# United States Patent Office

3,197,395
Patented July 27, 1965


1

2


3,197,395


## CARBON ELECTRODES


Joseph F. Nelson, Westfield, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware



No Drawing. Filed Mar. 13, 1961, Ser. No. 94,983
5 Claims. (Cl. 204—294)


This invention relates to the preparation of carbon electrodes and more particularly to the preparation of carbon electrodes made from fluid coke.

Carbon electrodes are used in large volume by the aluminum industry in the electrolysis of alumina by the Hall process to make metallic aluminum. Such electrodes must meet strict requirements in order to give economical troublesome-free operation. They must have high electrical conductivity, be resistant to cracking, be resistant to attack by air at the 950° C. operating temperature, and they must be consumed at a uniform rate in order to prevent dusting, i.e., sloughing off of carbon particles.

In the past most of the electrodes have been manufactured from petroleum coke made by the delayed coking process. Other petroleum cokes have been used. When using coke from the delayed coking processes, the coke is ground and various size range fractions are mixed together with a binder to produce the carbon electrodes. The delayed coke is of different sizes and pieces up to about one inch are used in the mixture. The ground delayed coke particles are non-uniform and have jagged edges and irregular surfaces with some large pieces and some extremely fine pieces which help to give a good compact mixture in the manufacture of carbon electrodes, providing a particle size distribution is used.

Fluid coke made by the fluid coke process as described for example in Pfeiffer et al., U.S. Patent No. 2,881,130, granted April 7, 1959, is made up of small spherical coke particles of a size such that the major proportion of the particles, that is about 60% to 90% by weight being between about 150 and 850 microns or in the range of about 20 to 80 mesh, with, of course, some being smaller than 150 microns and some being bigger than about 850 microns. Commercial fluid cokers can be operated to give various coke particle size distributions, but the amount coarser than 20 mesh can never be very large or the bed will "bog," i.e., cease to fluidize and with the result that the agglomeration will occur and seriously interfere with the operation. Some commercially produced fluid cokes have the following size distributions:

| | Example | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Weight percent on: | | | | |
| 20 Mesh | 8 | 4 | 6 | 1 |
| 30 Mesh | 26 | ------ | ------ | ------ |
| 40 Mesh | 28 | ------ | ------ | ------ |
| 50 Mesh | 20 | ------ | ------ | ------ |
| 60 Mesh | ------ | 15 | 23 | 13 |
| 80 Mesh | 15 | 28 | 36 | 17 |
| 100 Mesh | 3 | 18 | 14 | 26 |
| 140 Mesh | ------ | 20 | 15 | 15 |
| 200 Mesh | ------ | 15 | 6 | 20 |
| Through 200 Mesh | ------ | ------ | ------ | 8 |

It is more desirable to operate according to Example 1. In Examples 2 to 4 the coke was withdrawn from the coker before it had built up to a size similar to that in Example 1. The carbon electrode manufacturers have resisted use of the fluid coke because of its small size. The coke particles from the fluid coking process will be referred to hereinafter as "fluid coke."

The fluid coke passes from the fluid bed in the reactor to a burner to be reheated and then returned to the reactor. In this way layer upon layer of coke is deposited on the coke particles and heat hardened in the burner as the coke particles pass back and forth to the burner. As a result the coke particles from fluid coking are generally spherical and have an onion layer or shell upon shell structure. The fluid coke has a relatively low density between about 1.4 and 1.6 and this has been considered too low for use in carbon electrode manufacture.

The types of oil feed and temperature of operations and conditions set forth in said Pfeiffer et al. Patent No. 2,881,130 are incorporated herein by reference.

It has now been found that fluid coke from the fluid coking process may be used in the preparation of satisfactory carbon electrodes. Fluid coke as taken from the fluid coking process comprises relatively small spherical coke particles of which there are an insufficient number of large pieces of a size of about ⅛ to 1 inch. According to the present process and invention some or part of the fluid coke particles are ground in a conventional grinding mill such as a ball mill to particles of a size around 200 mesh or smaller to less than 325 mesh. A Raymond ring-rolled mill may also be used as described on pages 1155–1157 of Perry's "Chemical Engineers' Handbook" (1950). The coke may be calcined or raw (green) uncalcined fluid coke may be used. Not all the fluid coke but only a part of the fluid coke is ground but it is necessary to grind it to extremely small pieces.

The finely ground fluid coke is then mixed with unground fluid coke particles so that the fine coke particles fit in between the spaces left between the spherical unground particles. About 10% to 50 wt. percent of ground coke is mixed with about 90% to 50% by weight of unground coke. The mixture has further admixed with it a carbonaceous binder or pitch such as coal tar pitch, petroleum pitch, asphalt, or the like. About 10% to 40 wt. percent of a pitch of coal tar origin or an equivalent pitch is combined with the coke mixture consisting of 90% to 60% by weight of the coke mixture.

The mixing is done hot since pitches solid at room temperatures are generally of better quality. The mixing is done in kneader type mixer or a pug mill or the like. The resulting mixture is then briquetted or pelletized into pieces of a size of about 1 to 2 inches by being compressed. The briquettes or pellets (hereinafter referred to as briquettes) are then heated or baked at a temperature between about 1200° F. and 2600° F. for about 4 hours to two days. A Komarek-Graves briquetting machine can be used at a temperature of about 160° F. to 300° F. depending on the softening point of the pitch used. Or a hydraulic press using a pressure between about 2000 and 20,000 p.s.i. may be used as described in the chemical engineering article, "Agglomeration," of October 1951.

The briquettes are then partially crushed in a machine such as an ore crusher or a crusher such as used by the aluminum industry for crushed delayed coke and used as the coarse fraction in making an electrode along with ground and unground fluid coke in a desired particle size distribution. The resulting mixture is mixed with a suitable carbonaceous binder, compressed, and then baked to form what the trade calls a prebaked electrode or the coke-binder mixture before compressing may be fed to a Soderberg electrode.

Some fines will be produced, but not much, with the proper crushing equipment. These fines should be kept to a minimum to reduce cost. They can be removed and recycled or combined with the unground or ground fluid coke. The partially crushed briquettes can be used as such if the crushing is carefully done or screened coke pieces of a size between about ¼ and 1 inch can be separated to provide the real coarse particles which retard or prevent crack formation in the finished electrode product. It is important to crush the briquettes in order to produce irregular surfaces. The smooth surfaces of the briquette are undesirable since they facilitate crack formaton during baking and use of the electrode. By crushing a high ratio of irregular to smooth surface is produced.

It is essential to grind part of the fluid coke to real fine particles such as smaller than 200 mesh and to a considerable extent smaller than 325 mesh so that the particles fit in between the void spaces between the larger pieces of unground fluid coke. A maximum of coke should be incorporated into the electrode. In this way maximum packing density of the fluid coke particles is obtained and with this maximum packing density, a minimum of pitch binder is needed and better electrode properties are realized. If the fluid coke is only partly crushed into pieces such as halves, these pieces are not of the optimum shape to prevent electrode cracking. If too much binder is used or if the amount of binder used is much greater than in conventional practice or than desired, the porosity of the electrode is undesirably increased. The binder on decomposing and coking during baking produces a porous coke residue and this reduces the density of the electrode product and cuts down on the electrical conductivity of the electrode product. With the maximum packing density improved electrical conductivity is obtained in the electrode product.

The electrode mixture of the present invention comprises unground fluid coke particles, finely ground fluid coke particles and partly crushed briquettes made from fluid coke. The briquettes have a smooth surface and it is preferred to crush them as mentioned above to form irregular surfaces but in some instances a part or all of the coarse fraction may be made up of the unground or uncrushed briquettes.

In the preferred form of the invention the carbonaceous binder used in the final electrode product and in the briquettes is one that will leave a high carbon residue when baked.

The main portion or major part of the fluid coke mixture for the briquettes or compactions is made up of unground product coke as it comes from the flud coking unit and comprises spherical coke particles. This main portion is mixed with a minor portion of the extremely finely ground fluid coke particles from the fluid coking process to obtain the maximum packing density. A minor portion of the fluid coke mixture used in making the final electrode is made up of crushed briquette pieces which act as crack stoppers or retarders in the final electrode product.

The coke mixture used to make the electrode may be broadly defined as a "double dumbbell" mixture comprising essentially spherical unground or "as is" fluid coke particles, extremely fine ground fluid coke particles and coarse crushed fluid coke briquette particles held together by incorporating a carbonaceous binder. In the mixture there is a lean area of particles of a size between unground fluid coke particles and finely ground fluid coke particles. There is another lean area of particles of a size between unground fluid coke particles and the larger sized crushed briquette pieces. Hence it will be seen that there is not a gradation of size in the coke particles but gaps or lean areas to obtain the maximum packing density to permit the use of a minimum amount of carbonaceous binder in the electrode mixture.

Electrodes made with this "double dumbbell" mixture possess optimum properties. They are resistant to cracking, possess high electrical conductivity, and they are resistant to dusting and "burning" during the electrolysis operation. This "double dumbbell" mixture gives a 100% fluid coke electrode that is superior to electrodes



previously made with 100% fluid coke. Electrical resistivity and strength are good and resistance to cracking is greatly improved over the previous electrodes. Dusting during electrolysis is less than with delayed coke electrodes Thus all desirable properties are at an optimum combination in the electrodes of this invention.

The briquettes may have a size between about ½ inch to about 2 or 3 inches on an edge and be of any shape such as ovoid or the like and a thickness of about ¼ to 2 inches. Briquettes generally have a pillow shape and pellets which are an acceptable equivalent to briquettes are generally cylindrical in shape. The crushed or partially ground briquettes when starting with briquettes having a size of about 2 inches comprise particles having a size mostly of about ¼ to 1 inch. The crushed material generally contains a small amount of fines which can be left in the coarse aggregate but it is preferable to remove them by screening in order to avoid incorporation of an unknown amount of fines in the final coke mixture used to make the electrode. In lined out commercial experience the amount of the fines will be fairly constant and allowance can be made for them, and thereby avoid screening them out.

Instead of briquettes, the mixture of fluid coke and binder may be extruded or pelleted as mentioned above. The main purpose is to obtain larger pieces of fluid coke than are provided or produced in the normal operation of the fluid coking process. The briquettes or other compactions when partly crushed produce larger coke particles which are the largest pieces or lumps in the final electrode composite. These ground or crushed briquette pieces are of irregular shapes and sizes. These briquette pieces form a minor portion of the total electrode mixture.

The electrode mixture of fluid coke comprises real coarse material and real fine ground fluid coke with unground fluid coke particles in between the coarse and fine sizes so that there are two lean areas where there are not large concentrations of any particle sizes. One lean area is between the read coarse particles and the unground fluid coke particles and the other lean area is between the unground fluid coke particles and the finely ground fluid coke particles.

An example of one mixture of fluid coke particles for making carbon electrodes is as follows:

| | Weight percent |
|---|---|
| Coarse—¼ to 1 inch | 20 |
| Unground fluid coke particles—20 to 100 mesh | 55 |
| Finely ground fluid coke—smaller than 200 mesh | 25 |

It is desirable that about 40 to 60% of the finer than 200 mesh coke be finer than 325 mesh. The lean particle size distribution between 20 mesh and ¼ inch, and between 100 and 200 mesh allows the coke used to pack to give high weight of coke per unit volume. There can be small amounts of coke in the lean range but these should be kept to a minimum for best results.

In a specific example to make briquettes fluid coke particles which have been calcined at a temperature of about 2350° F. for about 1 hour having a particle size mostly between about 150–850 microns or about 20–100 standard mesh are used. Between about 70 to 90% by weight is between these sizes so that there are usually some larger and smaller particles than the range given. The calcined fluid coke particles have a real density between about 1.8 and 1.95 gm./cc. One portion of this fluid coke is used as such or unground and another portion is ground in a ball mill so that substantially all the ground particles are smaller than 200 mesh (75 microns) with 50% through or minus 325 mesh (45 microns). The ground and unground fluid coke particles are then mixed with an aromatic coal tar pitch binder having a melting point lying within the range of 158° F. and 248° F., a hydrogen content below about 5%, the concentration of benzene and nitrobenzene insoluble portions comprising about 20% to 35% and 5% to 15%, respectively, of the binder. The carbon residue of the pitch when coked by itself is over 50%. The following proportions were used:

| | |
|---|---|
| Unground fluid coke | 70 parts by weight. |
| Ground fluid coke | 30 parts by weight. |
| Coal tar pitch binder | 18 parts per 100 parts of mixture of unground and ground fluid coke. |

The fluid coke particles and pitch binder are then mixed in a kneader type mixer at a temperature of about 300° F. and then formed into briquettes about two inches in size with a conventional briquetting machine which produces pillow shaped briquettes of the type disclosed in Horvitz Patent No. 2,764,539 granted September 25, 1956. Roll briquetting machines such as are used in the coal briquetting can also be used.

The formed briquettes are then baked or heat hardened at a temperature above about 750° F., preferably about 1800° F. to 2400° F. for about ½ to 1 hour to decompose or crack the pitch binder to coke to form a hard briquette.

These briquettes are then cooled and partly crushed in a crusher such as used by the aluminum industry in crushing delayed coke to form coke particles of a size between about 30 mesh and 1 inch. The fines up to about 3/16 inch in size are removed by screening. The coarse particles formed by crushing the briquettes have a size between about 3/16 and 1 inch with most of the particles of a size of about ¼ to ½ inch. These briquette particles or pieces form the real coarse fraction in the electrode made according to the present invention and form a minor proportion of the electrode mixture. The selected crushed briquette pieces are then mixed with ground and unground calcined fluid coke particles and pitch binder to form the electrode mixture. Here preferably, but not necessarily, the same type of aromatic coal tar pitch is used as the binder.

As one example of a prebaked electrode the following information is given but the invention is not limited to this example.

| | Weight percent |
|---|---|
| Crushed briquettes—3/16 inch to 0.8 inch | 20 |
| Unground calcined fluid coke—20 mesh to 120 mesh | 56 |
| Ground calcined fluid coke—200 mesh to minus 325 mesh | 24 |
| Coal tar binder, 18% by weight on 100 parts by weight of coke charge including crushed briquettes, unground and ground calcined fluid coke. | |

In general, the prebaked electrodes made according to this invention contain the following range of materials:

Crushed briquettes about 15 to 30 wt. percent.
Unground fluid coke about 45 to 65 wt. percent.
Ground fluid coke about 20 to 30 wt. percent.

The mixing of all the above ingredients is done at a temperature of about 350° F. in a steam jacketed kneader type mixer. The mixture is then made into an electrode about 15 x 15 inches square and about 16 inches high by molding in a press at a pressure of about 3000 to 5000 p.s.i. and the molded electrode is then baked at a temperature of about 1820° F. for up to 21 to 30 days to carbonize the binder. Under carefully controlled rates of heat-up, baking times as short as 24 to 48 hours may be used.

The final prebaked electrode will have a compression strength or crushing strength of about 6500 p.s.i., and a density of about 1.54 g./cc. and an electrical resistivity of about $2.25 \times 10^{-3}$ ohm-inch.

Prebaked electrodes made according to the present invention have a crushing strength between about 5000 and 8000 p.s.i. and a bulk density between about 1.50 and 1.60 g./cc. and an electrical resistivity below about $2.5 \times 10^{-3}$ ohm inch.

The present invention may also be used in the preparation of Soderberg self-baking electrodes in which the paste comprises 70–72% coke charge and 28% to 30% pitch binder.



The temperature during mixing of the pitch binder in making the briquettes is between about 200° F. and 500° F. and in making the final prebaked electrode product is between about 200° F. and 800° F. The pressure in compressing the briquettes and the electrode mixture may be between about 1000 p.s.i. and 20,000 p.s.i. The temperature during baking of the briquettes or compactions is above about 750° and preferably between about 1200° F. and 2400° F. and the time of baking is between about ½ hour and 2 days and is sufficiently long to crack or decompose the pitch binder to coke and form a strong product. The temperature during baking of the electrode mixture is between about 1400° F. and 2400° F. and the time of baking may be between about 2 days to 30 days.

The briquettes and electrodes may be preheated at lower temperatures for up to 10 days while being brought up to the top baking temperature.

When calcined fluid coke particles are to be used, the calcination may be done at a temperature between about 2000° F. and 2800° F. for about 0.5 to 10 hours in a fluid, moving or fixed bed in an atmosphere of air (lean in oxygen), nitrogen, hydrogen or a gas such as carbon dioxide. The density of the calcined fluid coke particles is between about 1.80 and 2.00 g./cc.

The pitch binder in making the briquettes of compactions and the electrode may be a petroleum pitch but is preferably a coal tar pitch and is used in an amount of between 10 to 40 parts by weight of binder to 100 parts by weight of coke blend, preferably 16 to 32 parts by weight of binder to 100 parts by weight of coke blend in the case of electrodes and 12 to 22 in the case of briquettes.

What is claimed is:

**1.** A method of making a carbon electrode from fluid coke which comprises providing a batch of product fluid coke comprising spherical fluid coke particles mostly of a size between about 20 and 140 mesh, grinding a portion of said fluid coke particles to produce fluid coke particles of a size smaller than 200 mesh, mixing the ground fluid coke, unground fluid coke and a pitch binder in the proportions of about 20 to 40 wt. percent ground fluid coke, about 60 to 80 wt. percent unground fluid coke and between about 10 and 22 wt. percent on the mixed fluid cokes of pitch binder, forming and compressing briquettes and baking the resulting briquettes to crack or decompose the pitch binder to coke, partly crushing said briquettes to form fluid coke pieces larger than said unground fluid coke particles to obtain fluid coke pieces of a size between about 3/16 and 1 inch, mixing the crushed briquette pieces with unground and ground fluid coke in the proportion of about 20 to 30 wt. percent ground fluid coke particles, 45 to 65 wt. percent unground fluid coke particles, 15 to 30 wt. percent crushed briquette pieces, 16 to 25 wt. percent pitch binder on weight of said coke mixture, making electrodes from said mixture, compressing and baking to produce a prebaked carbon electrode of desired properties.

**2.** A process according to claim **1** wherein said finely ground fluid coke is ground to smaller than 325 mesh.

**3.** A process according to claim **1** wherein the temperature of baking said briquettes and said electrode is between about 1200° F. and 2400° F.

**4.** In a method of making carbon electrodes entirely from fluid coke particles and carbonaceous binder wherein the coke particles are mixed with a carbonaceous binder, formed into an electrode and baked, the improvement which comprises providing a mixture of fluid coke particles comprising 20 to 30 wt. percent of ground fluid coke particles of a size smaller than 200 mesh, about 45 to 65 wt. percent of unground spherical fluid coke particles mostly of a size between about 20 and 140 mesh, and about 15 to 30 wt. percent of crushed briquette pieces made from ground and unground fluid coke and carbonaceous binder and of a size between about $\frac{3}{16}''$ and 1″, said ground fluid coke fraction including 40 to 60% through 325 mesh.

5. A method according to claim 4 wherein there is a lean area of fluid coke particles of a size between unground spherical fluid coke particles and finely ground fluid coke particles and another lean area of fluid coke particles of a size between unground spherical fluid coke particles and said crushed briquette pieces to obtain maximum packing density of the coke particles and the use of a minimum amount of carbonaceous binder.




**References Cited by the Examiner**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 1,067,031 | 1/13 | Jewett | 204—294 |
| 1,517,819 | 12/24 | Beer | 204—294 |
| 2,527,595 | 10/50 | Swallen | 204—294 |
| 2,764,539 | 9/56 | Horvitz | 204—294 |
| 2,805,199 | 9/57 | Banes | 204—294 |


JOHN H. MACK, *Primary Examiner.*