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PROCESS FOR PRODUCING FORMED CARBON ARTICLES

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ABSTRACT OF THE DISCLOSURE

An inexpensive tar or pitch is transformed by a known treatment into a modified pitch having a hydrogen-to-carbon atomic ratio of from 0.2 to 0.6 and a softening point of at least 170 degrees C., which modified pitch in granular form is pressure formed into a formed article, which is then treated in an inert gas, whereupon a carbon formed article having a graphitization characteristic in the range of from easy graphitizability to difficult graphitizability and a structural texture in the range of from glass-like state to porous state is obtained. Prior to carbonization, the formed article is preferably heated in an oxygen-containing atmosphere to temperature of about 200 to 330° C.

BACKGROUND OF THE INVENTION

This invention relates generally to the field of formed structures or articles of carbon and techniques in the production thereof. More particularly, the invention concerns a new process for producing carbon formed articles having graphitisation characteristics and structural textures varying over wide ranges from modified pitches (defined hereinafter) as starting materials.

Heretofore, formed or shaped articles or structures of carbon of various kinds have been produced. Generally known examples of carbon in a glass-like state are the so-called cellulose carbon manufactured by G.E.C., Ltd., of England, the so-called glass carbon manufactured by Tokai Denkyou Company, Ltd., of Japan, and carbon products developed by Shigen Gijutsu Shiken-Jo of Japan for which acetone-furfural resins are used as starting material. In addition, numerous other carbon products including porous products and filaments have been produced. While most of these various carbon products have excellent characteristics, they have had one or more drawbacks such as complicated or time-consuming processes in the products thereof or the necessity of using expensive starting materials.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a relatively simple and inexpensive process for producing carbon formed articles having graphitisation characteristics selectable from a range of from easy graphitisability to difficult graphitisability and structural textures ranging from a glass-like state to porous state and having high uniformity and homogeneity through the use of relatively inexpensive modified pitches as raw material.

According to the present invention, briefly summarised, there is provided a process as stated above which is characterised by the steps of preparing a modified pitch (defined hereinafter) of a hydrogen-to-carbon (H/C) atomic ratio of from 0.2 to 0.6 and a softening point (as defined hereinafter) of at least 170 degrees C., forming this modified pitch as a principal starting material into a formed article, and subjecting this article to carbonisation and/or graphisation treatment in an inert gas, or

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first subjecting the article to an oxidation treatment and then subjecting the resulting article to carbonisation and/or graphitisation treatment in an inert gas.

The nature, details, and utility of the invention will be more clearly apparent from the following detailed description beginning with a consideration of the general aspects of the invention and concluding with specific examples of preferred embodiment thereof.

DETAILED DESCRIPTION OF THE INVENTION

The term "modified pitch" as herein used designates collectively pitches obtained by heat treatment, by treatment with a dehydrogenation agent such as ozone, oxygen, air, halogens, and sulphur, or by solvent extraction treatment of coal tar pitches, petroleum asphalts, and other tars and pitches produced industrially as byproducts, these modified pitches being further characterised in that their H/C atomic ratios and softening temperatures are from 0.2 to 0.60 and 170 degrees C. or higher, respectively.

The term "softening temperature" or "softening point" used herein designates that temperature, as measured by means of a micromelting-point-measuring apparatus, at which a sample in the form of fine powder of the order of 0.1 mm. within a sealed tube fully assumes a spherical form. A large number of modified pitches having H/C atomic ratios of the order of from 0.60 to 0.46 exhibit softening points of the order of from 170 to 300 degrees C.

Pitches of H/C atomic ratios of from 0.46 to 0.40 do not clearly exhibit a molten state when heated in powder form but, in many cases when they are heated in the form of pressure-moulded structures in an inert gas, undergo swelling caused by the formation of a semi-molten state and the generation of gases. While pitches of H/C atomic ratios of from 0.4 to 0.2 do not exhibit a clearly observable molten state when heated in powder form or a semi-molten state when heated as a moulded structure, these pitches exhibit ample sintering property.

The relationship between the H/C atomic ratio and softening point herein described vary to some extent depending on whether or not a functional group of high thermal reactivity is contained with the modified pitch.

While there are numerous processes for preparing modified pitches, as mentioned hereinbefore, a few processes representative thereof will now be described.

(A) First, in the case where dry distillation in an inert gas is to be utilised, the dry distillation residue between 380 and 500 degrees C. can be utilised as a modified pitch of the above defined characteristics.

(B) In the case where dry distillation is to be carried out as air is blown onto the pitch, the dry distillation residue corresponding to a temperature range of the order of from 380 to 430 degrees C. can be used.

In the modified pitch obtained by this process, no increase in oxygen is observable.

(C) One example of a process other than (A) and (B), above, for readily preparing a modified pitch having the objective characteristics is a treatment with chlorine gas. For example, when coal tar pitch in powder form is heated gradually from room temperature in an atmosphere of chlorine gas, a modified pitch of a softening point of the order of from 170 to 300 degrees C. is obtained by the treatment up to a temperature of from 150 to 270 degrees C. This modified pitch contains from 5 to 15 percent of chlorine.

It is possible, of course to use a combination of processes (A) and (C), above, a combination of (B) and (C), or any of the various processes mentioned hereinbefore either singly or in various combinations.

(D) A process comprising an ozone treatment at room temperature and an immediately following air oxidation treatment up to a temperature of the order of 250 degrees C. is particularly effective in raising the softening points and reducing the H/C atomic ratios of starting material pitches and, furthermore, in introducing a functional group containing oxygen of high thermal reactivity into a modified pitch already having characteristics within the aforestated ranges. By this process, oxygen in an amount up to approximately 30 percent can be readily introduced in this manner.

In the forming operation of the invention, a single modified pitch or a mixture of different pitches is ground to a suitable combination of sizes of particles, which are then formed, for example, by pressure moulding at a pressure of from 100 to 3,000 kg./cm.^{2}. A feature of this process is that the admixture of an aggregate such as coke particles of a binder such as pitch is not necessary. The admixture of additives such as coke and graphite is possible, of course, particularly in cases when the softening point of the pitch is relatively low.

The forming operation of the invention may be accomplished by extrusion or by moulding in a die or mould cavity. In either case, good results are obtained by adding approximately 10 percent or less of alcohol or some other suitable liquid to the modified pitch.

In the case of a modified pitch of a softening temperature of 300 degrees C. or less, the pitch is formed, then dried, and thereafter gradually heated up to from 200 to 300 degrees C. in air at a temperature rise rate of from 0.1 to 3 degrees C./minute. This temperature rise rate can be increased, and the maximum treatment temperature in air can be decreased in the case of a modified pitch of higher softening temperature and, moreover, in the case of a modified pitch having a thermal reactive functional group. Furthermore, for formed articles of larger size, lower temperature rise rates are preferable.

Even in the case of modified pitch of a softening temperature of 300 degrees C. or higher or a modified pitch which does not exhibit a definite softening temperature, if the H/C atomic ratio thereof is 0.4 or higher, this heating treatment in air is preferable for producing formed articles of high strength with high yield. In the case of a modified pitch containing a large quantity of a thermal reactive functional group, baking or firing is possible merely by heating in an inert gage at an amply low rate of temperature rise, and the step of firing in air can be omitted. With a modified pitch having a softening point which cannot be definitely determined and a H/C atomic ratio of from 0.2 to 0.4, there is no particular need for firing in air.

Carbonisation and graphitisation treatment, with respect to formed articles requiring this treatment, is carried out with a temperature rise rate of approximately 5 degrees C./minute in an inert gas after heat treatment in air.

The general features of carbon materials which can be produced by the process of the present invention are as follows.

(1) An article having any porosity in the range of from 8 to 60 percent can be produced, depending on the softening point of the modified pitch and the forming pressure.

(2) In general, these materials have a high degree of hardness. For example, as expressed in terms of Shore hardness (Hs), the hardness of an article of a carbide with a porosity of approximately 30 percent or less is from 80 to 130, and that of an article which has undergone graphitisation treatment (at 2,800 degrees C.) and has a porosity of approximately 30 percent or less is from 50 to 90.

(3) The bulk specific gravities of these articles are from 0.7 to 1.8.

(4) The mechanical strengths of these articles are affected by the values of their porosities and bulk specific gravities. In general, the strengths are high in carbonised articles and decrease as the articles are graphitised. In terms of maximum bending strength, articles of porosities of from 8 to 15 exhibit values of from 800 to 1,100 kg./cm.^{2}, articles of porosities of from 15 to 30 percent exhibit values of from 400 to 800 kg./cm.^{2}, and articles of porosities above 30 percent exhibit values of from 100 to 400 kg./cm.^{2}.

In the case of porosities of from 8 to 15 percent, articles fired at 600 degrees C. exhibit values of bending strength of from 100 to 200 kg./cm.^{2} and values of shore hardness (Hs) of from 100 to 130.

(5) Of the measured physical properties of these formed articles, the most unexpected result obtained was that of their graphitisation characteristics. For example, a formed article resulting from a modified pitch prepared by the aforementioned process (A) through the use of a temperature above 450 degrees followed by process (D) as the starting material exhibits a behavior with respect to X-rays typically characteristic of easily graphitised carbon materials in spite of an oxygen content of from 15 to 25 percent in the starting material modified pitch. Conversely, a formed article resulting from a starting material modified pitch prepared by process (B) through the use of a temperature above 380 degrees C. exhibits a behavior with respect to X-rays characteristic of carbon materials which are very difficult to graphitise in spite of the fact that no oxygen can be analytically observed in the starting material.

In order to clarify further the above stated features, we have made a study of the relationship between the process of modification of the starting material pitches and the graphitisation characteristics exhibited by the carbon materials thereby produced. As a result, we have found that:

(1) modified pitches prepared by the aforedescribed process (A) and modified pitches prepared by process (A) followed a process for introducing a thermal reactive functional group or another process, that is, processes (C) and (D) or some other process as stated above, result in easily graphitised carbon materials and carbon materials having slightly deficient graphitisation characteristics, and

(2) modified pitches prepared by process (B), process (C), process (D), or another treatment wherein a dehydrogenation agent is added and modified pitches prepared by combinations of these processes result in carbon materials ranging from those difficult to graphitise to those of intermediate graphitisation characteristics.

That is, as an effective result, we have found that it is possible to produce, readily, formed carbon articles ranging from those easily graphitised to those difficult to graphitise and having porosities ranging from 8 to 60 percent by using, as principal forming materials, modified pitches prepared by the various above described processes for preparing modified pitches having characteristics falling within the aforedefined ranges of H/C atomic ratio of from 0.2 to 0.60 and of softening point of 170 degrees C. or above.

In the carbonisation process step in the practice of the invention, the coefficient of linear contraction or shrinkage is from 5 to 20 percent, being from 10 to 15 percent in most cases.

Because of the wide ranges of physical properties of the carbon formed articles which can be produced in the above described manner, the present invention makes possible the production of a large variety of materials and products of formed carbon for a wide range of users.

For example, formed articles of low porosity produced by the process of the invention can be used as various electrodes, electrolytic plates, structural materials, refractory materials, and aggregates and obviate the necessity of processes involving repetitions of firing, impregnation, and refiring. Formed articles of high porosity can be used for products such as electrodes for fuel cells, filter elements, and heat insulation materials.

An important feature of the present invention is that it affords a process whereby it has become possible to produce readily carbon materials in a glass-like state of easily graphitisable or difficult to graphitise characteristic and porous carbon materials of easily graphitisable or difficult to graphitise characteristic, this is, carbon materials which, in structure, range from those approaching glass to those of high porosity and, at the same time, have any basic structure ranging from easily graphitisable to difficult to graphitise characteristic. This feature further widens the uses for glass-like carbon materials and porous carbon materials beyond the scope as conceivable heretofore.

A further advantageous feature of the invention is that use is made in the process thereof of pitches which are most economical from the industrial viewpoint as starting materials.

In order to indicate still more fully the nature and utility of the present invention, the following examples of actual practice representing preferred embodiments of the invention are set forth, it being understood that these examples are presented as illustrative only and that they are not intended to limit the scope of the invention.

PREFERRED EMBODIMENTS OF THE INVENTION

Example 1

Coal pitch of a softening point of 85 degrees C. produced by the Kawasaki Seitetsu (Kawasaki Iron and Steel) of Japan was dry distilled at 380 degrees C. for 60 minutes. Then 20 grams (g.) of residual substances of extraction remaining when the n-hexane-soluble component was removed from the resulting residue of dry distillation were dissolved in chloroform to form a solution, which was oxidised by causing air which contained ozone to bubble therethrough at room temperature. After removal of the chloroform, the remaining substance was ground. The H/C atomic ratio of this substance was 0.43.

This pitch-like substance was formed under a pressure of 400 kg./cm.^{2} into a disk of 20-mm. diameter and 10-mm. thickness, which was heated in air at a temperature rise rate of 2 degrees C./minute to 320 degrees C.

Thereafter, the atmosphere around the formed article was changed over to nitrogen gas, and the formed article was fired by heating at a temperature rise rate of 5 degrees C./minute to 1,000 degrees C.

The fired article thus obtained was very uniform, and when a surface thereof was polished, a mirror surface was obtained. The properties of this article were as follows:

Shore hardness (Hs)—100–115
Porosity—17%
Shrinkage—15%
Apparent specific gravity—1.4
Carbonisation yield—87%
Bending strength—600 kg./cm.^{2}

This article was graphitised by heating up to 2,800 degrees C. in an inert gas. The resulting article was found to have the following properties.

Shore hardness (Hs)—68
Porosity—16%
Bending strength—300 kg./cm.^{2}
Resistivity—7.0×10^{-4} ohm. cm.

The variations of lattice spacing resulting from treatment temperatures of 1,600 degrees C. and higher were those typical of easily graphitisable carbon materials and was 3.365 angstroms for an article treated at 2,800 degrees C.

Example 2

A polyvinyl chloride powder was fired at a temperature of from 400 to 430 degrees C. in nitrogen gas, whereupon a pitch-like substance of a softening point of from 195 to 202 degrees C. was obtained. This substance, used as a starting material in powder form, was spread as much as possible and, in this state, was heated up to 200 degrees C. in air at a temperature rise rate of from 2 to 3 degrees

C./minute thereby to cause oxidation thereof, whereupon a pitch of H/C atomic ratio of 0.48 was obtained.

This pitch was ground and then formed under a forming pressure of 450 kg./cm.^{2} into a formed disk of 20-mm. diameter and 4-mm. thickness, which disk was thereafter subjected to the same process steps prior to the graphitisation step as set forth in the preceding Example 1. The formed article thus obtained was uniform and could be polished to a mirror surface. Measured properties of this article were as follows:

Shore hardness (Hs)—108–120
Porosity—16%
Shrinkage—20%
Apparent specific gravity—1.42
Bending strength—800 kg./cm.^{2}

Example 3

A coal pitch of a softening point of 85 degrees C., produced by Kawasaki Seitetsu (Kawasaki Iron and Steel) of Japan was dry distilled at 380 degrees C. The resulting residue in the powder form as obtained was subjected to the action of ozone at room temperature and then oxidised by heating in air up to 200 degrees C. to prepare a first pitch material.

The component insoluble in chloroform of the Kawasaki Seitetsu coal pitch was air oxidised by heating up to 200 degrees C., in the powder form as obtained, to prepare a second material.

The resulting first and second materials were mixed in the weight ratio of 1:3, and the mixture was thoroughly ground, whereupon a pitch mixture having an average H/C atomic ratio of 0.50 was obtained. This mixture was formed under a pressure of 400 kg./cm.^{2} into a formed article, which was thereafter subjected to the same process steps prior to the graphitisation step as set forth in Example 1. The properties of the formed articles thus processed were as follows:

Shore hardness (Hs)—115–125
Porosity—13%
Shrinkage—10%
Apparent specific gravity—1.50
Carbonisation yield—89%
Bending strength—950 kg./cm.

Example 4

Coal pitch of the kind specified in Examples 1 and 3 (softening point 85 degrees C.) was dry distilled at 380 degrees C. for 60 minutes, and the residue, with 5 percent of tetramethylthiuram disulphide added thereto, was heat treated at 300 degrees C. for one hour and then ground, whereupon a pitch of H/C atomic ratio of 0.45 was obtained.

This pitch was formed under a pressure of 150 kg./cm.^{2} into a disk of 20-mm. diameter and 10-mm. thickness, which was thereafter subjected to the same process steps prior to the graphitisation step as set forth in Example 1. The formed disk thus produced was uniform and could be polished to a mirror surface. The properties of this disk were as follows:

Shore hardness (Hs)—110–125
Porosity—16%
Shrinkage—20%
Apparent specific gravity—1.45
Bending strength—600 kg./cm.^{2}

Example 5

Kawasaki Seitetsu coal pitch (softening point 85 degrees C.) was dry distilled at 380 degrees C. for 30 minutes, and the residue was ground and placed in contact with chlorine gas at room temperature for 30 minutes. The resulting pitch had a H/C atomic ratio of 0.41.

This pitch was formed under a pressure of 300 kg./cm.^{2} in the same manner as set forth in Example 1 and thereafter was subjected to the same process steps prior to the graphitisation step as set forth in Example 1.

The formed article thus produced was uniform and exhibited a mirror surface when polished. The properties of this article were as follows:

Shore hardness (Hs)—105–120
Porosity—20%
Shrinkage—20%
Apparent specific gravity—1.40
Bending strength—350 kg./cm.^{2}

Example 6

A pitch produced as a byproduct of cracking of petroleum naphtha and having a softening point of from 195 to 205 degrees C. and a H/C atomic ratio of 0.54 was used as a starting material pitch. This pitch was ground well and then formed under a pressure of 300 kg./cm.^{2} into a disk of 20-mm. diameter and 5-mm. thickness.

This disk was then heated in air up to 330 degrees C. at a temperature rise rate of from 1 to 2 degrees C./minute and then fired by heating in an inert gas up to 1,000 degrees C. at a temperature rise rate of 5 degrees C./minute.

The resulting formed article exhibited good uniformity and a mirror surface when polished and had the following properties.

Shore hardness (Hs)—98–112
Porosity—15%
Shrinkage—75%
Apparent specific gravity—1.46
Bending strength—600 kg./cm.^{2}

To this pitch material, 35 percent of graphite powder was admixed, and the mixture was formed under a pressure of 500 kg./cm.^{2} into a formed article, which was then heated in air up to 300 degrees C. at a temperature rise rate of 0.5 degrees C./minute and thereafter graphitised by heating in nitrogen gas up to 2,800 degrees C. The formed article thus produced had an easily graphitisable characteristic as determined by X-rays and had the following properties.

Shore hardness (Hs)—50
Porosity—16%
Bending strength—290 kg./cm.^{2}
Specific resistivity—6×10^{-4} ohm. cm.

Example 7

Kawasaki Seitetsu coal pitch (softening point 85 degrees C.) was ground into a fine powder form and heated in this form and in contact with chlorine gas up to 250 degrees C.

The sample thus obtained had a H/C atomic ratio of 0.38 and had no softening point up to a temperature of 360 degrees C.

This sample was ground into fine powder, which was then formed under a pressure of 400 kg./cm.^{2} into the same formed article as described in Example 4.

This formed article was heated in nitrogen gas up to 500 degrees C. at a temperature rise rate of from 2 to 3 degrees C./minute and then fired by heating to a higher temperature at a temperature rise rate of 5 degrees C./minute.

The resulting formed article had the same outer appearance as the corresponding articles in the foregoing examples and had the following properties.

Shore hardness (Hs)—75–85
Porosity—20%
Shrinkage—18%
Apparent specific gravity—1.35
Carbonisation yield—70%
Bending strength—400 kg./cm.^{2}

Example 8

The component insoluble in chloroform of Kawasaki Seitetsu coal pitch was used as a starting material.

This material in powder form was spread for good contact with air and oxidised by heat up to 220 degrees C., whereupon a pitch of a H/C atomic ratio of 0.50 was obtained.

This pitch was ground into a fine powder, which was then formed under a pressure of 450 kg./cm.^{2} into a disk of 20-mm. diameter and 7-mm. thickness, which was fired under the same conditions as set forth in Example 5. The resulting formed article had an outer appearance similar to those of the corresponding articles of the foregoing examples and had the following properties.

Shore hardness (Hs)—115–128
Porosity—13%
Shrinkage—9%
Apparent specific gravity—1.50
Carbonisation yield—88%
Bending strength—850 kg./cm.^{2}

Example 9

500 grams of coal tar pitch (softening point 85 degrees C.) was dry distilled at 400 degrees C. for 90 minutes as air was blown thereonto, whereupon a modified pitch of a softening point of from 238 to 245 degrees C. and a H/C atomic ratio of 0.46 was obtained. This pitch was ground and then formed under a pressure of 400 kg./cm.^{2} into a formed article, which was heated in air up to 300 degrees C. at a rate of 0.3 degree C./minute and then heated in nitrogen gas up to 2,800 degrees C. at a rate of 5 degrees C./minute. As a result a disk-shaped formed article of 40-mm. diameter and 10-mm. thickness having a Shore hardness of 95, porosity of 12 percent, and bending strength of 600 kg./cm.^{2} was obtained.

The lattice spacing as determined by the X-ray 002 diffraction line was 3.39 angstroms, and the specific resistivity was 3×10^{-3} ohm. cm. The product was a carbon material of difficult graphitisability.

Example 10

Petroleum asphalt was dry distilled at 390 degrees C. as air was blown thereonto. The resulting material was ground and treated in a chlorine gas atmosphere at temperatures up to 250 degrees C., whereupon a monified pitch of a H/C atomic ratio of 0.42 and a softening point which could not be definitely determined was obtained.

This pitch was formed under a pressure of 300 kg./cm.^{2} into a formed article, which was heated in air up to 300 degrees C. at a rate of 1 degree C./minute and then heated in nitrogen gas up to 2,800 degrees C. The carbon material thus produced had a shore hardness of 68, porosity of 48 percent, bending strength of 78 kg./cm.^{2}, and specific resistivity of 13×10^{-3} ohm. cm. and was found to have a difficult-to-graphitise characteristic as determined by X-rays.

It should be understood, of course, that the foregoing disclosure relates to only examples of preferred embodiment of the invention and that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purposes of the disclosure, which do not constitute departures from the spirit and scope of the invention as set forth in the appended claims.

What I claim is:

1. A process for producing carbon shaped articles from a modified pitch having an H/C atomic ratio of 0.2 to 0.6 and a softening point of at least 170° C. selected from the group consisting of (1) tars and pitches treated with chlorine, (2) tars and pitches treated with ozone immediately followed by air oxidation, (3) tars and pitches subjected to dry distillation in air at 380° C. to 430° C., and (4) tars and pitches subjected to dry

distillation in an inert gas at 380° C. to 500° C., which comprises:

(a) pulverising said modified pitch,
(b) pressure-forming the pulverised pitch into an article having a desired shape,
(c) gradually heating the shaped article in an oxygen-containing atmosphere to a temperature between about 200° C. and about 330° C., and
(d) carbonising the article of step (c).

2. The process of claim 1 in which step (c) is carried out by heating the shaped article to a temperature between 200° C. to 300° C.

3. The process of claim 1 in which the carbonised article of step (d) is graphitised.

4. The process according to claim 1, in which step (c) is carried out by heating the shaped article to a temperature between from 200° C. to 300° C. at a rate of from 0.1 to 3.0° C./minute.

5. The process according to claim 1, in which alcohol is added to the pulverised pitch in step (b) in an amount of less than 10% to the total quantity thereof.

References Cited

UNITED STATES PATENTS

2,560,642	7/1951	Greaves et al.	264—29
2,768,119	10/1956	Nash	208—45
3,392,216	8/1968	Otani	23—209.2X

FOREIGN PATENTS

858,132	1/1961	Great Britain	208—44

OTHER REFERENCES

Otani: "Carbon," vol. 3, 1965, pp. 31–38.
Otani et al.: "Carbon," vol. 4, 1966, pp. 425–432.

EDWARD J. MEROS, Primary Examiner

U.S. Cl. X.R.

264—29