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CARBONACEOUS COMPACTION USING HIGH TEMPERATURE FLUID COKE

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This invention relates to carbonaceous electrodes, especially to the preparation of electrodes from fluid coke. More particularly, it relates to the preparation of dusting-resistant electrodes from high temperature fluid coke and carbon black.

Carbon electrodes are used in large quantities 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 trouble-free operation. They must have high electrical conductivity, good resistance to cracking and must be consumed at a uniform rate in order to prevent dusting, i.e., sloughing off of carbonaceous particles.

In the past electrodes have been manufactured from coke formed at relatively low temperatures, generally below about 1200° F. A common form of low temperature coke is that known as delayed coke. In the manufacture of such coke, petroleum or other heavy hydrocarbons are cracked at low temperatures, i.e., from about 750° F. to about 950° F., to form coke and relatively light hydrocarbons. The heavy hydrocarbons are decomposed in a coking chamber, the coke accumulating therein while the light hydrocarbon products are evolved as a gaseous effluent. The delayed coke is removed from the chamber only with considerable difficulty, i.e., by actual physical dislodgment with crow bars, hydraulic jets and the like. In the process, the coking chambers are usually employed in pairs, one chamber being used for collecting coke while coke is being dislodged from the other.

When using coke from the delayed coking processes, it is necessary first to calcine the coke at 2000° F. to 2400° F. to eliminate volatiles and densify the carbon. Then it is necessary to grind the coke to various sizes and mix the various size range fractions together with a binder to produce "green" carbon electrodes. These "green" electrodes are recalcined to produce the final, electrically conductive 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 wide particle size distribution is used.

While delayed coke has admirable characteristics making it highly suitable as a raw material for manufacturing electrodes, the difficulties associated with the process of manufacture leave much to be desired. Among other things, the difficulties associated with the process make delayed coke quite expensive. Moreover, because a high quality feedstock is required, delayed coke is in short supply worldwide.

It has long been desirable to manufacture electrodes from a more conveniently available and less expensive form of low temperature coke and, in this regard, a limited degree of success has been achieved. Thus, e.g., U.S. Patents, 2,881,130, 3,043,753, and 3,197,395 describe the production of low temperature fluidized coke, i.e., coke formed by contact of hydrocarbons with hot fluidized coke solids at temperatures ranging from about 850° F. to about 1200° F., and the formulation of such coke, in whole or in part, with mixtures for forming electrodes.

Low temperature fluid coke has only limited utility and has not been generally accepted by carbon electrode manufacturers because it has been found not to meet stringent criteria on, e.g., conductivity and dust-free operability except when carefully tailored to critical particle size distributions. Such electrodes, for example, are described in U.S. 3,197,395 where acceptable electrodes are only produced by using a mixture of three distinct particle size fractions of low temperature coke.

Because of these process inconveniences and expenses the use in electrode manufacture of low temperature fluid coke has been quite limited, and the major source of electrode coke continues to be delayed coke.

Coke from a recently developed high temperature fluidized coking process could offer process advantages. This coke, formed only at temperatures above about 1800° F., however, has properties which are in sharp contrast with those of delayed coke and low temperature fluid coke, supra. High temperature fluid coke can be produced, for example, by the recently developed process disclosed in U.S. patent application S.N. 333,897 and now Patent No. 3,264,210. The differences in properties of coke formed at temperatures above 1800° F. compared to delayed coke and low temperature fluid coke are apparently due to the fact that at the high temperature the coke forms entirely by a gas phase reaction whereas in low temperature processes the coking reaction occurs in the liquid phase.

Since the high temperature coking process is applicable to the very low molecular weight feeds, e.g., methane, as well as high molecular weight feeds such as residua, and achieves much higher conversions than can be attained by either of the delayed coking or low temperature fluid coking processes, it would appear highly desirable to use the high temperature coke product in the manufacture of electrodes. This, of course, was heretofore considered to be impractical due to certain unique properties of high temperature fluid coke.

Thus, it has heretofore been considered impractical to produce commercially acceptable alumina reduction electrodes of either the prebaked or Soderberg types from high temperature fluid coke. It is known, e.g., that at the temperatures at which electrodes are prebaked or used, the binder material in the electrodes forms a type of coke very much like low temperature cokes and considerably different from high temperature fluid coke. The incompatibility of the binder coke and the high temperature fluid coke constituents is known to cause certain serious defects in the electrode. Thus, micro cracks form in the electrode due to the pulling apart of the binder from the fluid coke particles, which results from differences in adhesion and thermal expansion characteristics of the two types of coke. Moreover, the high temperature coke particles are extremely hard and have a low surface reactivity, in sharp contrast to the soft binder coke. Electrodes resulting from ingredients having such combination of characteristics are known to have a tendency to dust severely, i.e., slough off carbonaceous particles and cause the electrodes to break down prematurely in the alumina bath. This unduly increases electrode consumption and can result in short circuiting the bath. The dusting is believed to be caused by the selective action of evolved oxygen on the lower density, more reactive coke material derived from the binder in the finished electrode as compared to the carbon from the fluid coke. Although some dusting occurs with low temperature fluid coke electrodes, the problem is much more extreme in high temperature fluid coke because the latter is formed at the high temperatures as very hard, small spheres having an extremely hard surface with correspondingly low reactivity.

In view of the disadvantageous dusting characteristics of high temperature coke, it has heretofore been thought impossible to prepare commercially acceptable electrodes from this type of material. Such use of high temperature fluid coke was considered particularly unlikely since even certain forms of low temperature coke, i.e., low temperature fluid coke, have had only limited applicability in electrodes.

Surprisingly, however, it has now been found that high temperature fluid coke can be employed pursuant to the present invention to make satisfactory electrodes possessing minimal tendency toward dusting, and this can be done without laboriously tailoring the particle size distribution as required for low temperature coke. Further, in accordance herewith it is even feasible to greatly reduce or completely eliminate the necessity of grinding the high temperature fluid coke particles to produce fines. Furthermore, it has been unexpectedly found that electrodes of high crushing strength can be made from the high temperature coke using very low percentages of the relatively expensive carbonaceous binder.

In accordance with this invention high temperature fluid coke, carbon black, and a carbonaceous binder are mixed and formed into compactions suitable for use in alumina reduction electrodes. The compactions can be produced by admixing 100 parts high temperature fluid coke with from about 5 to about 10 parts by weight of carbon black and from about 10 to about 30 parts of binder followed by compacting the mixture in any convenient manner, e.g., by using a conventional briquetting machine at about 160° F. to 300° F. or a hydraulic press operated at about 2000 to 20,000 p.s.i. The compactions can then undergo conventional cures, e.g., by baking at temperatures ranging from about 1200° F. to about 2600° F. for about 48 hours to 14 days to coke the binder material and produce prebaked electrodes. Alternately, the compactions can, of course, be used in Soderberg electrode formulations without curing, since such electrodes are cured in situ in the alumina reduction cell. In either case the cured compactions comprise high temperature fluid coke, the coked residue of carbonaceous binder, and carbon black.

Optimum benefits of the carbon black are attained using about 10 parts of black per 100 parts of coke; however, lesser amounts may be employed with, of course, correspondingly reduced effectiveness. Electrode improvement, however, is nil below about 2 to 3 parts black. Similarly, greater amounts of carbon black can be used to impart still better non-dusting characteristics to the electrode; however, it is generally undesirable to use more than about 10 parts of black per 100 parts coke because at above this level the overall electrode resistivity is rapidly increased above acceptable levels for use in alumina reduction cells.

Any type of carbon black can be used; however, thermal blacks resulting from pyrolysis of hydrocarbons at about 1800° F. to 2400° F. are generally preferred. Blacks having an average particle size above about 1000 A., and preferably in the range of about 2000 A. to 4000 A., will give satisfactory improvement in the electrode resistance to dusting. Such blacks are also most economical to use since they can be produced as a by-product in high temperature fluid coking processes.

The carbon black can conveniently replace ground coke fines in specific formulations where such fines are called for, thus reducing or eliminating the expense of grinding coke. Moreover, a sometimes desirable increase in electrode density is obtained when carbon black is added to the formulations. Thus, in a typical example, when 10 wt. percent carbon black was added in place of a corresponding quantity of ground coke fines, the resulting electrode density was about 1.66 g./cc. compared with about 1.50 g./cc. when carbon black was omitted.

While applicants do not wish to be bound by any particular theory, it is believed that the salutary effect of carbon black is in part due to certain similarities between its surface characteristics and those of high temperature fluid coke. Thus, both are formed by gas phase reactions at the same temperatures, and both tend to have higher electrical contact resistivities than low temperature fluid or delayed cokes. Similarly, the carbon black and high temperature fluid coke generally have higher contact resistivities than the coke which forms from the electrode binder material when it is baked. Thus, when carbon black is not present current tends to pass into the alumina reduction cell through the low resistivity binder coke in preference to the high temperature fluid coke of the electrode, and the result is that the binder coke reacts and is used up at a faster rate than the fluid coke. This is believed to increase the tendency for the electrode to dust.

When carbon black is added, however, it apparently tends to change the character of the binder coke giving the latter a contact resistivity approximately the same as that of the high temperature fluid coke. Thus, the electrical current density tends to be more nearly uniform throughout the electrode with the result that there is no preferential destruction of binder; dusting is reduced, and, inter alia, electrode life is correspondingly increased.

A feature of the invention provides for the use of from about 10 to about 12 parts of carbonaceous binder per 100 parts of high temperature fluid coke in prebaked electrodes because this gives a much better baked compaction with respect to the density, electrical resistivity, and crushing strength than when greater quantities of binder are used. This is surprising because generally about 17 to 20 parts binder per 100 parts of coke are required when low temperature delayed coke is used. The savings in binder which is possible using high temperature fluid coke is particularly significant since the binder is often more expensive than the coke.

Any conventional carbonaceous binder can be used, including, e.g., coal tars, petroleum pitch and asphalt binders.

The high temperature fluid coke for use in making the electrodes of this invention is prepared in the conventional manner from petroleum feedstocks at about 1800° F. to 2500° F. Typical high temperature fluid cokes have the following particle size distributions:

Mesh size (Tyler)	Cumulative percent on screen	
	1	2
14	0.1−	0
20	0.2	0
28	0.4	0
35	1.0	0.7
48	8.6	1.5
55	47.3	4.9
100	86.9	18.8
150	98.7	48.9
200	99.9	78.5
325	99.9+	96.9

It is generally desirable to use the larger particle sizes; however, any of the products produced under the conventional high temperature coking conditions can be used.

Part of the high temperature fluid coke may be finely ground prior to using it in the electrode composition. Any conventional grinding technique can be employed, and any fraction of the coke used in the electrode up to about 50% may be ground to fines. Fines as used herein means coke ground sufficiently small that substantially all will pass through a 200 mesh screen (Tyler) and 40% will pass through a 325 mesh screen.

Also, a part of the fluid coke can be added to the compaction admixture as preformed agglomerates. Thus, agglomerates of fluid coke can be formed by mixing 100 parts of coke with from about 9 to about 15 parts by weight of a carbonaceous binder, which binder can be the same or different from the carbonaceous binder to be used in forming the final compaction. The agglomerates can then be formed in any conventional equipment, e.g.,

extruders, briquetters, etc., and then prebaked in the manner described above for the final compactions.

Up to about 75% of the fluid coke in the final compaction can be added as preformed agglomerates. The agglomerates should be no greater than about 10 mm. in size and preferably will be in the size range of about 1.5 to 10 mm., being produced directly within such size range or by crushing larger agglomerates, e.g., used electrode butts.

Although any conventional mixing technique may be employed, highest quality electrodes are produced if the carbon black is mixed with the carbonaceous binder material prior to mixing in the high temperature fluid coke. This technique provides intimate contact between binder and carbon black and may result in a binder coke more uniformly modified by the black than would otherwise be possible. Another variation of the invention is to include part or all of the carbon black in the performed agglomerates rather than adding it separately in the final mixing step before formulation of the electrodes.

In a specific example of this invention 12 parts by weight of coal tar pitch were mixed with 10 parts of thermal black having a particle size substantially in the range from about 1000 to 4000 A., averaging about 2500 A. To this mixture were then added 70 parts of unground high temperature fluid coke substantially in the size range from about 40 to about 400 microns and averaging about 100 microns. Twenty parts of coke fines were also added to the mixture, substantially all the fines being ground sufficiently small to pass through a 200 mesh (Tyler) screen, and 40% of which were sufficiently small to pass through a 325 mesh screen.

The binder, carbon black, fines, and unground coke were then mixed for about 60 min. at about 325° F., compressed into electrodes in a conventional laboratory electrode press, and prebaked for 48 hours at temperature up to about 2000° F. to coke the binder material.

The electrodes were then tested in a cryolite bath at 1800° F. under constant electrical current load. After 6 hours electrode consumption was 143% of the theoretical carbon consumption for the amount of electrical energy use.

In sharp contrast, when electrodes were prepared exactly as in the foregoing example except that the carbon black was replaced by additional ground coke fines, test results showed that electrode consumption in 6 hours was 150% of theoretical, an increase of 7% due to increased dusting.

It will be apparent that many variations are possible without departing from the spirit of this invention.

What is claimed is:

1. A carbonaceous compaction suitable for dusting-resistant alumina reduction cell electrode use comprising high temperature fluid coke, carbon black in an amount ranging from about 5 to about 10 parts per 100 parts by weight of high temperature fluid coke, and a carbonaceous material selected from the group consisting of carbonaceous binder and the coked residue thereof.

2. The compaction of claim 1 wherein said carbonaceous material is selected from the group consisting of carbonaceous binder in an amount ranging from about 9 to about 15 parts per 100 parts by weight of high temperature fluid coke and the coked residue thereof.

3. The compaction of claim 1 wherein said high temperature fluid coke comprises a mixture of ground coke of sufficiently small particle size to pass through a 200 mesh screen and unground coke ranging from about 40 to about 400 microns in size.

4. The compaction of claim 1 wherein said high temperature fluid coke comprises a mixture of agglomerates of coke ranging from about 1.5 to about 10 mm. in size and unground coke ranging from about 40 to about 400 microns in size.

5. The compaction of claim 1 wherein said high temperature fluid coke comprises a mixture of ground coke of sufficiently small size to pass through a 200 mesh screen, unground coke ranging from about 40 to 400 microns in size, and agglomerates of coke ranging from about 1.5 to about 10 mm. in size.

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