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PROCESS OF PREPARING CARBON ELECTRODES AND A PASTE THEREFOR

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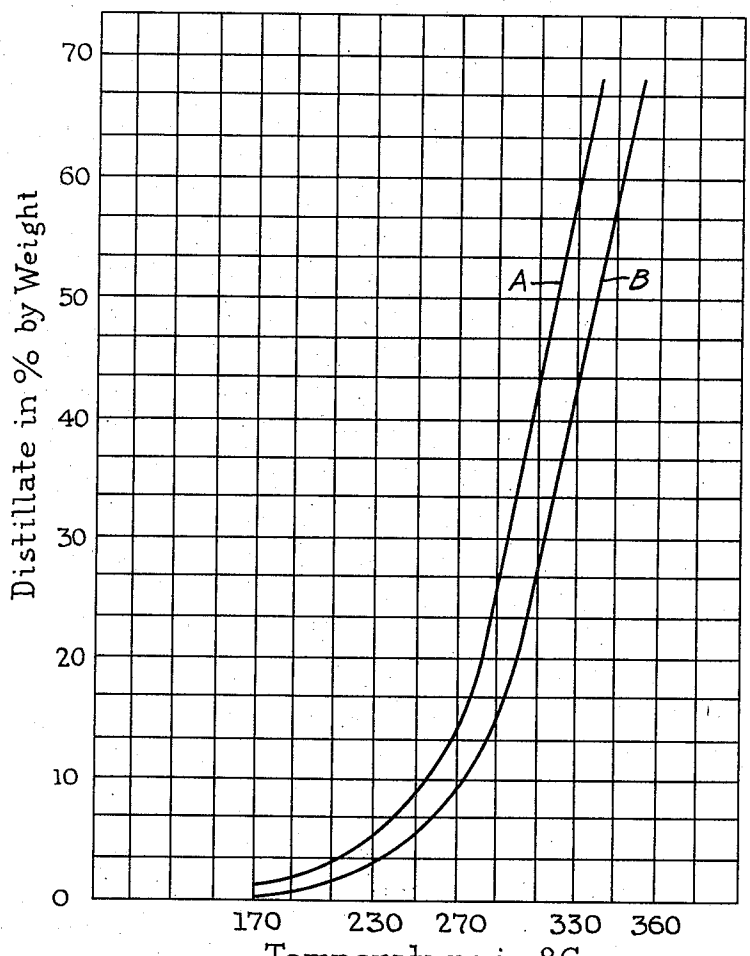

Distillation of Anthracene Oils Used

Distillation Curves of Anthracene Oils Used according to Invention fall between curves A,B.

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PROCESS OF PREPARING CARBON ELECTRODES AND A PASTE THEREFOR

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6 Claims. (Cl. 252—502)

In the production of aluminum by the electrolysis of alumina dissolved in molten cryolite, there are used anodes of agglomerated carbon which are immersed in the electrolyte kept at 950–980° C. The quality of these electrodes has a great influence upon the proper operation of the electrolysis; they must be of high purity, because the constituents of their ashes—metals and silicon—pass into the produced aluminum. It is also important that they be sound—that is to say, free from cracks which would disturb the current distribution—and that they be consumed uniformly, without introducing carbon dust into the electrolysis bath. Finally, they have to be able to resist, without breaking, sudden temperature variations, for example, as when they are introduced into the molten electrolyte where their temperature suddenly rises from that of ordinary temperature to 950° C.

In the course of the electrolysis, the anodes burn with the oxygen of the alumina, and their consumption amounts to an important part of the production costs of aluminum. Until now, a net consumption of less than 470 kilograms per ton of aluminum was exceptional. By net consumption is understood the figure obtained after deducting the waste portions attached to the current lead-in of preliminarily baked (prebaked) anodes, or after deducting the volatile matters of the pitch in the paste of continuous anodes of the Soderberg type.

The present invention, which results from applicant's researches, makes it possible to improve considerably the quality of anodes and to cut down their consumption per ton of aluminum produced.

The invention consists in using as binder a pitch that possesses well defined characteristics, and in adopting for the powdered carbon a continuous granulometry (particle distribution) comprising a minimum percentage of coarse grains having dimensions exceeding 5.5 mm., as well as a minimum percentage of fine grains smaller than 0.16 mm.; these percentages are not the same for prebaked anodes as for continuous anodes of the Soderberg type. Moreover, the invention comprises the adoption of a series of precautions and controls which will be defined hereafter.

The nature of the pitch used as binder has considerable influence upon the quality of the anodes intended for the production of aluminum. This pitch is most often coal pitch, but certain petroleum pitches can also be used.

According to the invention, the softening temperature of the pitch should exceed 70° C. and it should preferably range between 70° and 85° C. Pitch is a complex mixture of hydrocarbons, the composition of which is not well defined. The above mentioned softening temperature is measured by the Kramer-Sarnow method; it is the temperature at which a given weight of mercury (5 grams) passes through a column of pitch five cm. high which adheres perfectly to the lower end of a tube 6 mm. in diameter, the tube being vertically disposed within a vessel heated in such a manner that the temperature rises by 1° C. per minute.

The pitch itself serves as binder for the raw (unbaked) anode, but in the course of the baking it loses its volatile matters and it is its residual coke that binds the grains of carbon dust in the baked anode. Accordingly, this residue of the carbonization (coking) of the pitch has a vital effect on the quality of the baked anode.

According to the invention, a pitch is chosen which gives a residue on carbonization (coking) in excess of 50%. The coking residue is determined as follows: a sample of pitch is placed in a small crucible and slowly heated so as to attain a temperature of 460° to 470° C. within about twenty minutes. The small crucible is then covered with an adjusted cover and is introduced into another larger crucible, the space between the walls of the two crucibles being filled with grains of wood charcoal, so as to avoid entry of air. The assembly is heated in a muffle-furnace at 800° C. for five hours. Following cooling, out of contact with air, the coke residue is weighed; its weight should exceed 50% of that of the initial pitch sample.

Another important characteristic of the pitch is the proportion of benzene insoluble resins, and resins soluble in anthracene oils. Indeed, it is this portion of the pitch that contributes the binding qualities necessary to obtain a good anode. The resins should constitute more than 20% of the total weight of the pitch.

To determine the proportion of benzene soluble resins in the pitch, pure crystallizable benzene is employed (95% distilling between 79.5° C. and 80.5° C.).

The anthracene oils, extracted from coal tar, are complex mixtures; to control the quality of the pitch, there are used oils having the following characteristics:

Density at 15° C., 1.085;
Proportion of oil distilling below 250° C., less than 15%;
Water content, less than 0.5%.

The distillation curve of the anthracene oils used should fall between the two curves shown on the figure attached to the present specification.

Finally, it is important that the residue from the coking of the resins insoluble in benzene and soluble in anthracene oils exceed the proportion of 89%, as shown by the following Table I:

TABLE I

Pitch Sample No.	1	2	3	4	5	6	7
Softening temperature, °C.	82	79	79	83	76	77	78
Residue of coking, percent	52.11	52.24	50	58.6	52.85	47.04	50.2
Insoluble in benzene, percent	32.31	31.82	27.38	34.82	28.12	27.21	29.90
Insoluble in anthracene oils, percent	7.89	10.60	6.65	12.10	8.15	5.19	10.57
Resins insoluble in benzene and souble in anthracene oils, percent	24.42	21.22	20.73	22.72	19.97	22.02	19.33
Residue from coking the above resins, percent	91.30	92.67	91.47	87.74	87.67	86.41	84.39
Results obtained with anodes in the production of aluminum	excellent	very good	very good	poor	poor	bad	very bad

The residue from coking the resins is determined by the method described above for pitch.

It will be seen that pitch No. 4, all other character-

istics of which are excellent, produced nevertheless poor anodes, because the residue from coking the resins does not reach a proportion high enough.

It is preferable to use a pitch that has a very small fraction distilling at 360° C.

A pitch of good quality, conforming to the present invention, can be employed indifferently for producing either anodes pressed and baked before their use, or for producing carbon paste for feeding continuous anodes of the Soderberg type. On the other hand, the granulometry (particle distribution) that should be adopted for the carbon dust, is somewhat different for these two types of anodes, as will be studied successively below:

Pressed and prebaked anodes

Very pure cokes are used for manufacturing these anodes: pitch coke or petroleum coke, deprived of their voltatile matters by calcination in the absence of air and ground to dust. The real specific gravity of the dust should range between 2 and 2.05, preferably between 2.02 and 2.05, for petroleum coke, and between 1.94 and 1.97 for pitch coke.

The dust should have a continuous granulometry, that is to say, it should include grains of all dimensions from 15 mm. up to impalpable powder. Moreover, it should possess the following characteristics:

At least 45% of the total dust should be arrested by a sieve having openings of 0.83 mm. and 15% of the total dust should have dimensions ranging between 5.5 and 15 mm.

33 to 35% of the total dust should consist of particles passing through a sieve having openings of 0.16 mm., while 25% should pass through a sieve with openings of 0.089 mm.

The following granulometry, which is given by way of example, and does not limit the invention, is satisfactory:

Opening of the sieve in mm.	15	5.54	3.33	1.70	0.83	0.36	0.16	0.089
Percent	15	7	11	12	10	10	10	25
	45%						35%	

The proportion of pitch to be used with a powder (dust) of such granulometric composition is about 15%. Mixing of the powder with the pitch is carried out according to the process described in French Patent No. 992,508. That is, the oversize on a sieve with openings of 0.16 mm. is first charged into a mixer and mixed until the temperature reaches 140° C. Thereupon, the pitch is introduced and the mixing is renewed until all grains of coke are well wetted. It is only then that the grains passing through the sieve having 0.16 mm. openings are introduced and the mixing is completed.

The green (raw) anode is then formed by compressing the paste at a pressure of 400 to 700 kg. per square centimeter, and thereafter, it is so baked that the real specific gravity of the baked anode is greater than that of the coke employed for making the paste. In fact, experience shows that in this way anodes are obtained in which the binding coke derived from the pitch is burned by the oxygen of the alumina simultaneously with the grains of coke forming the mass of the anode, thereby avoiding loosening of these grains and formation of carbon dust in the electrolyte.

Using anodes made as described above, there has been obtained during a period of six months an average consumption of 430 kg. per ton of alumina produced.

After deducting the weight of the wastes, that is, the portion of the anode which remains attached to the current lead-in, the net consumption of the anode was: 430—40=390 kg. per ton of aluminum.

Carbon paste for continuous anode of the Soderberg type

Since the continuous anode is baked at the temperature of the electrolysis bath, that is at about 950° C., there should be used pitch coke or petroleum coke, the real specific gravity of which—following calcination in the absence of air—ranges between 1.94 and 2, if it be desired to avoid formation of carbon dust due to the loosening of grains in the electrolysis bath.

The granulometric composition of the particles (powder) should be characterized by the following features:

At least 15% of the total particles should have sizes ranging between 5.5 mm. and 15 mm.;

50 to 60% of the total particles should pass through a sieve having a mesh opening of 0.16 mm., and

40 to 48% of the total particles should also pass through a sieve with 0.089 mm. openings.

There is set out below a non-limitative example of a granulometric composition which produced good results:

Sieve Opening in mm.	15	5.54	3.33	1.71	0.83	0.36
Percent grains	15	4	7	4	6	8

Sieve Opening in mm.	0.16	0.089	0.075	0.040	0.020	0.010
Percent grains	9	13	10	8	7	9
	56%					

The mixing of the powder with the pitch binder is carried out according to the process described in French Patent No. 992,508, as stated above in connection with the paste for the prebaked anodes.

The proportion of pitch relative to the total weight of paste is about 30%; it should enable the paste to be sufficiently fluid so that the paste spreads completely on the upper surface of the continuous anode. This fluidity is particularly important when electric current is led to the anode by means of vertically disposed metallic studs.

The anode, the baked lower part of which is consumed as the electrolysis proceeds, slides within its fixed casing so as to compensate for the consumption. However, it has been observed that the upper part of the anode does not slide on the walls of the casing during this downward motion; there always remains a layer of raw paste, more or less thick, which stays stuck to the walls of the casing. As a result, separation occurs along the casing, between the part of the anode already hardened and the raw paste. It is essential that the paste, added at the top of the anode, be sufficiently fluid so as to be able to fill in the voids created by such separation. If this kind of "feeding" does not take place, the voids remain within the mass of the anode, and it has been established that air enters therein and the anode burns inside the casing, which interferes considerably with the proper operation of the electrolysis.

In order to have the paste fluid enough to avoid this drawback, the "spreading" of the paste is checked.

The spreading test is carried out in the following manner: Samples of paste taken from the mixer are molded by compression to obtain cylinders 50 mm. in length and 25 mm. in diameter. They are placed on a metal sheet (sheet iron) 120 mm. long which is slightly inclined and provided with recesses for receiving the samples, the upper end of which is 15 to 20 mm. from the upper end of the sheet. The lower ends of the samples can move downwards freely. The sheet with the samples is disposed, with an inclination of 6.5°, within a stove heated to 220° C.; it remains therein for two hours. After cooling, the elongation of each sample is measured.

The spreading=

$$\frac{\text{elongation}}{\text{initial length}} \times 100,$$

should range between 60 and 80%

By the use of continuous anodes of the Soderberg type made of paste as above described, it has been possible to obtain during a period of six months a consumption of 514 kg. carbon paste per ton of produced aluminum, which corresponds to 440 kg. of baked anode per ton aluminum.

As will be seen, the present invention represents a very important advance in the manufacture of anodes intended for use in the production of aluminum.

I claim:

1. A binder suitable in the preparation of carbon paste for use in the production of electrodes, consisting essentially of a pitch having the following characteristics:

Softening point, Kramer-Sarnow, between 70–85° C.;
Coking residue, in excess 50% by weight of the initial pitch;
Proportion of benzene insoluble resins and resins soluble in anthracene oils, not less than 20% by weight of the pitch;
Residue upon coking of said resins, not less than 89% by weight of said resins.

2. Carbon paste suitable in the production of compressed and prebaked anodes for aluminum manufacture comprising a binder and particles of petroleum coke, said binder consisting essentially of a pitch having the following characteristics:

Softening point, Kramer-Sarnow, between 70–85° C.;
Coking residues, in excess 50% by weight of the initial pitch;
Proportion of benzene insoluble resins and resins soluble in anthracene oils, not less than 20% by weight of the pitch;
Residue upon coking of said resins, not less than 89% by weight of said resins;

and said petroleum coke particles having the following characteristics:

Real density, between 2 and 2.05;
At least 45% of the total particles are arrested by a screen having openings of 0.83 mm.;
Approximately 15% of the total particles have sizes ranging between 5.5 and 15 mm.;
Between 33 and 35% of the total particles pass through a screen having openings of 0.16 mm.; and
25% of the total particles pass through a screen having openings of 0.089 mm.;

the proportion of the binder relative to the total weight of the paste being about 15%.

3. Carbon paste suitable in the production of compressed and prebaked anodes for aluminum manufacture, comprising a binder and particles of pitch coke, said binder consisting essentially of a pitch having the following characteristics:

Softening point, Kramer-Sarnow, between 70–85° C.;
Coking residues, in excess 50% by weight of the initial pitch;
Proportion of benzene insoluble resins and resins soluble in anthracene oils, not less than 20% by weight of the pitch;
Residue upon coking of said resins, not less than 89% by weight of said resins;

and said pitch coke particles having the following characteristics:

Real density, between 1.94 and 1.97;
At least 45% of the total particles are arrested by a screen having openings of 0.83 mm.;
Approximately 15% of the total particles have sizes ranging between 5.5 and 15 mm.;
Between 33 and 35% of the total particles pass through a screen having openings of 0.16 mm., and
25% of the total particles pass through a screen having openings of 0.089 mm.;

the proportion of the binder relative to the total weight of the paste being about 15%.

4. Carbon paste suitable in the production of continuous anodes of the Soderberg type, comprising a binder and coke particles, said binder consisting essentially of a pitch having the following characteristics:

Softening point, Kramer-Sarnow, between 70–85° C.;
Coking residues, in excess 50% by weight of the initial pitch;
Proportion of benzene insoluble resins and resins soluble in anthracene oils, not less than 20% by weight of the pitch;
Residue upon coking of said resins, not less than 89% by weight of said resins;

and the said coke particles having the following characteristics:

Real density, between 1.94 and 2;
Approximately 15% of the total particles have sizes ranging between 5.5 and 15 mm.;
50 to 60% of the total particles pass through a sieve having openings of 0.16 mm., and
40 to 48% of the total particles pass through a sieve having openings of 0.089 mm.;

the amount of binder added to the particles is such as to produce, following mixing, a fluid paste giving on a "spreading" test of a sample thereof, an elongation ranging between 60 and 80% of the length of a cylindrical sample 50 mm. in length and 25mm. in diameter, disposed on a plane with an inclination of 6.5° and heated to 220° C. for two hours.

5. Process of preparing carbon electrodes comprising the steps of: intimately mixing into a paste powdered coke, approximately 15% of which has dimensions ranging between 5.5 mm. and 15 mm., with a pitch binder having the following characteristics:

Softening point, Kramer-Sarnow, between 70–85° C.;
Coking residue, in excess 50% by weight of the initial pitch;
Proportion of benzene insoluble resins and resins soluble in anthracene oils, not less than 20% by weight of the pitch;
Residue upon coking of said resins, not less than 89% by weight of said resins;

shaping the paste into the desired form, and baking the shaped paste whereby, following baking of the paste, the real density of the baked anodes produced therefrom is greater than that of the coke used in producing the paste.

6. Process of preparing carbon electrodes of the Soderberg type, comprising the steps of: intimately mixing into a paste coke particles with a pitch binder having the following characteristics:

Softening point, Kramer-Sarnow, between 70–85° C.;
Coking residue, in excess 50% by weight of the initial pitch;
Proportion of benzene insoluble resins and resins soluble in anthracene oils, not less than 20% by weight of the pitch;
Residue upon coking of said resins, not less than 89% by weight of said resins;

the said coke particles having the following characteristics:

Real density, between 1.94 and 2;
Approximately 15% of the total particles have sizes ranging between 5.5 and 15 mm.;
50 to 60% of the total particles pass through a sieve having openings of 0.16 mm., and
40 to 48% of the total particles pass through a sieve having openings of 0.089 mm.;

the relative proportions of particles and binder being such that the fluid paste produced upon completion of

the mixing gives on a "spreading" test of a sample thereof, an elongation ranging between 60 and 80% of the length of a cylindrical sample 50 mm. in length and 25 mm. in diameter, disposed on a plane with an inclination of 6.5° and heated to 220° C. for two hours; shaping the mixed paste into the desired form and baking the shaped paste.

References Cited in the file of this patent

FOREIGN PATENTS

659,261 Great Britain ---------- Oct. 17, 1951

OTHER REFERENCES

Abrahams: "Asphalts and Allied Substances," vol. 1 (5th ed.), pages 4–2–406.

UNITED STATES PATENT OFFICE

Certificate of Correction

Patent No. 2,848,424 August 19, 1958

Stefan Stanko

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, lines 39 to 45 inclusive, the table should appear as shown below instead of as in the patent—

opening of the sieve in mm—	15mm	5.54	3.33	1.70	0.83	0.36	0.16	0.089
%	15%	7%	11%	12%	10%	10%	10%	25%
	45%						35%	

line 71, for "alumina" read —aluminum—; column 4, lines 20 to 29, the table should appear as shown below instead of as in the patent—

Sieve opening in mm % grains	15mm	5.54mm	3.33mm	1.71mm	0.83mm	0.36mm
	15%	4%	7%	4%	6%	8%
	0.16	0.089	0.075	0.040	0.020	0.010
	9%	13%	10%	8%	7%	9%
			56%			

Signed and sealed this 4th day of November 1958.

[SEAL]

Attest:
KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.