March 1, 1966 R. L. BICKERDIKE ETAL 3,238,054

METHOD FOR PRODUCING A COMPOSITE CARBON ARTICLE AND ARTICLES PRODUCED THEREBY

Filed June 22, 1960

2 Sheets-Sheet 1

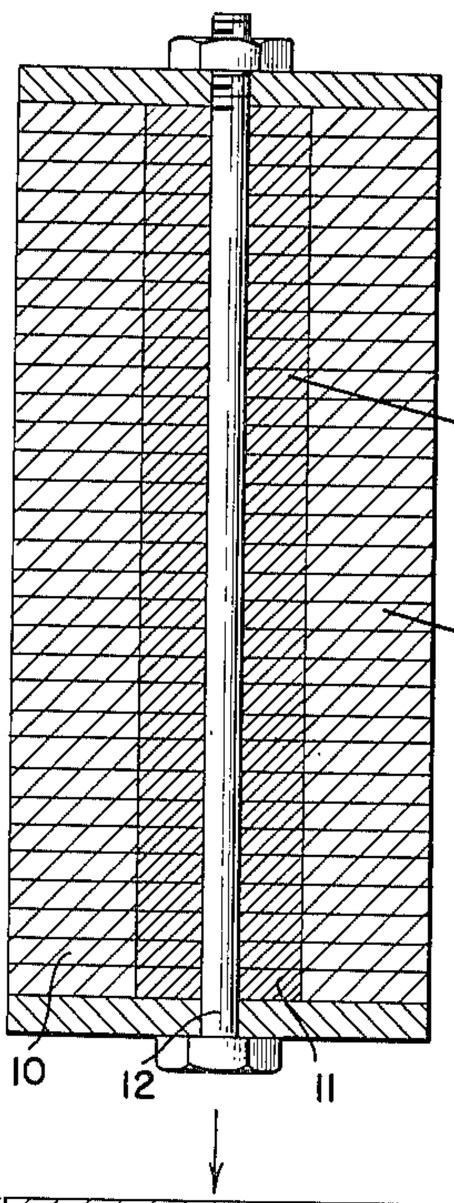

FIG. 1

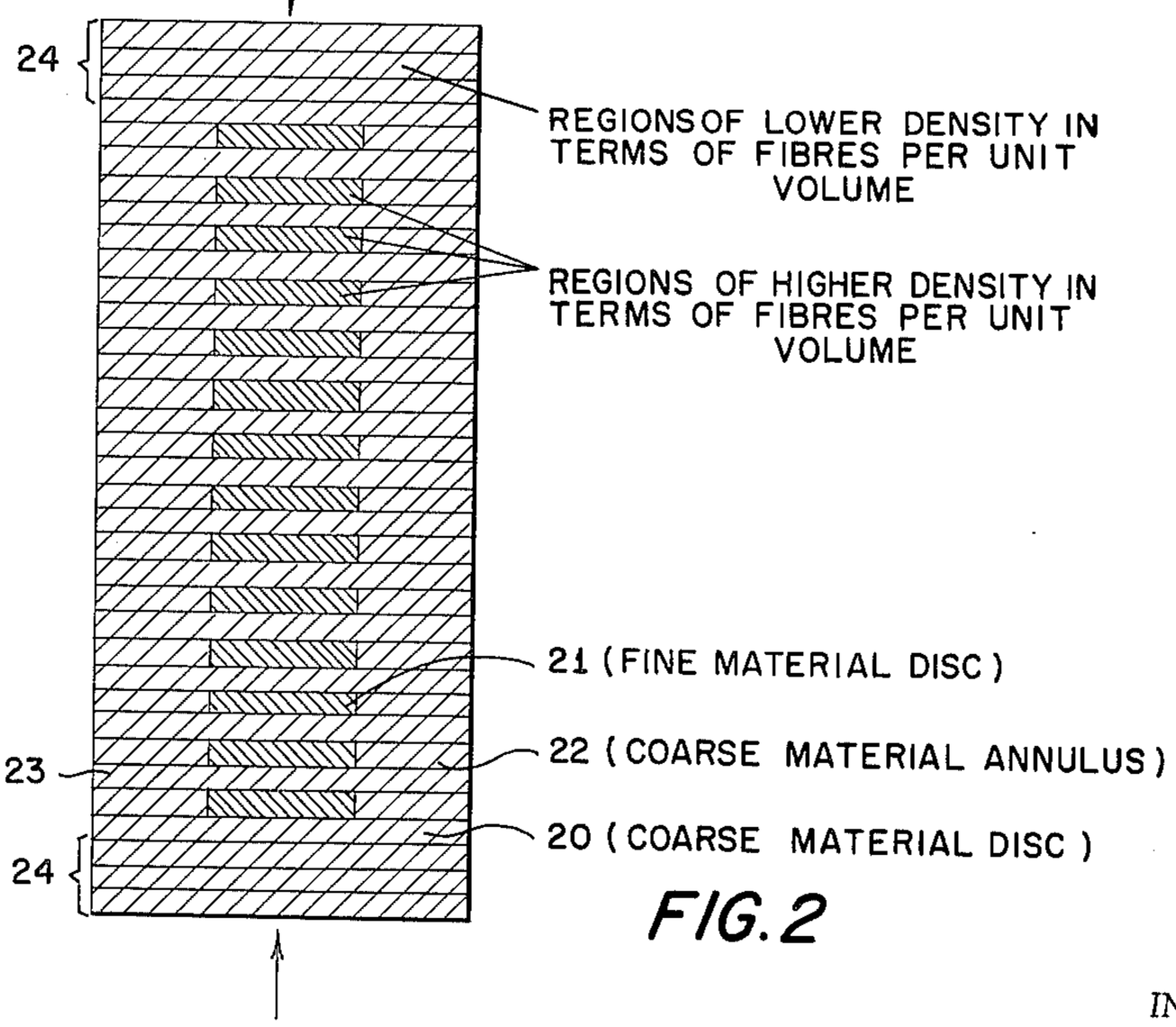

FIG. 2

INVENTORS

ROBERT L. BICKERDIKE

ANTHONY R. G. BROWN

BY Larson and Taylor

ATTORNEYS

March 1, 1966 R. L. BICKERDIKE ETAL 3,238,054

METHOD FOR PRODUCING A COMPOSITE CARBON ARTICLE AND ARTICLES PRODUCED THEREBY

Filed June 22, 1960 2 Sheets-Sheet 2

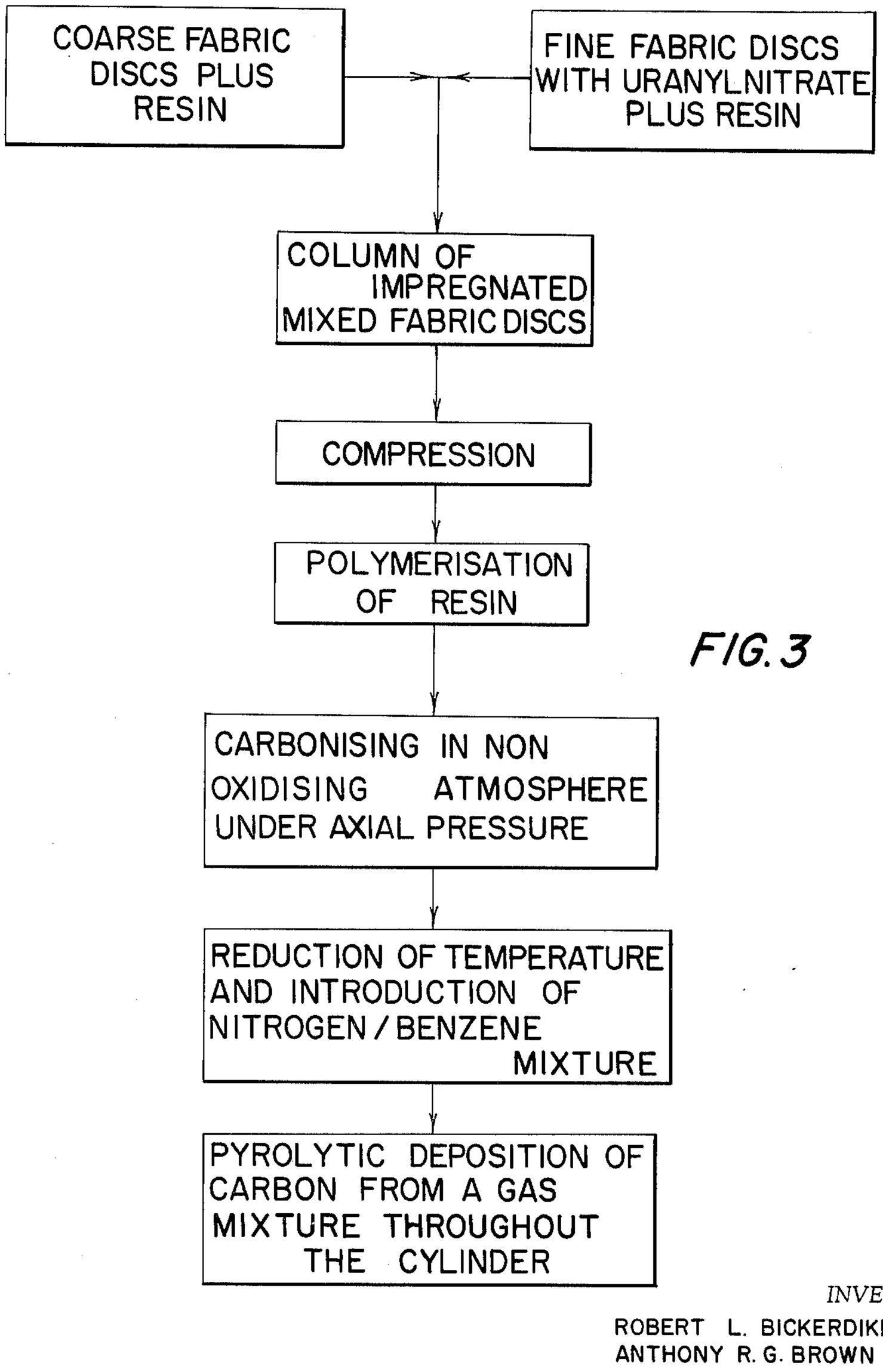

FIG. 3

INVENTORS
ROBERT L. BICKERDIKE
ANTHONY R. G. BROWN

BY Larson and Taylor

ATTORNEYS

United States Patent Office

3,238,054

Patented Mar. 1, 1966

3,238,054

METHOD FOR PRODUCING A COMPOSITE CARBON ARTICLE AND ARTICLES PRODUCED THEREBY

Robert Lewis Bickerdike and Anthony Reginald George Brown, Farnham, England, assignors to United Kingdom Atomic Energy Authority, London, England

Filed June 22, 1960, Ser. No. 37,831
Claims priority, application Great Britain, July 2, 1959, 22,748/59
7 Claims. (Cl. 117—46)

This invention relates to carbon and graphite materials. The term carbon will hereafter be used to describe both.

Some of the important characteristics of carbon are that its strength is considerably greater in the basal plane of the crystals than in a transverse direction and its physical properties vary considerably with the direction of the crystal. It is therefore necessary to consider the orientation of the structure of a carbon article with respect to its proposed mode of use so as to try and make best use of these directional properties and the present invention is concerned with a new approach to the problem of how to make best use of these properties.

Accordingly, the invention consists in massive fibrous carbon material comprising carbon fibres which are the thermal conversion products of natural or synthetic organic fibres.

The material may include reactive material dispersed throughout as the precipitate from a solution, or deposit from a vapour, or as particles, and the individual fibres may have on or around them a deposited skin or external layer of carbon which may envelope the reactive material and the fibres.

This skin may be derived from a liquid impregnant such as a synthetic resin which is converted to carbon or be laid down as carbon by the pyrolytic deposition of carbon from the vapour of a carbon compound. The skin may be impermeable.

In some cases the material is impermeable as a whole or substantially so, the impermeability being brought about by the continuance or a further application of the treatment employed for depositing the skin, this being continued or repeated to fill the spaces between the fibres until a satisfactory degree of impermeability is achieved.

The material of the invention may be in the form of shaped articles which may have regions of greater density than the remainder, these regions being impermeable if desired to constitute a barrier to the passage of reaction products. For example a tubular article may comprise an annular impermeable region which prevents the passage of reaction products through the wall of the tube.

The process of making fibrous carbon material according to the invention may include assembling a structure of the organic or synthetic fibres, heating them in non-oxidising conditions to carbonising temperature whilst held in the desired form and, if desired, depositing external carbon layers on or around the individual carbon fibres of the mass by, for example, a pyrolytic deposition process in which the mass is heated to a temperature above 500° C. in an atmosphere of, or in a stream of gas containing, a gaseous carbon compound. In such a process the total pressure may be about one atmosphere, but higher pressures may be beneficial for higher deposition rates. The partial pressure of the carbon compound should be adjusted to avoid the formation of soot in the furnace under the combination of conditions obtaining. Alternatively the mass of original organic fibres or the carbon fibres produced from them may be impregnated by a pressure or evacuation technique with a synthetic carbon yielding resin, preferably a furane derivative such as furfuryl alcohol, which is subsequently polymerised and carbonised. The process may include a final graphitising step at a temperature above 2000° C. if desired.

Pyrolytic deposition may be continued until a high density and strength are achieved, or the structure may be left with considerable residual porosity which has a beneficial effect on the physical properties of the product for some applications in that an unusually large deformation will occur before complete fracture thereof when put under load. Pyrolytic deposition may be continued for a sufficiently long time to render the body substantially impermeable, at least at the outer surface. The pyrolysis may be performed on a free standing article or whilst it is held in a mould or maintained under pressure.

The original fibres may be in the form of a random loose mass such as cotton wool, or they may be spun or woven or subjected to some other treatment to give them a required orientation or type of packing. If a loose fibre such as cotton wool is used, it is preferably compressed before carbonising, and it is desirable to restrict its expansion during carbonising by, for example, holding it in a clamp or press to prevent the opening up of laminar flaws.

Part way through the pyrolytic deposition step the material or article may be graphitised by heating to a high temperature for example 2000 to 2800° C. in a non-oxidising atmosphere. Further pyrolytic deposition may thereafter be performed and this produces a body with a duplex structure consisting partly of soft graphitic material and partly of harder pyrolytic deposit. Alternatively the graphitising treatment may be done when deposition has been completed.

After pyrolytic deposition to the required extent, the material or article, if still porous, may be treated with a furane derivative such as furfuryl alcohol as described above, the furfuryl alcohol being polymerised in the pores to a solid resin and this solid resin converted to carbon or graphite in the pores by heating it to a temperature not less than 950° C.

The step of depositing reactive material through the basic fibrous carbon material is advantageously performed before the step of depositing the carbon skin on or around the fibres so that the skin envelopes the fibres or conjointly envelopes and joins together contiguous fibres and their attached reactive material.

The process of forming a shaped article of the basic material may include the step of compressing the mass of organic fibres in a die before carbonising, at least during the period in which the mass is raised to a temperature at which decomposition of the fibres occurs in the first stage of their conversion to carbon.

Further, heating may be continued to the carbonising temperature whilst maintaining constant, or varying, or removing the pressure and/or the other conditions of the pyrolytic deposition process in a manner as described. Advantageously pyrolysis is performed after reducing the temperature slightly below the temperature employed during carbonising. In these conditions, with certain moulded shapes, if moulding pressure is maintained to above an optimum temperature in the carbonising cycle the spontaneous shrinkage of the fibre mass away from the walls of the mould may cause buckling or distortion of the final product.

In the case in which the process of making the material or article includes impregnating a mass of the organic natural synthetic fibres with a thermosetting adhesive resin, the process may comprise heating the mass to bring about cohesion of the fibres and set the adhesive and compressing the mass in a die during at least part of the stage of polymerising or hardening the resin to make the article rigid, whereafter further pressure may be applied during

carbonising. The adhesive resin is desirably one which gives a high yield of carbon when decomposed by heat. Furfuryl alcohol and phenol formaldehyde resins are particularly suitable.

In the production of tubular articles of the fibrous material of the invention which in the final form comprise a substantially impermeable region such as an annular impermeable region, the process may comprise arranging the original fibrous material to form a tube with at least a cylindrical intermediate zone having a higher fibre density than the remainder, carbonising the fibres and depositing layers of carbon on the carbonised fibres by a pyrolytic deposition process or by impregnation with a liquid synthetic resin as described.

The tubes may be conveniently formed by hydrostatically pressing a fibre mass in a rubber bag. To obtain the required high density of carbonised material in the middle of the wall, a loose layer of fibrous material is placed around the outside of a thin walled rubber tube. Outside this is placed a tube of closely woven material (either a natural or artificial woven yarn). The woven tube is moistened with a furfuryl alcohol-acid mixture, and outside it a further layer of loose fibrous material is placed, followed by an outer rubber tube. The two rubber tubes are then connected to a hydrostatic pressure source and pressure applied.

After releasing the pressure and extracting the pressed tube, it is fitted into a clamping device to prevent radial expansion of the outer surface or contraction of the inner, and carbonised. The carbonised tube is finally given a pyrolytic deposition treatment.

Machining to final dimensions is accomplished part way through the pyrolytic treatment, before the material has become too hard to turn satisfactorily on a lathe.

Articles and a process flow sheet according to the invention are illustrated in the accompanying drawings in which:

FIGURE 1 is a side view in cross section of a cylindrical tubular article,

FIGURE 2 is a side view in cross section of a cylindrical solid article, and

FIGURE 3 is a flow sheet of the process leading to the article of FIGURE 2 as further illustrated by Example III and described hereafter.

Referring to FIGURE 1, rings **10** of material woven to have a very dense fibre arrangement in a circular central zone **11** are arranged on a former **12** after moistening with adhesive, such as furfuryl alcohol or a phenol formaldehyde resin, and subjected to slight axial compression whilst heated to polymerise the resin, and if necessary, further pressure during the whole or part of a step subsequent heating to carbonise the fibres. The high density zone gives a high density cylinder within the tube as a whole. Thereafter the fibrous carbon tube may be treated by pyrolysis and/or given an impregnation and carbonising treatment in the manner described, by which treatment the dense inner cylinder rapidly becomes a substantially impermeable cylindrical barrier.

Ordinary commercial cotton wool gives good results when used as the surface layers of the tubes.

Several examples of the invention will now be described:

Example I

About 25 grams of compressed cotton wool was carbonised in lamp black in a silica vessel with a graphite sealing member by heating slowly up to 1000° C. in a Nichrome furnace and then cooling over a period of three days, yielding about 7 grams of carbon fibres. The carbon fibre mass had an apparent density of 0.35 gr./cc. The mass was heated in a stream of nitrogen saturated (at room temperature) with benzene at 890° C. for 24 hours, after which the weight was 20 grams and the density slightly greater than 1 gram/cc. On heating in a nitrogen and benzene mixture as before for a further 19 hours at 850° C. the density increased to 1.4 g./cc. A sample of the product had a breaking stress in compression of 4.3 ton/sq. in.

Example II

Cotton wall was compressed in a hydraulic press at a pressure of one ton per sq. in. into a slab approximately 3.75 x 1.5 x 1.5 inches. This was held in a graphite clamp then packed in lamp black in a silica tube with graphite end plugs and slowly heated to 1000° C. for 48 hours, and then cooled. The carbonised slab was given a pyrolytic carbon deposition treatment by heating it in a silica tube furnace in a stream of nitrogen saturated with benzene as follows:

Period, hours	Temperature, ° C.	Benzene partial pressure, cm. Hg
190	820–825	2.7
40	825–835	8.2

The surfaces of the slab were then filed to remove the skin and pyrolysis repeated for 21.5 hours at 845 to 850° C. at a benzene partial pressure of 8.2 cm. Hg and total gas pressure of 1 atmosphere.

The slab was then cut into three specimens and each was treated for 51.5 hours at 860 to 890° C. at a benzene partial pressure of 8.2 cm. Hg, total gas pressure 1 at mosphere.

Each specimen was filed to remove the surface skin and further gas treated for 66 hours at 870° C.

The density of the slab after carbonising and before pyrolysis was 0.25 gm./cc. and the final density of the specimens was 1.57 gm./cc. When tested by bending, Young's modulus was 2.07×10^6 p.s.i. and breaking stress in bending 11.6 tons/in.^{2}, compared with about 2 tons/in.^{2} for conventional carbon material.

Example III

It was desired to produce a solid cylinder of carbon containing a dispersion of uranium in the central region completely enclosed in a pyrolytic-carbon-filled outer case, the whole forming one integral mass.

Referring to FIGURE 2, on to a disc **20** of woven cellulose material was laid a small diameter second disc **21** of finer spun and woven material containing a dispersion of uranium laid down from a solution of uranyl nitrate and precipitated with ammonia. Round the edge of the smaller disc was laid a ring **22** of the coarser woven material of the same outer diameter as the lower disc. Another disc **23** of the coarser material was laid on top of the same diameter as the first disc, and the laying up procedure was repeated. In this way a column of material was built up, and by placing a number of discs **24** of the uranium-free material at the top and bottom of the column, the dispersed uranium was confined to the inner region of the column, leaving a uranium-free outer zone. All the discs were previously moistened slightly with acidified furfuryl alcohol and the column was held under slight axial compression while the alcohol was polymerised to produce a coherent column ready for carbonising. The column was held under slight axial pressure during carbonising and during the early part of a pyrolytic deposition process. Carbonising was carried out by heating in a non-oxidising atmosphere to 1000° C., and after adjustment of the temperature to 860° C. a stream of nitrogen containing benzene (total pressure 1 atmos., benzene partial pressure 8 cm. Hg) was led through the furnace to produce a deposit of pyrolytic carbon in the fibre mass. The outer uranium-free region, being of coarser fibre, was more easily penetrated by the diffusing gas than the inner region, with the result that the uranium-containing zone was sealed by pyrolysis before the outer zone became impermeable. Pyrolysis was continued until the surface was completely sealed.

Using woven cloth a uniform controlled pore size is achieved, and no abnormally large pores occur, so that it is relatively easy to treat a large piece and make it impermeable.

Example IV

About 20 grams of cotton linters were immersed at room temperature in a 10% solution of uranyl acetate in water. The surplus liquid was removed by light pressing and draining and the cotton was then put into 10% ammonia solution. After decanting and washing, the material was dried at 120° C. in an oven. Three 3 gram pellets were made by taking 2.25 grams of untreated linters and 0.75 gram of the material treated as described and compressing in a ¾′ dia. metal mould, the cotton being placed in the mould in such a way that the treated material was completely surrounded by the untreated material.

The pellets were placed in a graphite clamp to prevent exfoliation, packed in lamp black in a silica tube with a graphite closure, and carbonised by slow heating to 1000° C. over a period of 2 days. After cooling down and removing the lamp black, the specimens were given a carbon deposition treatment at 860° C. in a stream of nitrogen and benzene vapour in a silica tube furnace, part way through which they were removed from the furnace and ground flat. The total gas pressure was 1 atmosphere and the benzene partial pressure was 8 cms. Hg. Two of the specimens were given a pyrolytic carbon deposition treatment, one for 7½ days and one for 11½ days in the nitrogen-benzene atmosphere. The initial density (i.e., after carbonising), was about 0.5 gram/cc. and the final density (after carbon deposition) about 1.46 grams/cc. The specimens were found to have good fission product (derived from the U–235 portion of the impregnant) retention characteristics after irradiation in an atomic pile.

Example V

In an alternative to Example IV, 100 grams cotton linters was wetted with 280 cc. of a solution of uranyl nitrate in water (total uranyl nitrate content 5 grams) by pouring the liquid on to the cotton and squeezing and releasing the latter alternately until it was uniformly wetted. The damp cotton was then exposed to ammonia vapour by passing over it a stream of nitrogen containing ammonia. After several hours the ammonia content of the gas entering the vessel was reduced to zero, and the temperature was raised to 120° C. to dry the cotton, which was then compressed into pellet form both with and without extra undyed linters, for processing as in Example IV.

Example VI

A mass of cellulose fibre (cotton wool) was compressed under light pressure in a die whilst the temperature was held at approximately 450° C. At this temperature the fibers rapidly decomposed and an increase in apparent density of the mass occurred. When evolution of the volatiles at 450° C. had ceased the temperature was raised to 1,000° C. to complete carbonising and the pressure maintained as carbonisation proceeded. The next step was to reduce the temperature to 900° C., still maintaining the pressure and pass through the die a stream of nitrogen-benzene mixture (total pressure 1 atmos., benzene partial pressure 8 cms. Hg) whereby carbon was pyrolytically deposited on the carbon fibres of the mass. The deposited carbon thus bonded the fibres together into a coherent porous mass. Pyrolysis was stopped when there was a danger of bonding the mass to the die and the pressure and temperature reduced to normal. The fibrous article produced was structurally firm and strong enough to resist delamination.

Example VII

A pack of cloth discs were placed in a silica tube and slowly heated to 400° C. in a stream of nitrogen at 1

atmosphere under a constant mechanical pressure of 10 lbs./sq. inch. The temperature and pressure were maintained for 4½ hours until most of the volatiles had been driven off. After cooling from 400° C., the compact which was fairly well bonded was removed. At this stage the density was 0.29 gram/cc. It was then heated to 1000° C. in a stream of nitrogen to complete carbonisation, and on cooling to room temperature the density was found to be 0.31 gram/cc.

The specimen was then placed in a silica tube and heated to 860° C., and nitrogen saturated (at room temperature) with benzene was passed over the specimen for 90 hours. The total and partial gas pressures were as before. After cooling, the specimen was removed from the furnace and machined to give a regular shaped block of 3.7 cms. diameter x 2.1 cms. thick with a density of 1.0 grams/cc.

After a further 200 hours treatment at 860° C. in the gas deposition furnace the density of the block was 1.56 grams/cc.

Example VIII

20 layers of cotton wool 2½″ x 9″ x ¼″ were placed one on top of another and pressed under 50 tons. The compressed slab was held in a graphite clamp which was then packed in lampblack and heated up to 1000° C. over a period of 24 hours in order to carbonise the fibres. The slab was removed from the lampblack and then treated for 65 hours at about 860° C. in a stream of nitrogen saturated (at roof temperature) with benzene. After cooling, the slab was cut into bars measuring 18.5 cms. x 1.2 cms. x 1.2 cms., the density being 0.84 gram/cc. The bars were then given a further 196 hours treatment at 860° C. in the gas deposition furnace before grinding into test bars measuring 5/16″ square cross section and 3 inches long. After a further 138 hours of similar treatment in the gas deposition furnace the density was 1.66 grams/cc.

Young's modulus determined by cantilever method gave an average value of 3.41×10^6 p.s.i. An average value of the bend strength measured by four point loading was 6.7 tons/sq. inch. The compressive strength with the plane of compression perpendicular to the fibre length gave an average value of 13.9 tons/sq. inch and when parallel to the fibre length the average value was 19.5 tons/sq. inch.

After the final treatment in the gas deposition furnace some of the bars were graphitised by heating to 2800° C. for ½ hour in a graphite tube furnace and mechanical tests then carried out on these bars in the graphitised condition. The density of these bars was now 1.65 grams/cc. An average value of the Young's modulus was 1.96×10^6 p.s.i., and that of the bend strength 4.7 tons/sq. inch. An average value of the compressive strength when the plane of compression was perpendicular to the fibre length was 6.1 tons/sq. inch, and when the plane of compression was parallel to the fibre length the average value was 8.1 tons/sq. inch.

Example IX

A tube having high thermal conductivity across the wall thickness was made by stacking rings of woven cellulose yarn on a spindle to form a tube, each piece being lightly moistened with acidified furfuryl alcohol. The stack was then subjected to slight axial pressure and heated gently to polymerise the alcohol. When polymerisation was complete the stack was carbonised by heating to 1000° C. in non-oxidising conditions and then treated by a pyrolytic deposition process by heating it in a stream of nitrogen and benzene (total pressure 1 atmos., benzene partial pressure 8 cm. Hg) at a temperature of 890° C. After 48 hours, the stack was then heated to 2000° C. in non-oxidising conditions to convert the carbon into graphite.

Example X

In an alternative to Example IX, finely powdered phenol-formaldehyde resin was mixed with the original fibrous material and compressed whilst heated to 180° C. to polymerise the resin. Blocks of the resulting resin-impregnated fibrous solid were then carbonised and treated by pyrolysis as in Example IX.

Example XI

Small pieces of cotton wool were loosely packed into a silica tube and slowly heated to 1000° C. in an atmosphere of nitrogen in order to carbonise the fibres. When the furnace temperature was between 250 and 500° C. light pressure was applied to graphite plungers at each end of the silica tube in order to compact the cotton wool and the mechanical pressure was maintained until the carbonising was almost complete. After carbonising initially at 1000° C. the temperature of the furnace was lowered to about 860° C., and nitrogen saturated (at room temperature) with benzene when passed through the compact for 17 hours. After cooling, the compact which was well bonded was removed from the tube. At this stage the material was easily machinable, and a tube 1.25 cms., inner diameter 2.70 cms., outside diameter 3.5 cms. long was machined from the compact, the density of tube being 0.72 gram/cc. The tube was then given a further treatment for 275 hours at 860° C. in the gas deposition furnace, the final density being 1.58 grams/cc.

The permeability to air of the tube was then determined and found to be 2.12×10^{-8} cm.^{2}/sec. at room temperature.

It is to be noted that in the cases in which the product of the invention includes carbon deposited by pyrolysis that advantage is being taken of the orientated structure of carbon laid down in this way. Thus the fact that the basal plane of the crystal of the deposited carbon makes only a small angle with the underlying deposition surface has the effect of restraining or impeding the movement of foreign atoms such as reaction products in a direction normal to the fibre axis. Thus the products of nuclear fission reactions would be largely retained within the deposited carbon skin.

A further advantage with respect to the inclusion in the fibrous material of reactive material is that a uniform and finely divided dispersion of reactive elements may be obtained throughout a carbon block giving the advantages as regards reaction potential equivalent to using a fine powder of reaction material but avoiding the physical disadvantages of handling and uniformly dispersing the powder in any medium.

The preceding description is for the purpose of illustrating our invention, the scope of which is defined in the following claims.

It is to be noted that matter described and not claimed is the subject of one or more of copending patent applications numbers filed on the same date as the present application.

We claim:

1. A process for producing a composite carbon article with discrete, isolated regions of predetermined density comprising forming a first charge of densely packed intermingled organic fibers, completely surrounding said first charge with a second charge of intermingled organic fibers having a low density relative to the density of said first charge to form a unit, holding the unit under compression, providing and maintaining a non-oxidizing environment for the unit, applying heat to carbonize the fibers while applying pressure to said unit and maintaining said pressure during at least part of the carbonizing step.

2. A process for producing a composite carbon article with discrete isolated areas of predetermined density with an impermeable outer shell comprising forming a first charge of densely packed intermingled organic fibers, completely surrounding said first charge with a second charge of intermingled organic fibers to form a unit, said second charge having a low bulk density relative to said first charge, holding the unit under compression, providing and maintaining a non-oxidizing environment for the unit, applying heat to carbonize the fibers while applying pressure to said unit, maintaining said pressure during at least part of the carbonizing step, and depositing pyrolytic carbon in the pores of said second charge whereby the first charge is sealed by an relatively non-porous carbon second charge.

3. A process for producing a composite carbon article with discrete isolated areas of predetermined density comprising forming a first charge of densely packed intermingled organic fibers, impregnating said first charge with a thermosetting resin which will produce a substantially carbon residue when decomposed by heat, completely surrounding said first charge with a second charge of intermingled organic fibers to form a unit, said second charge having a low bulk density relative to said first charge, impregnating said second charge with a thermosetting resin which will form a substantially carbon residue upon decomposition by heat, holding the unit under compression, applying heat to crosslink said resin, providing and maintaining a non-oxidizing environment for the unit, applying heat to carbonize the fibers and resin while applying pressure to said unit during at least part of the carbonizing step to produce said carbonized article having regions of different density corresponding to the arrangement of said first and second charges.

4. A process for producing a composite carbon article with discrete isolated regions of predetermined density comprising forming first charges of intermingled organic fibers of a given density, providing a second charge of intermingled organic fibers having a substantial difference in density from said first charge, assembling said charges in mutual contact in predetermined stacked relation to form an assembly wherein the first charges are completely surrounded by the second charges, placing the assembly between pressure applying members, providing and maintaining a non-oxidizing environment for the assembly, applying heat to the assembly to carbonize the fibers and simultaneously urging at least one member to apply pressure to the assembly, and maintaining the pressure during at least part of the carbonizing step to produce a carbon assembly having regions of density corresponding to the arrangement of said first and second charges.

5. The process of claim 4 including depositing a pyrolytic carbon in the pores of said second charge during the final stages of said carbonizing step.

6. The product formed by the process as claimed in claim 4.

7. A process for producing a composite carbon article with discrete regions of predetermined density comprising forming dense first charges of intermingled organic fibers, surrounding said first charges with an annular second charge of intermingled organic fibers having a low density relative to the density of said first charge to form a unit, assembling the units in stacked relation whereby the first charges are in mutual contact, surrounding all remaining exposed surfaces of first charges with material of said second charge, placing the assembly between pressure applying members, providing and maintaining a non-oxidizing environment for the assembly, applying heat to the assembly to carbonize the fibers and simultaneously urging at least one member to apply pressure to the assembly, maintaining said pressure during at least part of the carbonizing step to produce a carbonized article having regions of different density.

References Cited by the Examiner

UNITED STATES PATENTS

280,341	7/1883	Bernstein	202—25 X
349,572	9/1886	Dick	202—26

(Other references on following page)

9

UNITED STATES PATENTS

580,308	4/1897	Fenby	117—46
869,012	10/1907	McOuat et al.	117—220
2,817,605	12/1957	Sanz et al.	117—228
2,922,722	1/1960	Hutcheon	117—46
2,962,386	11/1960	Doll et al.	117—46
2,972,552	2/1961	Winter	117—226 X
2,977,997	4/1961	Seltzer	139—383
2,986,173	5/1961	Johnson	139—383
3,011,981	12/1961	Soltes	252—502

10

OTHER REFERENCES

Chem. Eng. 64, No. 10, pg. 172 (1957).

Bickerdike et al.: Production of Impermeable Graphite, "Nuclear Power," February 1959, pp. 86–88.

High Temperature Fibers: Felts Now Made of Pure Graphite, "Materials In Design Engineering," May 1959, pg. 149.

RICHARD D. NEVIUS, *Primary Examiner.*