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HIGH TEMPERATURE FLUID COKE ELECTRODES

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This invention relates to carbonaceous electrodes. More particularly, it relates to the preparation of electrodes having improved resistance to dusting or consumption during use.

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 alumina bath.

In the past electrodes have been manufactured from coke formed at relatively low temperatures, generally below about 1200° F. One common form of low temperature coke is that known as delayed coke; another is low temperature fluid coke. Delayed coke is manufactured by cracking petroleum or other heavy hydrocarbons in a coking chamber at temperatures ranging from about 750–950° F., the coke accumulating therein while light hydrocarbon products are evolved as a gaseous effluent. The delayed coke is then removed batchwise from the chamber by actual physical disolgment with crow bars, hydraulic jets and the like.

Low temperature fluid coke is formed by contact of hydrocarbons with hot fluidized coke solids at temperatures ranging from about 850–1200° F. The production of low temperature fluid coke and its use in electrode formulations are described, e.g., in U.S. Patents 2,881,130; 3,043,753; and 3,197,395.

When using coke from the delayed coking process or the low temperature coking process, it is necessary first to calcine the coke at 2000–2400° 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.

While both delayed coke and low temperature fluid coke have admirable characteristics making them suitable as raw materials for manufacturing electrodes, the difficulties or expenses associated with their manufacture leave much to be desired. Among other things, the difficulties associated with the delayed coking process make delayed coke quite expensive. Moreover, because a high quality feedstock is required, delayed coke is in short supply worldwide.

Low temperature fluid coke, on the other hand, 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 resistance to dusting 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.

Moreover, because the conversion of hydrocarbon feed to coke is generally quite low at low coking temperatures, operating expenses in both the low temperature coking process and the delayed coking process are undesirably high.

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 somewhat different from those of the delayed coke and low temperature fluid coke, supra. The high temperature fluid coke can be produced, e.g., by the recently developed process disclosed in U.S. patent application Ser. No. 333,897, and now Patent No. 3,264,210. The characteristic differences between coke formed at temperatures above 1800° F. as compared with delayed coke or low temperature fluid coke is 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 important features of such high temperature fluid coke.

Thus, it has heretofore been considered impractical, if not impossible, to produce commercially acceptable alumina reduction electrodes of either the prebaked or Soderberg types from high temperature forms of coke. It is known, e.g., that at the temperatures at which an electrode is prebaked or used, the binder material in electrodes forms a type of coke very much like low temperature 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, microcracks 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 and a high electrical contact resistivity, in sharp contrast with 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, inter alia, 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 serious 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 fluid coke, it has heretofore been thought impractical to prepare commercial alumina reduction 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. In our copending application Ser. No. 550,591, filed of even date herewith, a method is disclosed for modifying high temperature coke electrode formulations by the addition of carbon black. Electrodes prepared from such formulations have greatly improved resistance to dusting and a correspondingly low rate of consumption as compared with high temperature coke electrodes prepared without carbon black.

In accordance with the present invention, it is possible to use high temperature fluid coke to make electrodes having an even greater resistance to dusting than heretofore believed possible.

Pursuant to this invention, coke, binder and inorganic additives are mixed and formed into compactions suitable for use in alumina reduction electrodes. Suitable additives include halide salts and oxides of metals selected from Groups I–A, II–A, and III–A of the Periodic Table (see Periodic Chart of the Elements, page 392 of "Handbook of Chemistry and Physics," 35th edition, published by the Chemical Rubber Publishing Co.). Preferred additives are the oxides and halide salts of the light metals of Groups I–A, II–A, and III–A having atomic numbers ranging from 3 to 20, viz. lithium, beryllium, boron, sodium, magnesium, aluminum, potassium, and calcium.

The particular inorganic additives selected will depend on the exact condition under which the coke compaction is to be used. Thus, in an alumina reduction cell where temperatures will generally be above about 1810° F., it is necessary to use additives which do not vaporize at such temperatures.

Examples of the metal oxides of this invention are Li_2O, BeO, B_2O_3, NaO, Al_2O_3, MgO, and the like. The term "oxides" as used herein also includes mixed or complex metal oxides containing a plurality of metals, e.g., aluminates, such as $MgAl_2O_4$ (magnesium aluminate), $CaAl_2O_4$ (calcium aluminate), $Ca_3Al_2O_6$ (tricalcium aluminate) and the like, and borates such as $NaBO_2$ (sodium metaborate), $Na_2B_4O_7$ (sodium tetraborate), $Ca(BO_2)_2$ (calcium metaborate), CaB_4O_7 (calcium tetraborate), KBO_2 (potassium metaborate), $K(AlO)_2(BO_2)_3$ (potassium aluminum borate), and the like.

Outstanding examples of the halide salts which are suitable additives in this invention are the fluorides, chlorides, bromides, and iodides of lithium, sodium, and potassium. Other useful salts are the fluorides of magnesium, calcium and aluminum; also magnesium chloride, magnesium bromide, calcium chloride, and the like. Mixed or complex salts such as Na_3AlF_6 (cryolite), $KCl{\cdot}CaCl_2$ (potassium chlorocalcite), and $Na_3Al_2F_9$ (chiolite) are also intended to be included in the term "salts" as used herein.

The additives of the invention also include precursors which liberate or form the above salts and oxides in situ in the coke compaction at the temperatures at which it is used, e.g., hydrates or carbonates which liberate water or carbon dioxide at alumina reduction or electrode baking temperatures. Examples of such precursors are magnesium carbonate, calcium carbonate, sodium carbonate, etc., and hydrated borates and aluminates such as $Ca(BO_2)_2{\cdot}2H_2O$, $Mg(BO_2)_2{\cdot}3H_2O$, $KAlO_2{\cdot}\frac{1}{2}H_2O$, and the like; $Al_2O_3{\cdot}3H_2O$ (hydrated alumina); and hydrated metal halide salts such as $AlCl_3{\cdot}6H_2O$, and also $CaO_2{\cdot}8H_2O$ (calcium peroxide); $CaCl_2{\cdot}2H_2O$, and the like.

Generally the most preferred additives for use in alumina reduction electrodes are alumina, cryolite, and the chlorides and fluorides of lithium, sodium, and potassium.

The compactions of this invention can be produced by admixing 100 parts coke with from about 0.1 to about 3 parts by weight of inorganic additive and from about 9 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 flowing type electrode, e.g., Soderberg electrode, formulations without curing, since such electrodes are cured in situ in the alumina reduction cell. In either case, the cured compactions comprise coke, the coked residue of carbonaceous binder, and the inorganic additive.

Optimum benefits of the inorganic additive are attained using about 0.5 to 1.0 part of additive per 100 parts of coke; however, lesser amounts may be employed with, of course, correspondingly reduced effectiveness. Electrode improvement, however, is nil below about 0.1 part additive. Similarly, greater amounts of additive can be used to impart still better nondusting characteristics to the electrode; however, it is generally undesirable to use more than about 3 parts per 100 parts coke because at above this level the electrode may be too brittle for use in alumina reduction cells. Moreover, the additive is generally more expensive than the coke itself.

While outstanding electrodes can be prepared pursuant to this invention using any type of petroleum coke, the greatest effect of the inorganic additive on electrode consumption is obtained using high temperature fluid coke. The reasons for the outstanding improvement in resistance to dusting are not clear; however, in the case of high temperature coke electrodes it is believed to be due to the ability of the additive to improve the wettability of the coke, greatest improvement being obtained using additives which melt at or below the operating temperature of the reduction cell. Thus high temperature coke particles have very hard surfaces with correspondingly low wettability and reactivity such that in an alumina reduction cell the electric current passes preferentially into the cryolite bath through the easily wetted binder material in the electrode with the result that the binder coke is used up at a faster rate than the high temperature fluid coke. This increases the tendency of the electrode to dust.

The inorganic additives of this invention apparently tend to improve the wettability of the high temperature coke with the result that the surfaces of the high temperature coke have improved reactivity, and its consumption rate becomes similar to that of the binder.

When high temperature coke is used, an important feature of this invention is to incorporate about 5 to 10 parts by weight of carbon black per 100 parts of coke in an electrode formulation containing the inorganic additives. Electrodes of outstanding quality can thus be prepared deriving high resistance to dusting or consumption from both the carbon black and the inorganic additive. Optimum benefits of the carbon black are obtained 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 nondusting 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., are especially convenient and satisfactory in improving 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, an increase in electrode density can be obtained by incorporation of desirable amounts of carbon black in 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 somewhat different from the effect of the inorganic additive, supra, and is in part due to certain similarities between the surface characteristics of the black 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 9 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 of 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 feed stocks at about 1800° 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
65	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 is preferably 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, briquettes, 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 can 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 preformed agglomerates rather than adding it separately in the final mixing step before formulation of the electrodes.

The best use contemplated for the electrodes of this invention is in combination with an alumina reduction cell in the manufacture of aluminum. In a typical operation an electrode or bank of electrodes, of either the prebaked or Soderberg type, are mounted in a bath of molten electrolyte, e.g., cryolite, containing dissolved alumina, at a temperature of about 1800–2000° F., electric current is passed through the electrodes (which serve as anodes) into the electrolyte bath and out through one or more cathode electrodes. The alumina is reduced to molten aluminum which settles to the bottom of the cell and can be drawn off as product. The cathodes are also generally carbon or coke and can be formed as a layer along the walls of the reduction cell. Since the cathodes are not consumed at any appreciable rate, no inorganic additive is needed in their formulation, and conventional cathodes can be used.

In a specific example of this invention 12 parts by weight of coal tar pitch is mixed with 70 parts of high temperature fluid coke substantially in the size range from about 40 to about 400 microns and averaging about 100 microns. Thirty parts of ground coke fines are then added to the mixture, substantially all the fines being ground sufficiently small to pass through a 200 mesh (Tyler) screen, and 40% of which is sufficiently small to pass through a 325 mesh screen.

The binder, fines, and unground coke are then mixed with 1.0 part by weight of cryolite for about 60 minutes at about 325° F., compressed into electrodes in a conventional laboratory electrode press, and prebaked for 48 hours at temperatures of about 2000° F. to coke the binder material.

The electrodes are weighed and then tested under constant electrical current load in an alumina reduction cell comprising a cryolite bath at 1800° F. containing 0.5 wt. percent dissolved alumina. After 6 hours the electrodes are reweighed to determine the electrode consumption. The results of this test as shown below indicate that outstanding electrodes can be produced using only a very small amount of additive according to the invention. This is in sharp contrast to the results obtained with electrodes prepared without the inorganic additive.

Wt. percent inorganic additive:	Percent of theoretical consumption
None	150
1.0	130

Still greater improvements in electrode consumption are obtained when the inorganic additives of this invention are used in combination with carbon black. Thus, when electrodes are prepared exactly as described above except that 5–10 parts of ground coke fines are replaced by thermal black having particle sizes substantially in the

range from about 1000 to 4000 A., averaging about 2500 A., electrode consumption is still further reduced.

It will be apparent that many combinations and variations are possible without departing from the bounds of this invention. Thus, mixtures of inorganic additives can be used with equivalent effectiveness. While the greatest effect is seen using high temperature fluid coke, improvements in electrodes are also possible according to this invention using low temperature fluid coke, delayed coke, or mixtures of the various types of coke. Moreover, benefits are also obtained when the additives of this invention are used either alone or in combination with carbon black in standard Soderberg electrode formulations. Thus, it is contemplated that this invention can be used to advantage in any process in which coke electrodes are used and consumed in contact with a liquid electrolyte. The homogeneity of the composition throughout the electrode provides consistent and uniform resistance to consumption as the electrode is used.

What is claimed is:

1. A carbonaceous compaction having improved resistance to consumption in alumina reduction cell electrode use comprising high temperature fluid coke, inorganic additive selected from the group consisting of salts and oxides of metals selected from Groups I–A, II–A, and III–A of the Periodic Table, and mixtures thereof, ranging from about 0.1 to about 3 parts additive per 100 parts by weight of 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 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.

3. The compaction of claim **1** wherein carbon black is present in an amount ranging from about 5 to about 10 parts per 100 parts by weight of coke.

4. The compaction of claim **1** wherein said 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 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 about 400 microns in size, and agglomerates of coke ranging from about 1.5 to about 10 mm. in size.

6. 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.

7. The compaction of claim **6** wherein said inorganic additive is present in an amount ranging from about 0.5 to about 1.0 part of additive per 100 parts of coke.

8. The compaction of claim **1** wherein said additive is present in an amount ranging from about 0.5 to about 1.0 part per 100 parts of coke.

9. The compaction of claim **8** wherein said additive comprises cryolite.

10. The compaction of claim **8** wherein said additive comprises alumina.

11. The compaction of claim **8** wherein said additive comprises CaF_2.

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