

UNITED STATES PATENT OFFICE

2,653,878

PROCESS FOR THE PRODUCTION OF
ELECTRODES

Johannes Sejersted and Oluf Christian Bóckman,
Oslo, Norway, assignors to Elektrokemisk A/S,
Oslo, Norway, a corporation of Norway

No Drawing. Application November 18, 1949, Se-
rial No. 128,252. In Norway November 20,
1948

4 Claims. (Cl. 106—56)

1

This application relates to the production of carbon electrodes for the electrolysis of molten salts. More particularly, it relates to the production of carbon anodes used in the electrolytic production of aluminum metal. Our invention is of particular importance when the anode is of the self-baking or so-called Soederberg type, but it is also useful with other types of electrodes such as the so-called "prebaked" types.

In the electrolytic production of aluminum, the carbon anode serves for introducing the electric current into the bath and at the same time acts as a reductant. The oxygen liberated by electrolysis at the anode reacts with the carbon of the anode to form a mixture of carbon dioxide and carbon monoxide which leaves the furnace as the anode gas. The consumption of anode carbon is fairly high and amounts in commercial operation to 50 to 60% of the weight of the produced aluminum metal.

The carbon anode consists of pitch coke, petroleum coke, purified anthracite or the like known as the "dry material" of the electrode. This dry material is crushed and screened to a suitable size and then mixed with a binder such as coal tar, coal tar pitch or the like. The resulting mixture is then shaped and carbonized to transform the binder into coke thus producing a coherent carbon anode.

In some installations the mixture of dry material and binder is compressed to shape and then carbonized in a special furnace made for that purpose. Such electrodes are known as "prebaked" electrodes. Under another system the mixture of dry material and paste is used for forming continuous electrodes which are sometimes called "self-baking" or Soederberg electrodes. The present invention is of particular value in connection with the latter type of electrodes.

One of the difficulties with the carbon electrodes is their tendency to form carbon dust in the molten electrolyte. The carbon dust in the electrolyte does not take part in the electrolysis and represents a loss of anode carbon. What is even more important is that the carbon dust accumulates in the electrolytic bath and tends to cause trouble in the operation of the furnace so that it is necessary to remove the dust from the bath at intervals. This removal disturbs operations and tends to cause serious losses of the valuable fluoride salts which make up the electrolytic bath. It is therefore of great importance to be able to produce carbon anodes which

2

produce as little carbon dust as possible in the electrolytic bath.

We have discovered that the tendency to form carbon dust in the bath is due to different qualities in the ground coke or so-called "dry material" of the electrode as compared with the baked binder with which the dry material has been bound together. We have further discovered that anodes which are greatly superior as regards the formation of dust can be produced if the dry material of the electrode has been given its preliminary calcining at a temperature of not over 1200° C. (and preferably at a temperature not over 1100° C.) and if the coke from such dry material has a reactivity to carbon dioxide (determined in the manner hereinafter set forth) which is at least 75% of the reactivity (determined in the same manner) of the coke resulting from the baking of the binder.

We have discovered that there are three characteristics or qualities of the coke making up the entire electrode which tend to cause the coked binder to be eaten away before the particles of coke introduced as the dry material. When the binder is thus eaten away, particles of the dry material coke are released and fall into the bath forming the carbon dust which we seek to avoid.

The first of these characteristics is the behavior of the coke when the so-called "anode effect" occurs. It is well recognized that as the quantity of alumina dissolved in the bath is reduced, a point is gradually reached at which the bath does not adequately wet the electrode and the voltage necessary to cause the current to pass through the cell rises rapidly. We have found that in electrodes now in use the anode effect occurs more rapidly with the particles of coke introduced into the electrode as the dry material than with the coke resulting from the baking of the binder. Thus there is a period when virtually all of the activity of the electrode is working through the binder coke due to the fact that the bath is no longer wetting the bound particles. This tends to cause the binder coke to be eaten away more rapidly than the other particles, with the result that dust is released.

The second characteristic has to do with the difference in anodic electro-chemical over-voltage between the two types of coke. The over-voltage in a bath of this type means the voltage over and above the theoretical necessary to produce the desired electrolysis. We have found that a greater over-voltage is required with the

usual particles of coke introduced as dry material than with the coke resulting from baking of the binder. Again, this causes more rapid disintegration of the binder coke.

The third characteristic is the difference between the two cokes in reactivity toward carbon dioxide. When, through electrolysis, the oxygen is disassociated from the alumina in the bath it tends to form carbon dioxide with the carbon of the electrode mass and this carbon dioxide tends to act on additional quantities of carbon present to form carbon monoxide. We have found that ordinarily there is a difference in the reactivity toward carbon dioxide of the coke resulting from the dry material and the coke resulting from the baking of the binder. This difference in reactivity ordinarily is quite appreciable, with the binder coke showing the greater reactivity so that again it tends to be eaten away more rapidly.

While the three characteristics may be separately determined, we have found that for practical purposes all of them can be approximately measured by measuring the reactivity of the coke to carbon dioxide. Using this test, we have found in general that where the coke is given a preliminary baking at high temperature its reactivity is reduced and at the same time its action relative to the anode effect and electrochemical over-voltage are made less desirable.

Ordinarily the coke used as the dry material is calcined at a temperature of 1400° C. to 1500° C. and it must be remembered that in producing aluminum by the Soederberg system of continuous electrodes the temperature at which the binder is calcined never exceeds 950° C. As a result, there is a great difference in the characteristics of the two types of coke found at the operating surfaces of the electrode. Even in the case of prebaked electrodes the calcining temperature of the finished electrode does not exceed about 1300° C. so that in this case also there is a marked difference in the coke characteristics.

We have determined that as a practical matter the critical line where the difference in characteristics of the two types of coke becomes effective is found where the reactivity of the coke resulting from the dry material is at least 75% of the reactivity of the coke actually resulting from the calcination of the binder. With a smaller difference in characteristics the formation of dust is so small as to be substantially negligible but beginning at about the figure named, the tendency to form dust increases rapidly. We have found that for general operating conditions in order to get the necessary similarity of coke characteristics, the dry material should not be calcined at a temperature above about 1100° C. However, by careful selection and control, it is possible to get the desired results at a somewhat higher temperature, and therefore we set as our top limit for the calcination of the dry material the temperature of 1200° C.

For the purposes of determining reactivity as we use the term in this application, we have developed a particular type of test as follows:

A known volume of the coke to be tested is crushed and screened between sieves of values of 20 and 35 on the Tyler screen scale. This coke is placed inside a closed silica tube (the one which we employed was 17 mm. inside diameter), the coke resting on a perforated disk of alloy metal. The tube is heated to a tempera-

ture of 950° C. in a vertical tube furnace, the temperature being measured by a thermocouple in the center of the sample. A stream of pure carbon dioxide is passed through the bed of coke at a known rate. For example 100 mg. of CO₂ are passed through in 5 minutes. This rate of flow of CO₂ going into the tube we call *a*. At the temperature employed, a certain amount of the carbon dioxide reacts with the coke sample to form carbon monoxide. To determine the amount reacted we determine the rate of flow of CO₂ coming out of the tube (by gravimetric determination) and call this value *b*. In other words, the amount of CO₂ reacted by the coke is (*a-b*).

For our purposes we use the natural logarithm of the ratio of the amount of CO₂ going into the tube during a given time interval (*a*) to the amount of CO₂ found to be coming out of the tube during the same time interval (*b*). Thus stated as a formula and terming the rate of reactivity as *Y* we have

$$Y = \text{nat. log. } \frac{a}{b}$$

In determining the relative reactivities of various samples the same amounts of the coke should be employed in each case and they should be ground to the same fineness.

By using this method we have determined the relative reactivity of different cokes. Some of the results are given below:

A number of different binders of the types employed commercially were coked and calcined at 950° C. These gave reactivities of *Y* ranging between .31 and .59.

On the other hand, raw petrol coke calcined at different temperatures has given the following values:

Temperature of Calcination, ° C.	Reactivity <i>Y</i>
950.....	0.38
1,100.....	0.26
1,300.....	0.20
1,500.....	0.18

From the foregoing figures if we consider a carbon anode composed of coke calcined at 1500° C. (a usual temperature) as the dry material and a binder coke giving a relatively high degree of reactivity calcined at 950°, it will be seen that the relative reactivities of the two will differ very substantially. In fact, from the table shown, the reactivity of the binder coke may be more than three times that of the dry material. By maintaining the calcination temperature of the dry material below 1200° its reactivity is materially increased. At the same time, a binder should be selected such that the reactivity of the dry material coke is at least 75% of the reactivity of the binder coke. By using the method specified above the relative reactivity of the two materials can readily be determined.

As is well understood in the art of making the carbon electrodes the electrode ordinarily consists of pitch coke, petroleum coke or purified anthracite coal. The binders are made of such materials as coal tar, coal tar pitch or the like all of which may be classified as "bituminous pitches."

In carrying out our invention the desired material for the dry coke is calcined at a temperature of between 1000° C. and 1200° C. A sample

5

6

of binder material is then calcined at the temperature at which the electrode is to be formed, which in the case of a continuous electrode will be 950° C. The relative reactivities of the two cokes are then tested. If the coke from the dry material has a reactivity of at least 75% of the test sample of binder material coke, then the selected binder and coke can be combined and used in the usual manner.

In the case where the coke is to be used in the continuous electrode system, a so-called "paste" is formed following in general the instructions of U. S. Patent No. 1,670,052, issued May 15, 1928. By terming the material a "paste" we do not intend to imply that the material is necessarily pasty at ordinary room temperatures. In fact, it is now customary to use a binder having a melting point in the order of about 100° C. so that at normal temperatures the electrode material is solid for handling. The important thing is that the mass when heated in the electrode holder shall become soft enough to assume the shape of the holder without tamping.

If when the test described above is run, it is found that there is too great a difference in reactivity between the dry material coke and the sample of binder coke, it may be possible to select a different binder coke, but it ordinarily will be easier and preferable to lower the temperature at which the dry material coke is originally calcined.

Paste made in this manner is a great improvement on the pastes now being used and when these instructions are followed, it will be found that the resulting electrode will have an appreciably greater life than those heretofore formed and will result in much less carbon dust being formed in the electrode bath.

What we claim is:

1. A method of preparing mixes for use in electrodes which comprises selecting bituminous pitch as a binder material, carbonizing a sample

of such binder material at approximately the temperature at which the electrode is to be carbonized, testing the reactivity of such sample to CO₂ as herein defined, calcining dry material selected from the group consisting of pitch coke, petroleum coke and purified anthracite at a temperature below 1200° C. and at a temperature low enough so that the reactivity thereof to CO₂ as herein defined is at least 75% of the reactivity of the test sample of binder material and combining such dry material in powdered form with the binder material.

2. A method as specified in claim 1 in which the binder material sample is carbonized at a temperature of about 950° C.

3. A method as specified in claim 1 in which the binder material sample is carbonized at a temperature of about 950° C. and the dry material is calcined at a temperature below 1100° C.

4. A method of preparing so-called paste for use in electrodes which comprises combining together bituminous pitch as binder material and dry pulverulent carbonaceous material selected from the group consisting of pitch coke, petroleum coke and purified anthracite, such dry material having been calcined at a temperature not in excess of 1200° C. and having a reactivity to CO₂ as herein defined equal to at least 75% of the reactivity to CO₂ of a sample of the binder material carbonized at 950° C.

JOHANNES SEJERSTED.

OLUF CHRISTIAN BÖCKMAN.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
655,920	Burke	Aug. 14, 1900
887,123	Price et al.	May 12, 1908
1,317,497	Hinckley	Sept. 30, 1919
1,670,052	Soderberg	May 15, 1928