

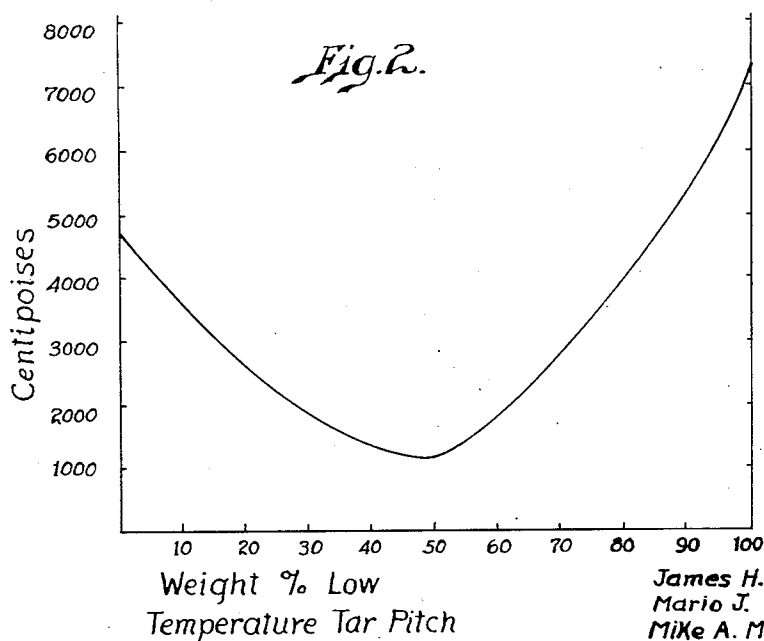
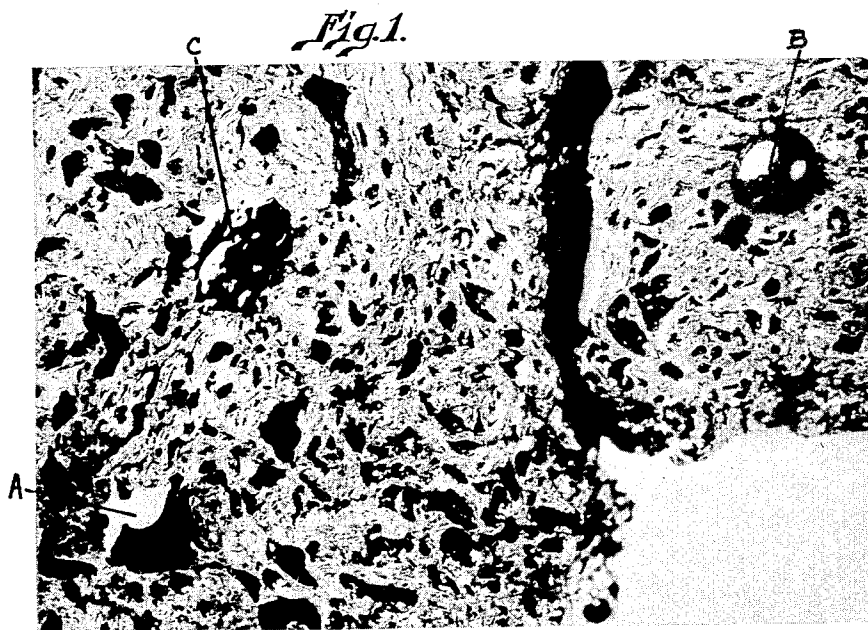
May 22, 1962

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ELECTRODE BINDER PITCH

3,035,932

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2 Sheets-Sheet 1



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2 Sheets-Sheet 2

Fig. 3.

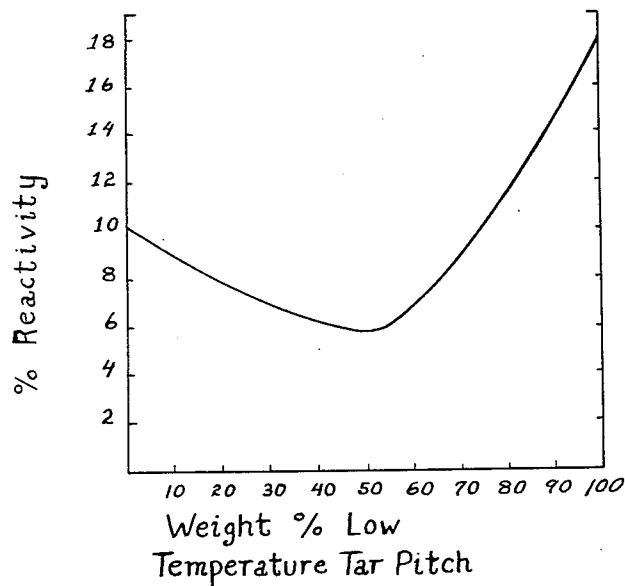
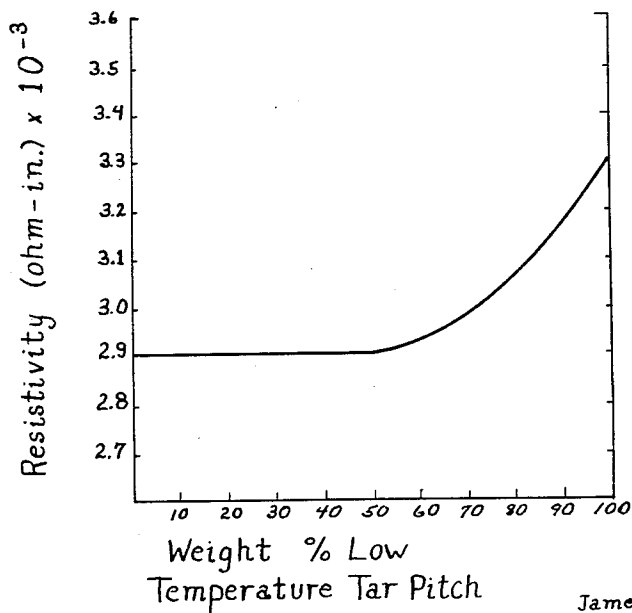


Fig. 4.



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ELECTRODE BINDER PITCH

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4 Claims. (Cl. 106-284)

This invention relates to the utilization of tars produced in the carbonization of bituminous materials. More particularly, it is directed to an electrode binder comprised of a low-temperature tar pitch and a high-temperature tar pitch.

Peat, brown coal, lignite, sub-bituminous and bituminous coals are bituminous materials which have been proposed as feedstocks for low-temperature carbonization processes to secure chars or cokes for use as fuel, and tars from which valuable products might be obtained. The present invention is directed to the utilization of such low-temperature tars in the production of electrode binder pitch.

The term "low-temperature carbonization," as used herein, refers to carbonization of bituminous materials at temperatures lower than about 1300° F. Representative of such a process is that described by V. F. Parry in U.S. Patent 2,773,018 and in "Drying and Carbonizing Fine Coal in Entrained and Fluidized State," Bureau of Mines Report of Investigations 4954, U.S. Department of Interior, dated April 1953.

The term "low-temperature tar," as used herein, refers to tars produced by low-temperature carbonization of peat, brown coal, lignite, sub-bituminous or bituminous coals. Such tars are generally oily, tarry organic masses ranging from viscous liquids to soft semi-solid materials at room temperature and may contain small quantities of char, ash or other inert material, dissolved gases and water.

The term "low-temperature tar pitch," as used herein, refers to pitch obtained by distillation of low-temperature tars.

The term "high-temperature tar," as used herein, refers to tars produced by carbonization of peat, brown coal, lignite, sub-bituminous or bituminous coals at temperatures above about 1600° F. The most prevalent variety are the "coke-oven" tars.

The term "high-temperature tar pitch," as used herein, refers to pitch obtained by distillation of high-temperature tars.

A typical analysis of low-temperature tar obtained by carbonization of Texas lignite at 946° F. utilizing the Parry process, supra, is shown in Table 1 below.

TABLE 1

Analysis of Crude Tar

Ash, weight percent	0.35
Specific gravity, 60°/60° F	0.9867
Moisture, weight percent	2.9
C-I (quinoline-insolubles), weight percent	1.41
Distillation, ASTM D20-52, dry basis, weight percent:	
To 170° C.	2.2
170-235° C.	18.4
235-270° C.	12.6
270-300° C.	12.8
300° C. to decomposition temperature	31.3
Residue at decomposition temperature	19.7
Loss	3.0
Decomposition temperature, ° C.	329
Analysis of distillate, vol. percent:	
Tar bases	4.3
Tar acids	23.9
Neutral oil	71.8
Hydrocarbon types: ¹	
Saturates	14
Olefins	40
Aromatics	46

¹ Method disclosed in article by G. U. Dinneen et al., "Shale Oil Naphthas: Analysis of Small Samples by Silica Gel Adsorption Method," Analytical Chemistry, vol. 19, p. 992 (1947).

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Low-temperature carbonization is generally favored for the production of large quantities of tar as compared to high-temperature processes, thus permitting recovery of considerably greater amounts of tar oils. However, considerable differences exist in the nature of the tars. High-temperature tars are completely aromatic and contain only about 2 to 10 percent of phenolic constituents, but substantially all of these are low-boiling tar acids. Low-temperature tar is of lower specific gravity and is only partially aromatic, i.e. about 10-45 percent; it contains relatively large quantities of phenolic constituents, ranging from 20 to 40 percent of the tar. The pitches obtained by distillation of these tars are chemically similar to the initial feedstock, the lower molecular weight compounds having been removed. Further information regarding the nature of these two tars can be found in "Chemistry of Coal Utilization," vol. II, chapter 31, edited by H. H. Lowry, and "Asphalts and Allied Substances," by Herbert Abraham, vol. I, chapter XVII.

Generally, the product recovery treatment of low-temperature tars involves a distillation process to recover oils from which the tar acids are removed. These phenolic constituents are usually a readily marketable commodity and constitute a definite enhancement to the process. Tar bases may also be extracted from the distillate although of lesser commercial significance. The neutral oil remaining after such extraction has been proposed as a fuel, or as a feedstock for various refining operations, or for separation into its constituent fractions. The pitch residue which constitutes a great percentage of the original tar, about 25 to 80 percent, has been considered of poor economic value and used as a fuel or briquetting binder. Much experimental work has been devoted to the development of more valuable use for this pitch, including the preparation of binders for carbon products.

Binder pitches for carbon electrodes, especially anodes for the electrolytic production of aluminum, must meet certain criteria. Generally, they must produce electrodes having low resistivity and satisfactory reactivity, and it has heretofore been considered that these properties could only be obtained by a high-temperature pitch binder. Accordingly, pitches derived from high-temperature tars, generally coke-oven pitches, have been used in the production of these anodes.

The usual procedure for the production of pre-baked carbon anodes consists of mixing a high-temperature tar pitch (coke-oven) binder with the coke or carbon aggregate (usually petroleum coke) at a temperature high enough so that the pitch binder is fluid. The green electrode mix is then molded into the desired shape under pressure, and then the plastic-shaped articles or green electrodes are baked at a slowly rising temperature to an ultimate temperature above about 1000° C. so that the pitch binder is carbonized and the anode achieves the desired physical strength.

Because of the economics of low-temperature carbonization processes, it would be greatly advantageous if low-temperature tar products could be used to produce anode binders. However, attempts to use pitches derived from the distillation of low-temperature tars have resulted in totally unsatisfactory anodes. Several processes have been developed for conversion of the low-temperature tar into a more aromatic substance from which satisfactory binders have been derived; however, these conversion processes are costly.

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It is an object of this invention to utilize low-temperature tars in the production of binder pitches for carbon electrodes.

It is also an object to provide an improved electrode binder pitch composition in which low-temperature tar pitch is employed.

Other objects and advantages will be obvious from the following detailed specification and attached drawings wherein:

FIG. 1 is a photomicrograph illustrating the wetting power of various pitch binders on petroleum coke;

FIG. 2 is a graph representing the viscosity of various pitch blends;

FIG. 3 is a graph showing the effect of the percentage of low-temperature tar pitch on the reactivity of anodes made therewith;

FIG. 4 is a graph illustrating the variation in anode resistivity occasioned by varying amounts of low-temperature tar pitch in the anode binder.

It has now been found that a desirable binder pitch for carbon electrodes can be prepared by admixing pitch prepared by distillation of low-temperature tars with pitch obtained from high-temperature tars and wherein the low-temperature material constitutes about 25 to 90 percent by weight of the binder, and preferably about 40 to 75 percent.

This pitch mixture has been found to effect greater wetting of the coke or carbon aggregate. The properties of the anodes produced therefrom are equal and often superior to those of anodes prepared with the standard high-temperature or coke-oven pitch binders, especially with respect to reactivity.

By microscopic examination, it has been observed that the pure low-temperature tar pitches fail to wet the petroleum coke particles and that the high-temperature or coke-oven pitch effects only a small amount of wetting. However, blends of the two materials in the hereindescribed range are noted to penetrate into the coke pores and wet the coke surface. As stated previously, the mere addition of solvents to reduce the viscosity of the pitches is not comparable since the wetting power is not necessarily improved. Illustrating this improved wetting effect is the photomicrograph of FIG. 1 wherein three binder pitches have been placed upon petroleum coke which is at a temperature of 160° C. A is a coke-oven or high-temperature tar pitch of 110° C. softening point (cube-in-air); B is a low-temperature lignite pitch having a softening point of 120° C.; C is a composite binder pitch of the present invention containing 50 percent of the low-temperature material and 50 percent of the high-temperature tar pitch. As is evident from the photomicrograph, the low-temperature material (B) remains in a ball upon the surface of the petroleum coke aggregate and has apparently not wet the coke. The high-temperature pitch (A) remains in substantially the same condition indicating little or no wetting of the coke. However, the composite pitch (C) of the present invention has substantially completely penetrated into the pores of the coke.

The wetting effect is of importance since non-porous and/or high-density anodes are desired to obtain low resistivities and low reactivity. The pitch blend tends to penetrate deeply into the pores of the coke aggregate wherein it is subsequently carbonized during anode baking.

The nature of the cooperation between the aromatic high-temperature tar pitch and the normally deleterious low-temperature material is not completely understood. Anodes made from binders containing above 50% of the low-temperature material exhibit progressively increasing

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resistivity¹ and reactivity² as the proportion of low-temperature material is increased, as shown by FIGS. 3 and 4, and as a result binders containing not more than 75% of the low-temperature tar pitch are preferred. However, as FIGS. 3 and 4 show, use of as little as 10% of high-temperature material results in a sharp drop in reactivity and resistivity. Binders containing as much as 90% of low-temperature pitch can be used depending on the economics of pitch and power at a particular location. Binder pitches having less than 25 percent by weight of low-temperature tar pitch produce anodes with higher reactivity, as shown in FIG. 3, and reduced wetting power. Also, the economic advantage in using the less costly low-temperature material is minimized.

It has been noted that the optimum in the blend formulation approximates the optimum in a viscosity³ curve, as shown in FIG. 2. To this extent, reduction in the viscosity of the pitch is of significance, although not controlling since attempts to duplicate the improved wetting power of the blend by adding various solvent fractions to the high-temperature tar pitches were without success.

The pitch viscosity is related to the properties of anodes produced therefrom. Anode reactivity reaches its optimum range at approximately the optimum in the viscosity curve, as is shown by FIG. 3, and the resistivity rapidly rises above about 60 percent, as is shown by FIG. 4. The test anodes were prepared according to usual commercial practice from petroleum coke and 18.5 percent of a binder containing various amounts of lignite low-temperature tar pitch in admixture with the standard coke-oven pitch.

Either whole low-temperature tar, or so-called "single phase" extracts thereof, such as the hexane-soluble portion, may be distilled to obtain the pitch. Atmospheric batch type of distillation is preferably employed, although vacuum flash distillation may also be used. The pitch obtained should preferably have a softening point (cube-in-air) between about 80° C. and 130° C. for present commercial practices, although higher softening points may also be used.

The optimum blend within the previously described range should be determined for each mixture of starting material since there is some variance in the nature of the pitches generally available. As mentioned previously, the low point of the viscosity curve for the mixture is generally a good indication of the optimum composition.

The two pitch components are preferably admixed in

¹ A current of known amperage is passed through a cylindrical anode, and a set of probes is used to determine the voltage drop along the longitudinal axis. Resistivity is then calculated by the formula:

$$\rho = \frac{(E)(A)}{(I)(D)}$$

where

ρ = resistivity in ohm-inches

E = average voltage drop across probes

A = cross-sectional area of sample (sq. in.)

I = current passed through samples (amperes)

D = distance between probes (inches)

² The reactivity of anodes in a fluoride electrolyte bath for the production of aluminum from alumina has been successfully approximated in the laboratory by a sulfate reactivity test. This test measures the loss in weight of a carbon specimen, 1 inch in diameter by ½ inch, when immersed in molten sodium sulfate at 960° C. It is considered an excellent measure of the reactivity of an anode in a bath for the production of aluminum by the Hall process.

³ The viscosity of a binder pitch can easily be determined by the following method. Eight hundred grams of pitch are placed in a container and heated to 140° C. pitch temperature at which time a thermocouple, stirrer and the spindle of a "rotating bob" type viscometer are placed in the pitch, the heating of which is continued until 190° C. is reached with intermittent stirring to reduce air bubbles. At 190° C., the heating is discontinued, the mixture stirred a definite amount of strokes, and the temperature and the torque on the viscometer read. After 4½ minutes, the mixture is again stirred the same amount, the temperature is read, and at exactly five minutes the viscometer is read; this procedure is repeated until the pitch reaches 100° C. From the data obtained, a viscosity-temperature plot for the pitch tested may be obtained.

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the fluid or molten state and may then be added to the coke aggregate in either molten or solid state.

Although about 17.5 percent by weight of the high-temperature pitch binder in the green electrode mix has been generally used in the fabrication of pre-baked anodes for the electrolytic production of aluminum, it has been found that 18.5 percent by weight is preferable for the blends of this invention, and amounts of 15 to 20% by weight can be used.

In accordance with the present invention, a lignite low-temperature tar was distilled at atmospheric pressure to obtain a pitch having a softening point of 112° C. It was then admixed with a commercially available coke-oven or high-temperature tar pitch having a softening point of 110° C. Equal parts of each were used and the blending was in the molten or fluid state to achieve uniformity.

The composite pitch binder was then added to petroleum coke aggregate in the amount of 18.5 percent by weight and anodes were prepared in accordance with usual commercial practice, the final baking temperature being about 1084° C. Reference anodes utilizing a 100 percent coke-oven pitch binder were similarly prepared. On evaluation, the properties shown in Table 2 were obtained.

TABLE 2
Anode Properties

Binder	Percent Binder	Baked Apparent Density, ¹ g./cc. (av.)	Resistivity, ohms-in. (av.)	Percent Reactivity (av.)
High-temperature (coke-oven) pitch, 110° C., S.P.	17.5	1.44	0.0028	13
Low-temperature (lignite) pitch, 112° C., S.P.	17.5	1.37	0.0032	28
Low-temperature pitch	18.5	1.36	0.0034	21
50% Low-temperature pitch	18.5	1.42	0.0029	6
50% High-temperature pitch				

¹ The anode is weighed dry, then soaked for 24 hours in water containing a few drops of a detergent solution. It is suspended in water and weighed; then it is removed, dried with a towel and weighed while wet. The difference between the weight in water and wet weight is determined and then this figure is divided into the dry weight to give the baked apparent density.

In a further instance, low-temperature tar pitch hav-

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ing a softening point of 117° C., a commercial high-temperature tar pitch having a softening point of 110° C., and petroleum coke aggregate were mixed together thoroughly at 153° C. The total pitch comprised 83% by weight low-temperature tar pitch and 17% high-temperature tar pitch, and constituted 17% of the mix. Anodes were prepared from the mix in accordance with usual commercial practice, and were baked at 1100° C. Reference anodes were similarly prepared in which a 100% high-temperature tar pitch binder, and the above-mentioned petroleum coke aggregate, were used. When the anodes were evaluated, those made with the mixture of pitches showed resistivity only 7% higher than those made with only high-temperature pitch as the binder, and there was no substantial difference in reactivity. Such an increase in resistivity can be tolerated economically in some localities depending on the relative cost of binder and power.

This application is a continuation-in-part of our application Serial No. 752,013, filed July 30, 1958, now abandoned.

Having thus described the invention, we claim:

1. A binder for carbon electrodes, consisting essentially of an admixture of low-temperature tar pitch and high-temperature tar pitch and wherein said low-temperature tar pitch constitutes 25 to 90 percent by weight of the admixture.

2. A binder for carbon electrodes, consisting essentially of an admixture of low-temperature tar pitch and high-temperature tar pitch and wherein said low-temperature tar pitch constitutes 40 to 75 percent by weight of the admixture.

3. A green electrode mix consisting essentially of a mixture of carbon aggregate and a binder consisting of low-temperature tar pitch and high-temperature tar pitch, said low-temperature tar pitch constituting 25 to 90 percent by weight of the binder.

4. A green electrode mix for anodes used in the electrolytic production of aluminum, consisting essentially of a mixture of carbon aggregate and 15 to 20 percent of a binder consisting of low-temperature tar pitch and high-temperature tar pitch, said low-temperature tar pitch constituting 25 to 90 percent by weight of the binder.

No references cited.