.
Sulfur, wt. percent	About 1.1.
Oxygen, wt. percent	1.
H/C	1.2 atomic ratio.
Gravity	1.1° A. P. I.

This feed is then admixed with a highly aromatic petroleum fraction containing at least about 50 weight percent aromatics and boiling above about 700° F. which has been partially hydrogenated as explained in further detail below. The cracked fractions previously disclosed as being utilized for the feed can thus also be utilized as the component for hydrogenation as long as the minimum boiling point of about 700° F. is observed. The hydrogenated component can also include, however, virgin fractions such as aromatic extracts of lubricating oils. The feed can thus be admixed with an identical component which has been hydrogenated or another fraction meeting the stated requirements.

Hydrogenation is commonly conducted in the liquid phase over such sulfur insensitive catalysts as molybdenum sulfide or nickel tungsten sulfide at 500 to 3000 p. s. i. g., 650° to 750° F., 0.3 to 5 v./v./hr., incorporating 100 to not more than 800 s. c. f. of H₂ per barrel of feed. The effect of hydrogenation on a typical diluent (700°–900° F. clarified oil thermal tar) is shown below:

	700–900° F. Tar (A)	A+400 S. C. F. H ₂ /Bbl.
ASTM Distillation—Vol. percent at °F. Conv. to 760 mm.:		
I. B. P.	550	455
5%	660	590
50%	740	718
95%	875	840
Sp. Gr. 60/60	1.043	1.015
Wt. percent Hydrogen	8.60	9.46
Wt. percent Carbon	88.25	90.29
H/C atomic ratio	1.17	1.25
Wt. percent Sulfur	1.81	0.81
An. Pt. °F	98.6	91.4

The thermal cracking is preferably carried out non-catalytically in a coil and soaking drum at 800°–1000° F., 0.25 to 10 v./v./hr. depending on temperature, 100–2500 p. s. i. g. depending in part on diluent boiling range. In general operation at higher pressure, long residence time

and low temperature is preferred, e. g., 2000 lbs., 1 v./v./hr. and 820° F.

The amount of cracked aromatic petroleum fraction utilized as compared to the hydrogenated diluent is in the range of 1/2 to 6/1. It is to be noted that no extraneous hydrogen is added during the cracking operation and that the thermal cracking is non-catalytic. There is thus no problem of catalyst contamination during this step.

The thus cracked thermal tar can then be stripped at reduced subatmospheric pressures, less than 20 mm. Hg and at temperatures of up to 525° F. at the specified pressure, so as to obtain materials of the desired softening points. This operation is performed in a flash distillation apparatus having minor rectifying capacity.

The properties of the binder product are:

Softening pt., ° C. (cube in air)-----	70-120
Specific gravity-----	1.2-1.3
Nitrobenzene insolubles, percent-----	0.00-12.00
Acetone insolubles less nitrobenzene insolubles, percent-----	24.00-36.00
Benzene insolubles, percent-----	18-34
Residue upon heating 4 hrs. at 1200° F., percent-----	50
H/C atomic ratio-----	Less than 1/1

The drawing is a schematic illustration of a cyclic process by which the binder can be prepared.

The advantages of this invention are demonstrated in the following example.

Two identical samples of thermal tar having the required properties and the following characteristics were thermally cracked:

Percent carbon-----	91.68
Percent hydrogen-----	8.79
Gravity, ° A. P. I.-----	1.1
Aromatics, wt. percent-----	79.8
Conradson carbon-----	14.36
Viscosity at 210° F.-----	70

The control was cracked by itself, whereas the other sample was thermally cracked together with an equal part by weight of a 700° to 900° F. hydrogenated (400 S. C. F./bbl.) thermal tar as a source of the condensed ring aromatic naphthenic compound. The reaction was carried out in a 1.8 liter cracking bomb at a temperature of 830° to 844° F. for 45 minutes. A maximum pressure of 1800 p. s. i. g. was attained. The products were then stripped at 2-12 mm. Hg to obtain a pitch of softening point of 113° C. The pitch yields were 46.3 wt. percent for the control and 61.5 wt. percent for the product prepared as taught herein, or an increase in yield of almost 33 1/3 %. The pitch produced by this procedure possessed the following properties:

Softening point ----- ° C-----	113
Gravity -----	1.22
Nitrobenzene insolubles -----	0.00
Acetone insolubles less nitrobenzene insolubles percent-----	34.1
Residue after heating ----- do-----	52.8
Benzene insolubles ----- do-----	8.24
H/C -----	0.76

It should be particularly noted that while the H/C ratio of the initial feed was 1.13, the same ratio of the product produced according to this invention was 0.76. There was thus actually a desirable decrease in this ratio despite the fact that the thermal cracking took place with a material which supplied hydrogen.

In the manufacture of the carbon electrode itself the coke is charged together with the carbonaceous binder to

the fabrication system. The binder is normally utilized in an amount of 18 to 45 wt. percent based on the coke.

In general two types of electrodes are employed by the aluminum industry—(a) prebaked, and (b) Soderberg self-baking electrode. In the former, a mixture comprising, for example, 78-82% of calcined coke aggregate and 18-22% of pitch is molded at pressures of about 5000 p. s. i. or extruded and then baked for periods up to 30 days at 1800°-2400° F. These preformed electrodes are then used in electrolytic cells, being slowly lowered into the molten alumina-cryolite bath as they are consumed. Butts of the unconsumed electrodes are reground and used in subsequent electrode preparations.

The Soderberg process involves the continuous or intermittent addition of a pitch paste to the top of the cell as the electrode components in the lower part of the cell are consumed. In this operation the paste represents a blend, for example, of about 70-72% coke aggregate and 28-30% of pitch. The cells operate at temperatures of 1740°-1760° F. and electrodes are consumed at the rate of about 0.5-1.0 inch per day. The paste is baked into an electrode by the hot cell gases in the two months' period between the time it is added at the top and the time it is used. The net consumption of coke represents 0.4 to 0.5 lb. per pound of aluminum metal produced. It can be seen that the actual manner of fabricating the electrodes is not the essence of this invention. Both methods have in common the baking of the charge coke and binder at a temperature in the range of 1700° to 2400° F.

The advantages of this invention will be apparent to those skilled in the art. A new process of providing electrode binders is made available. High yields are obtained and there is no problem of catalyst contamination in the process itself.

It is to be understood that this invention is not limited to the specific examples which have been offered merely as illustrations and that modification may be made without departing from the spirit of the invention.

What is claimed is:

1. A process for preparing a carbonaceous binder for carbon electrodes said binder having a softening point in the range of 70° to 120° C., a hydrogen to carbon atom ratio of less than 1 and less than the feed and a specific gravity of 1.2 to 1.3 which consists of the steps of admixing from 1/2 to 6/1 parts of a cracked, highly aromatic petroleum fraction containing at least about 50 weight percent aromatics and having a minimum boiling point of about 650° F. with a partially hydrogenated, to the extent of 100 to 800 s. c. f. of hydrogen/bbl., cracked, highly aromatic petroleum fraction said aromatic fraction containing at least about 50 weight percent aromatics and having a minimum boiling point of about 700° F.; thermally and non-catalytically cracking the mixture in the liquid phase at 0.25-10 v./v./hr., a pressure in the range of 100 to 2500 p. s. i. g., at a temperature in the range of 800° to 1000° F. and stripping the resultant product at a maximum temperature of 525° F. and subatmospheric pressure of less than 20 mm. Hg to produce the desired binder.

2. The process of claim 1 in which the aromatic fractions employed are clarified oil, thermal tars.

3. A composition suitable as a binder for carbon electrodes said binder having a softening point in the range of 70° to 120° C., a hydrogen to carbon atom ratio of less than 1 and less than the feed and a specific gravity of 1.2 to 1.3, said binder being prepared by admixing from 1/2 to 6/1 parts of a clarified oil thermal tar feed containing at least 50 weight percent aromatics with a clarified oil thermal tar boiling above about 700° F. which has been hydrogenated catalytically with from 100 to 800 s. c. f. of hydrogen/bbl.; thermally and non-catalytically cracking the mixture in the liquid phase at 0.25-10 v./v./hr., a pressure in the range of 100 to 2500 p. s. i. g., at a temperature in the range of 800° to 1000°

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F. and stripping the resultant product at a maximum temperature of 525° F. and at subatmospheric pressure of less than 20 mm. Hg to produce the desired product.

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