UNITED STATES PATENT OFFICE.

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GRAPHITIZED ELECTRODE AND PROCESS OF MAKING THE SAME.

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To all whom it may concern:

Be it known that I, ARTHUR T. HINCKLEY, a citizen of the United States, residing at Niagara Falls, in the county of Niagara and State of New York, have invented a certain new and useful Improvement in Graphitized Electrodes and Processes of Making the Same, of which the following is a full, clear, and exact description.

This invention relates to improved graphitized electrodes and to processes of making such electrodes. By means of the invention it is rendered possible successfully to graphitize electrodes of much larger cross-sectional area than heretofore, and the invention relates more particularly to these larger electrodes, applicable especially for electric furnace use.

It is well understood in this art that the graphitization of electrodes, without excessive loss by breakage, becomes progressively more difficult as the diameter of the electrode increases; and the present limit of industrial graphitization is reached at a diameter of approximately 12 inches, either for round or square sections. As this limit is approached the proportion of losses through breakage or by the development of cracks or other defects undergoes a relatively very rapid increase, with the result that there exists a rather definite size limitation, above mentioned, beyond which graphitization has not up to the present time been commercially practised. The breakage and the development of defects referred to occur partly during the baking of the electrodes prior to graphitization, and partly in the graphitizing operation itself.

The manufacture of graphitized electrodes up to and including the 12 inch sizes which are the present commercial size-limit, involves the following essential steps: Petroleum coke, a low-ash residue from petroleum distillation, is crushed and then calcined or "shrunk" by heating to approximately 1000–1100° C., usually in a gas- or oil-fired kiln. Thereby the hydrocarbons which are volatile at or below the calcining temperature are largely expelled. The calcined material is again crushed, graded, bonded with pitch or similar heavy hydrocarbon, and molded or extruded through dies into the appropriate electrode sections. The resulting so-called green electrodes are then baked in gas-fired kilns, usually at a maximum temperature of about 1000° C. They are then ready for graphitization which is carried out in electric resistance furnaces at a much higher temperature range (above 2000° C.) The principal advantages secured through graphitization are a large increase in electrical conductivity, and a marked decrease in the tendency to oxidation at the working temperature of the furnace.

In case graphitization is not desired it is for many purposes advantageous to use in the electrode mix, instead of the low-ash petroleum coke, certain forms of carbon particles which are higher in ash but more compact, and of greater mechanical strength, notably hard coal of the anthracite type. This coal is preliminarily calcined or shrunk to expel volatile matter, this operation being most advantageously carried out in electric calcining furnaces at relatively very high temperatures, up to 1600–1800° C. This material is then crushed, graded, bonded and shaped, substantially as above described, and the green electrodes are then baked at about 1000° C. to form the finished commercial article. It has heretofore, so far as I am aware, been the universally accepted view of those skilled in this art that these so-called hard coal electrodes could not be advantageously graphitized; and so far as I am aware graphitization of hard coal electrodes has never been commercially practised, either for large or small electrode sizes.

I have discovered that electrodes compounded from a properly proportioned mixture including anthracite coal particles which have been fully shrunk, as for example by subjecting them to a calcining temperature of about 1500° C. or upward, may be graphitized under the usual furnacing conditions, without encountering the heavy losses through breakage and other causes which have heretofore served to fix a practical limit to the size of commercial graphitized electrodes. In accordance with my invention it becomes therefore industrially practicable, for the first time, to prepare graphitized electrodes of large size, that is to say upward of 12 inches in diameter. No upper limit of practicable size can now be assigned, but my invention is applicable to the manufacture of graphitized electrodes

in sizes up to at least 24 inches in diameter, that is to say the largest electrode sizes which are now commercial articles in the non-graphitized state.

I have discovered that certain other types of carbon particle which more or less closely resemble fully shrunk anthracite in the qualities of compactness, mechanical strength, and thermal conductivity, may be used to replace anthracite, either wholly or in part, in the electrode composition, with similar results so far as the successful conduct of the graphitizing operation is concerned. For example such particles may be artificially prepared from non-compact or cellular forms of carbon, such for instance as petroleum coke, or other forms of coke, by fine-milling, adding just sufficient hard pitch or other carbonaceous binder to prepare a plastic mass, shaping into briquets, and baking at a sufficient temperature to expel the volatile matters. A baking temperature around 1000° C. will ordinarily suffice for this purpose, although higher temperatures may of course be used and may be advantageous. The baked composition, owing to the heavy shrinkage of the carbon, particularly if this has not been preliminarily shrunk in bulk, will usually be misshapen and more or less cracked or broken; but is nevertheless suitable for crushing into fabricated carbon particles adapted to replace the fully shrunk anthracite for the purposes of this invention.

Or instead of petroleum coke or other cellular carbon, anthracite coal itself, or other compact form of carbon, either before or after shrinking, may be ground, bonded, shaped and baked, and the baked briquets thereafter crushed to produce fabricated anthracite particles which possess the advantage over the natural anthracite particles, for the purposes of this invention, that they are free from the laminated structure or cleavage tendency which is characteristic of most or all natural anthracites, and possess substantially uniform strength and thermal conductivity in all directions.

In one embodiment of my invention, I subject hard coal to a preliminary calcination or shrinking, preferably at a very high temperature, about 1500° C. or upward, This is preferably done in an electric calcining furnace which may be of any of the known types now used for the calcination of carbon. The time and temperature conditions during calcination are so controlled as substantially to complete the shrinking of the carbon; that is to say the time and temperature should be such that substantially no further shrinking of the carbon fragments will take place during the subsequent graphitization. This result may be measurably attained by bringing the carbon to the specified temperature of 1500° C. I am not restricted, however, to this specific temperature, inasmuch as a longer heating at a lower temperature may accomplish a like result.

This fully shrunk anthracite carbon is then crushed to a size suitable for the electrode in question. For electrodes of 10–12 inches in diameter the preferred size of particle is about .08–.16 inch in diameter. For larger sizes the diameter of the particles will preferably be somewhat increased, say up to .32–.64 inch for 24 inch electrodes. These particles are mixed with sufficient fine carbon, which may also be fully shrunk anthracitic carbon, to substantially fill the voids, and the whole is then mixed with pitch, or other suitable hydrocarbon binder, shaped and baked, preferably at a temperature of about 1000° C. The resulting baked electrode may then be directly graphitized.

One suitable mix for the purposes of this invention, for a 24 inch electrode, may comprise for example:

Fully shrunk anthracitic carbon particles 0.3 to 0.6″	about 500 parts
Fully shrunk fine carbon (100 mesh and under)	300 "
Hard pitch	200 "

My invention is not limited to carrying out the baking and graphitizing steps in separate furnaces or in interrupted sequence, inasmuch as I may subject the green electrodes to increasing temperatures in an electric resistance furnace, whereby the baking and graphitizing operations are carried out as successive steps of a continuous heat.

The fact that electrodes prepared as hereinabove described may be subjected to the successive operations of baking and graphitizing without serious loss through breakage or the development of cracks has been established. The following tentative explanation of the observed fact is offered without restriction of the invention:

Carbon particles suitable for use in accordance with this invention possess sufficient tensile strength to endure without fracture the strains set up in the electrode during the heating and cooling operations incident both to baking and graphitizing: at the same time they are of sufficient size to constitute a substantial interruption to incipient cracks which may tend to develop in the electrode. They retain these characteristics to a sufficient degree not only during the baking operation, but also during and after the graphitizing operation; in other words the graphite particles derived from previously shrunk anthracite coal and equivalent forms of carbon possess sufficient strength to withstand the stresses developed during the cooling and subsequent use of the

graphitized electrode. It should of course be understood that the great increase in the thermal conductivity of the carbon particle, due to the high temperature shrinking and subsequent graphitization, tends to rapid equalization of temperature throughout the electrode and thereby greatly reduces the strains set up in the electrode by temperature changes.

My invention is not limited to the use, in the electrode to be graphitized, of carbon particles derived from anthracite coal, inasmuch as other kinds of carbon particle having equal or sufficient tensile strength both before and after graphitization may be substituted therefor, as above set forth. Such other kinds of carbon particle are therefore to be regarded for the purposes of this invention as an artificial or fabricated anthracitic carbon; and the term "anthracitic carbon" is employed in the present claims to designate any kind of carbon particle, whether natural or fabricated, which possesses that quality of fully shrunk anthracite which is essential for the purposes of this invention, to wit: sufficient tensile strength, both before and after graphitization, to enable the particle to resist the strains which are set up in large electrodes during the baking and graphitizing operations and subsequent use. As before stated, the strains set up within the electrode by the temperature changes incident to the above operations will be less as the thermal conductivity of the electrode is greater. Hence a carbon particle, for the purposes of this invention, should combine mechanic strength with high thermal conductivity.

I claim:

1. A graphitized electrode comprising coarser and finer particles of graphitized carbon and a graphitized binder, the coarser particles having the essential quality of graphitized anthracitic carbon.

2. A graphitized electrode having a diameter in excess of 12 inches, said electrode comprising coarser and finer particles of graphitized carbon and a graphitized binder, said coarser particles having a diameter of about .08–.64 inch, and having the essential quality of graphitized anthracitic carbon.

3. Process of making graphitized electrodes comprising commingling coarser and finer particles of carbon with a hydrocarbon binder, said coarser particles having the essential quality of fully shrunk anthracitic carbon, shaping the mix into electrode forms, and baking and graphitizing the same.

4. Process of making graphitized electrodes having a diameter in excess of 12 inches, comprising commingling coarser and finer particles of carbon with a hydrocarbon binder, said coarser particles having a diameter of about .08–.64 inch, and having the essential quality of fully shrunk anthracitic carbon, shaping the mix into electrode forms, and baking and graphitizing the same.

In testimony whereof, I hereunto affix my signature.

ARTHUR T. HINCKLEY.