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PROCESS OF FORMING A CARBON ARTICLE FROM FURFURAL ALCOHOL AND CARBON PARTICLES

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This invention relates to a process of manufacturing carbon articles.

It is to be understood that the term "carbon" used herein extends to the various forms of the material, especially graphite.

In the known processes of manufacture of carbon articles, coal tar pitch has been commonly employed as a binder with a filler of carbon or coke particles, e.g. pitch coke and petroleum coke, these constituents forming a mixture which is subsequently processed to form solid material and shaped articles.

Although careful control of the quality and properties of the binder and filler has permitted the production of carbon articles having a wide range of physical properties, the process has been relatively expensive because of the difficulty in predicting the effect that the characteristics of a complex material such as pitch will have on the finished artcile. One characteristic of pitch is that on heating it goes through a liquid stage in which volatiles are given off and on further heating slowly turns to a viscous liquid and then to a highly porous solid, and consequently carbon articles made from pitch tend to suffer from similar porosity.

The present invention is concerned with the use of a novel binder in a process of making carbon articles, in which process, according to the invention, a liquid is employed as the sole binder for the particles of carbon and/or other filler material, which liquid consists essentially of furfuryl alcohol or mixtures thereof with furfuraldehyde in proportions depending on the desired properties of the article.

Resinification and hardening of the binder may be effected by heat and/or admixture therewith of a known hardening agent such as, in the case of furane derivatives, small quantities of a mineral acid in accordance with the desired rate of reaction. The proportions of filler and binder may be varied in accordance with the desired nature of the article.

The mixture may comprise a relatively small proportion of binder, say up to 20% by weight, the mixture being cast or extruded to form the article and then heat treated in non-oxidizing conditions to convert the binder to carbon. The heat treatment may be performed in two stages the first being a baking treatment to a temperature in the range 400–800° C. and the second being a graphitizing treatment at a temperature in the range 2000 to 3000° C.

The invention also includes the manufacture of shaped articles of carbon by making a mixture of the liquid binder and particles of carbon and/or other filler material, and forming the article by an extrusion process with or without heat as required. The extruded article may then be baked and graphitized as desired.

A particular advantage of the use of the novel binder materials of this invention is that mixtures thereof with carbon particles may be easily extruded at comparatively low temperatures and pressures, and thereupon converted into carbon articles comprising an infusible binder material by resinification of the binder. In an extrusion process employing a die having a 2¾ inch diameter, conventional mixtures of carbon particles and coal tar pitch require temperatures of about 150° C. and total extrusion forces in the range of 300 to 2000 tons. By using the liquid binders of this invention, extrusion through the same diameter die may be carried out at room temperature and with total extrusion forces in the range of only 50 to 100 tons. For similar extrusion diameters, the extrusion pressure required may be reduced by a factor of about 10. As the pressure is exerted over a die having a 2¾ inch diameter, this lower range may be expressed as from about 8 to 17 tons per square inch. This reduction in extrusion pressure enables the use of continuous screw extrusion presses for the extrusion of mixtures comprising the novel binders. It is believed that this is the first practical realization of a continuous process for the extrusion of carbon articles, without the introduction of non-carbonizable materials such as water.

Carbon articles produced by the extrusion process of this invention heated to a baking temperature, e.g. 800° C., have a high apparent density, i.e. in the region of 1.7 gm./cc. and after graphitizing, e.g. at 2700° C., have a density in the region of 1.8 gm./cc. The permeability to gases of graphite produced thereby is extremely low, the Darcy permeability being of the order of 10^{-13} sq. cm. or less, compared with 10^{-11} to 10^{-12} sq. cm. for the least permeable graphites produced from conventional pitch-bonded mixtures.

The invention is further illustrated by the following examples:

Example I

An intimate mixture was made of 2 parts by weight of ground reactor graphite powder containing substantially no particles greater than 60 mesh (British Standard Test Sieve) and 1 part of medium grade, thermal carbon black, of average particle size 0.3 micron. To 80 parts of this mixture was added 20 parts of liquid furfuryl alcohol containing 0.3% by volume of concentrated hydrochloric acid as catalyst added immediately prior to the addition of the alcohol to the carbon mixture. After thorough mixing, at room temperature, with cooling if necessary, the mix was extruded at room temperature through a cooled circular die of 2¾ inches diameter, which required a maximum force of only 55 tons. The extruded mass was received by a supporting tube and heated therein to 150° C. to complete resinification of the furfuryl alcohol. After cooling air to room temperature, the rigid mass was removed from the tube, cut into convenient lengths and baked by heating in a non-oxidizing atmosphere at the rate of 6° per hour to 800° C., at atmospheric pressure. The baked articles were then graphitized by heating to 2700° C. in an argon atmosphere. The average density of the baked articles was 1.71 gm./cc. and that of the graphitized articles was 1.81 gm./cc. The average Darcy permeability of the baked articles in the radial direction was 7×10^{-14} sq. cm. and that of the graphitized articles was 2×10^{-13} sq. cm.

Example II

An intimate mixture was made of 3 parts of electrographite powder containing substantially no particles greater than 60 mesh and 2 parts of the same carbon black as used in Example I. To 82 parts of this mixture was added 18 parts of liquid furfuryl alcohol containing 0.3% of concentrated hydrochloric acid as catalyst, as in Example I. After thorough mixing, the mix was extruded, as in Example I except that a maximum pressure of 85 tons was required. After curing and baking as in Example I, the carbon articles produced had an average density of 1.715 gm./cc. and a Darcy permeability in the radial direction of 2×10^{-14} sq. cm. After graphitizing as in Example I, the articles had an average density of 1.83 gm./cc. and a Darcy permeability of 7×10^{-14} sq. cm.

The invention also includes a combination of, firstly, a process as hereinbefore described with, subsequently, a process as described in British patent application No. 37,106/57 (U.S.A. Serial No. 777,682) whereby the impermeability of the articles of the first process is further improved by impregnation with a carbonizable liquid impregnant as in the subsequent process.

The invention may be applied to the solution of problems arising in atomic energy power plant, in one instance to the production of substantially impermeable carbon articles, and in another to the production of substantially impermeable fuel elements comprising carbon and a fissionable material such as a metal or carbide, the fuel element being formed by a process according to the invention in which the fissionable material is added in powdered form to the initial carbon and binder mixture.

I claim:

1. A process of manufacturing a carbon article having high density and low permeability comprising the steps of forming a mixture of carbon particles and up to about 20% by weight of a liquid binder material consisting essentially of furfuryl alcohol and being polymerizable to yield a thermosetting resinous material, and which gives a high yield of dense relatively low permeability carbon on decomposition by heat, extruding the formed mixture at room temperature and at an extrusion pressure of from about 8 to about 17 tons per square inch and without the introduction of non-carbonizable material, polymerizing the binder material in said mixture, and heating said mixture to carbonize the binder material.

2. A process as claimed in claim **1**, in which polymerization is effected by heating the extruded article to a temperature of about 150° C. in air until resinification of the binder occurs.

3. A process as claimed in claim **2** in which carbonizing is effected by heating the article in non-oxidizing conditions at a rate of increase of about 60 C. per hour to a temperature of about 800° C. and subsequently heating it in non-oxidizing conditions at a temperature in the range 2000–3000° C.

4. A process as claimed in claim **1** in which the mixture is heated during the extrusion process to partially polymerize the binder.

5. A process of manufacturing a carbon article having high density and low permeability comprising the steps of forming at room temperature a mixture of carbon particles and a binder material consisting essentially of carbon particles and up to about 20% by weight of a binder material consisting of furfuryl alcohol and an acid polymerization catalyst therefore, extruding said mixture at room temperature and at an extrusion pressure of from about 8 to about 17 tons per square inch without the introduction of non-carbonizable materials, heating said mixture to polymerize the furfuryl alcohol, and further heating said mixture to carbonize said binder material.

6. A process as claimed in claim **5** in polymerization is effected by heating the extruded article to a temperature of about 150° C. in air until resinification of the binder occurs.

7. A process as claimed in claim **6** in which carbonizing is effected by heating the article in non-oxidizing conditions at a rate of increase of about 6° C. per hour to a temperature of about 800° C. and subsequently heating it in non-oxidizing conditions at a temperature in the range 2000–3000° C.

8. A process as claimed in claim **5** in which the mixture is heated during the extrusion process to partially polymerize the binder.

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