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METHOD FOR PRODUCING GRAPHITE ELECTRODES

Grigory Konstantinovich Bannikov, Talalikhin Str. I/2, kor. 5, Apt. 332; Grigory Gavrilovich Brusko, I Vladimirskaya Str., 20a, Apt. 19; Abram Lazarevich Livshits, 5-Verkhne-Michailovsky proezd 28, Apt. 9; and Alexander Mironovich Sigariov, Talalikhin Str. I/2, Apt. 244, all of Moscow, U.S.S.R.

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The invention relates to an improvement in the art of making shaped carbon articles. It relates particularly to an improvement in the manufacture of graphite electrodes.

This is a continuation-in-part of our application Serial No. 112,746, now abandoned, filed May 19, 1961, entitled: Carbon Graphitic Materials for Electrodes-Tools.

By means of prior art methods similar graphitic articles are manufactured from a charge comprising a powder of mixed solid carbonic materials, such as, coke, soot, coal and graphite. The materials are cohesively compacted by a fusible resin, such as, pitch and resin. Articles produced by such prior art methods have excessive wear in electric pulse working.

It has now been discovered that an electric pulse working electrodes may wear 5–10 times longer when such electrodes are manufactured from raw materials including a solid filler and a binding agent devoid of fusible substances. Such binding agents are encountered in petroleum, pitch semi-coke and semi-coke obtained from pitch which is a product of shale gasification.

The term "petroleum pitch semi-coke" refers to a product being a heavy hydraulic pitch residue obtained from petroleum stills heated without the admission of air at a temperature of the order of 470° C.

The term "pitch semi-coke" defines a product obtained from stills or coke furnaces from coal pitch, said coal pitch itself is a residue product of distillates in coal coking.

Semi-coke obtained by either method contains 8 to 23 percent volatile components which are liberated upon heating to 800° C. The semi-coke utilized in the present invention does not contain ingredients fusible below 395–425° C. When heated, semi-coke is subjected to softening and caking.

A preferred composition comprises 95 percent of semi-coke having 9 to 12 percent of volatiles and 5 percent artificial graphite. A preferable range of graphite crushings is from 5 to 15 percent by weight.

A semi-coke with over 12 percent of volatiles, after grinding and moulding the blanks, does not ensure normal caking thereof during annealing. Such a blank has closed pores, which expand during annealing on account of liberated volatiles.

It has been discovered that closed pores, formed during annealing, may be prevented by mixing powdered semi-coke with leaning additives, such as finely ground coke; through partial oxidization of the semi-coke at temperatures up to 300° C. or adding salts of high hydrolysis, for instance $FeCl_3$ and $AlCl_3$.

It is, therefore, an object of the present invention to provide a method for manufacturing electrode material of excellent quality exclusively from charge that does not include fusible binding agents and whose principal component is semi-coke.

According to the above-stated object, for reducing and stabilizing the required caking capacity of the charge, apart from semi-coke and graphite crushings added thereto, a heat-stabilized substance (for instance, coke with under 7 percent of volatiles) or solutions of salts of high

hydrolysis are also added, said components being preferred in proportions ensuring in the material annealed-open porosity, which is about to begin a disappearance, i.e., open porosity turns into closed porosity.

Salt ions and coke fractions encircle semi-coke fractions and change the surface characteristics thereof and serve as a caking inhibitor.

Slower caking of semi-coke fractions is also achieved by preliminarily oxidizing their surfaces through heating the semi-coke to 200–300° C. and stirring the same in a mixer.

It has also been established that the best properties required in electric pulse working are encountered in a material possessing open porosity about to begin a disappearance. This consideration, or more precisely a rule in a wider application, means that the exact proportion for a charge comprising a principal filler (semi-coke) and a heat-stabilized substance (coke and graphite crushings), may vary in reference to the natural properties of the raw material. However, the change should always yield a product with little closed porosity being in the order of 1 to 2 percent, which, in other words, is about to begin a disappearance or fading away, since this product alone develops the best results in electric pulse working. The more substantial is the closed porosity of the material (which increases the mechanical strength of the material), the worse are the electric erosion conditions, because the pores are subjected to micro-explosions from within and, consequently, graphitic material is pulverized. With no closed porosity at low content of semi-coke in the charge or reduced caking capacity thereof, the properties of the product deteriorate due to insufficient mechanical strength of cohesion between fractions of the material. Consequently, the charge components proportion ensuring open porosity about to begin disappearance, while the moulded blanks are annealed, is a definite dosage applied to the manufacture of the electrode material according to the invention. For determining the optimal relation between semi-coke and heat-stabilized carbonaceous substances or salts of high hydrolysis, rapid experiments are conducted for each lot of the raw material, and the mixture ensuring the optimal limit for disappearance of closed porosity is adopted in industrial production.

The optimal relation of components is found through the preparation of several sample charges with variable semi-coke content in every charge to check their coking capacity. The disappearance limit for the closed porosity is established according to the specific weight, mechanical strength and aspect of the samples, moulded from test charges and subjected to rapid annealing.

For better understanding the idea of the invention for those skilled in the art, we herein provide further elucidation.

(1) The initial procedure is confined to determining the volatile content in semi-coke and coke samples, heated in a muffle furnace at 850±20° C. through measurements of weight losses.

(2) With consideration of the volatile content in the samples (see item 1) calculate the weight of semi-coke and coke components, required for preparing 100 g. of charge with an average 10–15 percent of volatiles. Also, the amount of artificial graphite in the charge should be within 5 to 15 percent.

Charge is composed by coke, semi-coke and artificial graphite crushed to the size of grains sieved through 0.09–0.15 mm. mesh.

(3) Apart from the principal charge prepared in accordance with item 2, prepare additional 3 or 4 charges of 100 g. each, and the weight of coke in each of them should increase or decrease by 5 percent.

The weight of coke in the charge also changes. The

amount of artificial graphite in the charge is constant.

(4) Each charge is mixed thoroughly and sieved twice through 0.3 mm. sieve.

(5) Two cylindrical samples 20 mm. high and 20 mm. diameter are moulded in a matrix from each charge. The maximum specific moulding pressure shall be 500 kg./cm.^{2}, with 30 seconds holding at maximum pressure.

(6) The samples are placed into metal crucibles. A sample is arranged in the centre of the crucible and is insulated therefrom all around by a layer of calcined petrol coke. The crucible is covered with a metal lid.

(7) The metal base with loaded crucibles is introduced into a muffle furnace at 400° C. The furnace is closed and increased in heat to 800° C. at the rate of 2° C. per second by means of a programming governor.

The temperature is controlled by a chrome-aluminum or platinum-iridium thermocouple. The thermocouple is inserted through the back wall of the muffle at half the height of the crucible.

At 800° C. the furnace is switched off and the crucibles are removed therefrom.

(8) On cooling, the samples are removed from the crucibles.

The good samples are weighed for determining the apparent specific weight and tested for mechanical strength of compression.

The optimal relation of the charge components ensures clean surface of the calcined samples. Excessive semi-coke causes swelling of the sample body and blows therein, while the shortage of semi-coke results in lower density and mechanical strength of the material.

The samples which have a volumetric weight of at least 1.25 g./cm.^{3} and strength of compression of at least 500 kg./sq. cm. are preferred.

For better illustration of the concept of the invention, but not limiting the same, we hereunder offer exemplary proportions of the moulding powder composition and technology for obtaining electrode material at optimal proportions of the components.

EXAMPLE 1

	Percent
(1) Semi-coke with 9–12 percent of volatiles	95
(2) Graphitic crushings	5

EXAMPLE 2

(1) Semi-coke with 18 percent of volatiles	84
(2) Graphitic crushings	15
(3) Iron chloride	1

EXAMPLE 3

(1) Semi-coke with 23 percent of volatiles	50
(2) Coke with 4 percent of volatiles	35
(3) Graphitic crushings	15

The initial raw materials—semi-coke with 8–23 percent of volatiles, coke with under 7 percent of volatiles and graphite (graphitic chips or waste crushings of graphitic articles)—are subjected to separate preliminary crushing in roll crushers to the 4 mm. fractions.

The material is then subjected (also separately) to fine grinding in tubular ball mills with pneumatic discharge of the dust.

The adjustment of the tubular mills and the qualitative control of grinding should be adapted for less than 0.09 mm. fractions.

The amount of 0.09 mm. and smaller fractions in the finely ground material should be within 90±3 percent, besides the maximum size of fractions should be no more than 0.15 mm.

Such crushed semi-coke, coke and artificial graphite are selected in proportions, provided by the dosage procedure.

The ground charge components are mixed in mixing machines having Z-shaped blades without heating. During this procedure salts of high hydrolysis are added. The salts are primarily dissolved in water (with view of obtaining saturated solutions at room temperature) and the solution obtained is added into the mixer.

To destroy the compacted semi-coke fractions, the charge is allowed through a sieve with a 0.3 mm. mesh.

Moulding of blanks

Matrixes with well-ground and chrome-plated surfaces are used in moulding. The taper of the matrixes should be as 0.2 to the height thereof.

Blanks are moulded without heat applied to the charge at a hydraulic vertical press in a press-mould or matrix. The specific pressure of moulding should be 500 to 700 kg./sq. cm. with 30 sec. holding at maximum pressure.

Annealing of blanks

Annealing increases strength and density of the blanks on account of substantial shrinkage and caking of the initial materials.

In annealing, the blanks are protected from oxidization in the multi-chamber gas kiln.

The blanks are packed in metallic boxes or other receptacles without admission of air. The bottom of the blanks, arranged vertically, should securely contact the filling

In choosing filling, preference is given to wastes from graphitic furnaces having a particle size of 0.3–0.4 mm.

Annealing temperature graph

Temperature (under the arch of the chamber):	Duration of temperature rise for the specified range (in hrs.)
0–400	90–120
400–600	80
600–700	33
700–800	33
800–900	25
900–1000	20
1000–1100	17
1100–1300	25
Holding at 1,300±25° C.	20
Total	343–373

Graphitization

The blanks are graphitized in electric resistance furnaces developing 2,500 to 2,800° C. The electric power supplied to the furnace is converted into thermal power at current flow in the core, consisting of the blanks to be graphitized, statified with carbonic filling, possessing substantial electric resistance.

The furnace hearth is removed prior to every new graphitization process.

The hearth is framed from coke size of 0.5 mm., which is primarily desiccated until its moisture content is no more than 5 percent.

The hearth is leveled and covered with the lower layer of coke (5–10 mm. large) to the height of 100–150 mm., and the core of blanks selected for graphitization is arranged thereon.

The core is arranged symemtrically with respect to the furnace longitudinal walls and the current conductors.

For temperature measurements, taken by an optic pyrometer, a graphitic tube is attached to the core.

For a 30 ton weight of blanks, charged into the furnace, graphitization is conducted under the following electric quantities:

(1) Initial power of the furnace	800 kw.
(2) Rate of furnace power increment	200 kw. per hr.
(3) The furnace is disconnected when the temperature has reached 2,500 ±50° C. at the middle of the core.	

The manufactured graphitic articles are packed in boxes with wrapping paper or cardboard and shipped to the consumer by any transportation, guaranteeing the articles from physical damage.

In manufacturing graphitized material according to the present invention the following characteristics are achieved in the articles:

(1) Volumetric weight at least 1.65 g./cu. cm.
(2) Mechanical strength of compression at least 600 kg./sq. cm.
(3) Mechanical bending strength at least 300 kg./sq. cm.
(4) Specific electric resistance 12–20 ohm mm.^{2}/m.
(5) Relative volumetric wear in electric pulse working no more than 0.3 percent.

It should be noted that under similar circumstances the wear of all electrodes obtained otherwise than in the manner described heretofore from the charge comprising fusible binding agents (such as pitch, resin) amounts to 1.5–5 percent.

Consequently the present invention provides reduction in electrode wear and has advantages over other methods of manufacturing carbonic materials.

Although the present invention has been disclosed according to the preferred embodiment, it will be understood by those skilled in the art that changes and variations may occur without departing from the spirit and scope of the invention.

These variations are considered to be within the idea and scope of the invention and the appended claims.

What is claimed:

1. The method of producing an electrode article consisting essentially of charging a mold with the following ingredients: a 50–95% by weight pitch semi-coke having 8–23% by weight voltatile components which are liberated upon heating to 800° C. and does not contain ingredients fusible below 425° C., 0–35% by weight coke, 5–15% by weight graphite, and 0–1% of a salt selected from the group consisting of iron chloride and aluminum chloride; and then molding said charge under a pressure of 500–700 kg./cm.^{2}, then substantially continuously gradually increasingly heating said mold containing charge to approximately 1,300° C. over a period of between 343–373 hours, thereafter the thereby produced blanks are graphitized by heat treatment until the core of the blank reaches a temperature of between 2,450°–2,550° C.

2. The method of producing an electrode article consisting essentially of charging a mold with the following ingredients having a particle size of less than 0.3 mm.: a 50–95% by weight semi-coke, having 8–23% by weight pitch volatile components which are liberated upon heating to 800° C. and does not contain ingredients fusible below 425° C., 0–35% by weight coke, 5–15% by weight graphite, and 0–1% of a salt selected from the group consisting of iron chloride and aluminum chloride; and then molding said charge under a pressure of 500–700 kg./cm.^{2}, then substantially continuously gradually increasingly heating said mold containing charge to approximately 1,300° C. over a period of between 343–373 hours, thereafter the thereby produced blanks are graphitized by heat treatment until the core of the blank reaches a temperature of between 2,450°–2,550° C.

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LEON D. ROSDOL, *Primary Examiner.*

JULIUS GREENWALD, *Examiner.*

J. D. WELSH, *Assistant Examiner.*