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MANUFACTURE OF CARBON ELECTRODES

Frederick L. Shea, Jr., Chicago, and Leslie H. Juel, Morton Grove, Ill., assignors to Great Lakes Carbon Corporation, New York, N. Y., a corporation of Delaware

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This invention is concerned with methods for improving the manufacture and quality of carbon articles such as carbon electrodes.

Carbon articles with which this invention is concerned are made from carbon or coke solids such as calcined petroleum coke, anthracite, electrode scrap, lampblack, graphite and the like, said materials being in a state of initial division termed in the electrode art as "particles" and "flour."

To make clear what is meant in regard to the sizes of the carbon solids employed, "particles," are defined as those sizes which are retained on a 20 to 35 mesh sieve, and may be as large as 0.75 inch in diameter. "Flour" is defined as the solids composed of sizes which pass such a sieve, and generally have 40-60% of 200 mesh or finer.

The cokes preferably used for electrodes and anodes are generally substantially volatile-free petroleum cokes, coal tar pitch cokes, anthracite cokes, etc. which are comparatively porous in the calcined state. These have generally been calcined at temperatures of 900-1100° C. Sizes of 3/4 inch diameter to 50 mesh are employed, especially in the manufacture of larger electrodes of 15-40 inch diameter.

The usual procedure in making carbon electrodes has been to mix a suitable amount of binder such as pitch with the entire carbon solids aggregate usually at an elevated temperature to insure the binder being fluid. A molding lubricant such as black oil may be added in small proportions just before mixing is completed. The mixture is usually cooled somewhat below the mixing temperature, but only to a point where it is still plastic, and then molded or extruded to the desired size and shape. The molded articles are baked at a slowly rising temperature to about 1000° C. to carbonize the binder, and may then be subjected to further heating at 2400-3000° C. for graphitization depending upon use to which they are put.

In the above practice, the use of any particular binder has its limitations because of difficulties which may arise during the baking of the molded article, especially those containing the particle-sized solids. For instance, swelling of the molded mass may occur in baking which often results in loss of useful product. Swelling appears to result from an improper penetration of the binder into the particles, particularly with high melting point binders. These are not sufficiently fluid at the mixing temperature to penetrate the particle pores and displace the air

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therein. Also, when the proportion of particles in the mix is relatively large, another effect may take place wherein the resulting product, although satisfactory as to shape and freedom from cracks or other defects, does not have the desired electrical conductivity and/or mechanical strength. The reason for the latter effect may be that the large particles tend to selectively absorb the more fluid components of the binder leaving an interstitial residue which does not adequately bond the carbon aggregate when carbonized. This is not overcome either by increasing the quantity of binder, nor adding a more liquid component to the mix.

We have found that by impregnating the larger particles first with a suitably fluid heavy hydrocarbon material before the addition of flour solids and binder, we are able to overcome the detrimental behavior in baking and also secure a better quality carbon article.

It is an object of this invention to provide methods of compounding carbonaceous mixtures for eliminating swelling during baking of the molded article therefrom.

Another object is to enable the use of more than one binder material in a mixture containing particles and flour carbon solids in such a way as to secure the best advantage of each for improving the manufacture and quality of carbon articles.

Another object is to enable use of desirably high coking hydrocarbonaceous materials for the binder. Coal tar pitches with a softening point above about 130° C. may be used. Heretofore these have not been regarded generally as satisfactory because of too great a viscosity even at high mixing temperatures, for proper mixing and penetration of the porous carbon solids.

Certain other materials which increase coke residue of pitches, e. g., phenol-aldehyde condensation products, pitch materials with added reactive nitro-aromatics, aldehydic material, etc., and which may have suitable viscosity at mixing temperatures are so heat sensitive as to "set up" or become too viscous before proper penetration of porous solids in mixing has taken place. These materials can be employed satisfactorily according to the practice of this invention.

In one embodiment the invention comprises the general procedure of making a carbon solids-binder mixture ready for molding comprising the following steps: First, the calcined coke particle fraction is mixed at a suitable elevated temperature with at least a sufficient proportion of a

heavy hydrocarbon material, such as the so-called coal tar pitch resins, to thoroughly impregnate the particles and fill the maximum number of the available pores thereof, then mixing the impregnated particles with coke flour and pitch binder at a temperature above the melting point of the latter, forming the mixture into the desired shape and baking it.

Heavy hydrocarbon materials which may be used as the impregnant include the pitch resins obtained as distillates of coal tars and pitches; the so-called "single phase" extracts of carbonaceous materials, for example, a benzol-soluble fraction of pitch; and the like. In any event such impregnant preferably melts below about 80° C. and should be of a relatively low viscosity when fluid. It should be substantially all distillable and/or contain no appreciable proportion of residues insoluble in benzol or carbon disulfide. The impregnant should be used in volumetric proportions to fill any desired percentage of the available pore voids of the coarse particles. Depending upon the particle size, the per cent of the total voids present in the particles which are available for purposes of impregnation will vary from about 50 to 90%. In general a slight excess of the impregnating agent over and above the total which is able to penetrate the aforesaid voids is employed, said excess being preferably about 5 to 10% over and above the total impregnant. The proportion of impregnant, based on the weight of the particles, is generally about 12 to 16% by weight.

The impregnated particles may then be mixed with a binder material at a suitable temperature above its melting point, in an amount necessary for the final molding mixture generally in the range of 17% to 28% by weight, based on the total weight of particles plus flour present in the final product. The flour carbon solids may then be mixed with the binder and impregnated particles, while still in heated condition. A small amount of the black oil or other suitable lubricant is added shortly before the mixing is completed, if the article is to be extruded. This is not necessary when molding under pressure.

An alternative procedure comprises mixing the coke or carbon flour with the impregnated particles and then adding the binder. Lubricant may be added.

This latter procedure is advantageous especially where an excess of impregnant is employed with the coke particles and it is desired to impregnate the flour to some extent before adding the binder. There is another advantage in the case of heat sensitive binders such as the phenol-aldehyde condensation products; or tars and pitch in which reactive additives such as aldehydes and nitroaromatics, and the like have been incorporated. This permits shorter time of exposure of the binder to heat during mixing. Mixing may be carried out at a lower temperature than in the usual practice.

It is essential that the coke particles be properly combined with the suitable heavy hydrocarbon impregnant in order to secure the improvements of the finished carbon product.

For example, the porous carbon particles may be impregnated by immersing them at about 125–200° C. and preferably at about 160° C. in a pitch resin which melts at about 60° C. and is substantially all distillable at 280–360° C. at 15 mm. of mercury pressure. The mixture is mildly agitated for a short time with continued heating

and thereafter excess impregnant may be drained off.

Alternatively, the impregnant may be added as increments to the agitated particles in a mixer at 160° C. until sufficient material has been added to fill the available pores and wet the particles.

The impregnation of the particle coke may be conveniently accomplished at atmospheric pressure, although in some instances the penetration thereof by the impregnant may be facilitated by applying a vacuum to the particles in a closed mixing vessel in the presence of the impregnant, and restoring the pressure to normal or even slightly super atmospheric, say to about 50 pounds gage. This aids in displacing air and filling the pores of the calcined coke or other particles with the impregnant.

The temperature for the impregnation of the particle coke is above the melting point of the heavy hydrocarbon material used, but below its coking or volatilization temperature.

A wider variety of binder materials than generally employed heretofore may be used advantageously in the production of carbon electrodes and other similarly produced molded or extruded carbon articles when practicing this invention. Examples of the binder materials, in addition to the commonly used soft and medium hard pitches which have softening points below about 120° C., are the pitches softening between about 120 and 150° C.; the liquifiable heat sensitive phenolic resins; the reactive mixtures of tars and pitches with aldehydes, nitro-aromatic compounds, and the like, such as are disclosed in our copending applications Serial No. 681,594, filed July 5, 1946, now U. S. Patent No. 2,500,208, and Serial No. 682,924, filed July 11, 1946, now U. S. Patent No. 2,500,209.

Example I

According to this invention electrodes were prepared as follows: To 60 parts by weight of calcined petroleum coke of 8 to 20 mesh particle size, was slowly added during 15 minutes, 7.2 parts by weight of a tar distillate resin having a melting point of 60° C. The mixture was agitated during mixing and was held at 160° C. The temperature was then raised to 200° C. and 19.2 parts by weight of a coal tar pitch distillation residue having a softening point of 180° C. was blended with the impregnated coke particles with agitation during 15 minutes to form a homogeneous mixture. To this hot mixture was added 40 parts by weight of calcined coke flour which was milled into it during 30 minutes to produce uniform distribution. Finally 2 parts by weight of an oil lubricant was worked in to assist in extrusion of the green electrodes which was carried out at about 150° C. and 3,500 pounds per square inch pressure. The extruded pieces were baked in the usual way to a temperature of 1000° C. The apparent density of the baked electrode was 1.55, and a resistivity of 0.00196 ohm per inch cube.

By way of comparison, baked electrodes were produced from identical components under otherwise similar conditions by first blending the impregnant and the pitch distillation residue together, then adding in sequence the coke particles, the coke flour and finally the lubricant. The properties of the resulting baked electrodes were considerably inferior, apparent density being 1.53, and resistivity being 0.00214 ohm per inch cube.

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Upon graphitizing the two baked electrodes just described, the results were even more favorable to electrodes of this invention. The electrode of this invention had an apparent density of 1.56 and a resistivity of 0.00033 ohm per inch cube. The values respectively for the non-impregnated electrodes were, 1.53 and .00035 ohms.

Example II

In order to compare the effect of particle impregnation described in Example I, a conventional mixture of 60 parts of the particles, 40 parts of the flour and 25 parts of the usual coal tar pitch (softening point 88° C.) was formed into electrodes. The baked and graphitized properties are shown as follows:

	Apparent Density	Resistivity ohms/inch ³	Crushing Strength
Baked.....	1.57	0.0020	-----
Graphitized.....	1.55	0.00036	-----

Example III

Utilization of certain binders resolves itself into the use of impregnated particles together with that amount of binder which will give an external porosity capable of permitting the escape of gases during baking without creating an internal pressure and consequent swelling of the electrode in baking. For example, a coke aggregate comprising 60 parts by weight of 4 to 20 mesh particles and 40 parts by weight of flour was mixed with 27 parts by weight of a binder consisting of fuel pitch having a cube in air melting point of 150° C., and 20% of its weight of a nitronaphthalene. This mixture was extruded into electrodes and upon baking, a volume swelling occurred amounting to 1.3%. The resistivity of the resulting baked electrode was 0.0025 ohm per in.³.

However, when another mixture otherwise comparable to this one was made up by first impregnating the particles with 8.3 parts of a pitch resin (melting point about 60° C.) and then combining with 17.1 parts by weight of the indicated nitro-modified binder and the coke flour, the resulting molded mixture did not swell but underwent shrinkage in baking amounting to 2.5% and an appreciable lower resistivity resulted at 0.0022 ohm per in.³. The total proportions of binder or binder plus impregnant in these two tests though differing on a weight basis were approximately equal in volume. Therefore, these examples show the advantages resulting from the practice of this invention.

When manufacturing carbon electrodes in excess of 20 inches in diameter according to the method described in the first paragraph of Example I, improvements of about 10% in apparent density, about 20% in conductivity and about 25% in crushing strength are obtained.

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We claim as our invention:

1. A process for forming a carbon electrode which comprises separating calcined coke into particles larger than about 50 mesh and coke flour smaller than about 50 mesh, mixing the particles with a hydrocarbonaceous impregnant, said impregnant characterized by being normally solid, melting below about 80° C. and boiling at about 280° C. to about 360° C. at 15 mm. of mercury pressure, said mixing being carried out at a temperature at which the impregnant is freely fluid, to impregnate said particles, thereafter mixing the unimpregnated coke flour and a pitch binder melting higher than said impregnant, with the impregnated particles at a temperature above the melting point of said binder, forming the mixture while hot into an electrode and baking it.

2. The process of claim 1 wherein the impregnant is in the proportions of 12-16%.

3. The process of claim 1 wherein the impregnant is in the proportions of 12-16% and the binder in proportions of 17-28% both by weight of the total coke in the mixture.

4. The process of claim 1 wherein the flour is mixed with the impregnated particles and the binder is then added.

5. The process of claim 1 wherein the flour and binder are added simultaneously.

6. The process of claim 1 wherein the impregnant is substantially completely soluble in benzene.

7. The process of claim 1 wherein the impregnant is a coal tar distillate.

8. A process for forming a composition suitable for making a carbon electrode which comprises separating calcined coke into particles larger than about 50 mesh and coke flour smaller than about 50 mesh, mixing the particles with a hydrocarbonaceous impregnant, said impregnant characterized by being normally solid, melting below about 80° C. and boiling at about 280° C. to about 360° C. at 15 mm. of mercury pressure, said mixing being carried out at a temperature at which the impregnant is freely fluid, to impregnate said particles, thereafter mixing the unimpregnated coke flour and a pitch binder melting higher than said impregnant, with the impregnated particles at a temperature above the melting point of said binder.

FREDERICK L. SHEA, JR.
LESLIE H. JUEL,

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