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METHOD OF CARBONIZING ANIMAL FIBER MATERIALS

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3 Sheets-Sheet 1

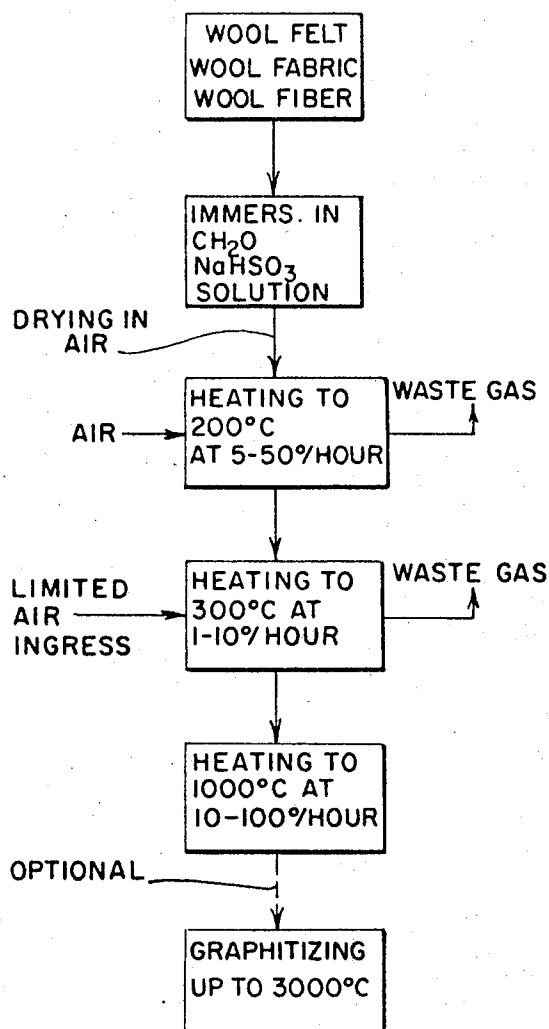


Fig. 1

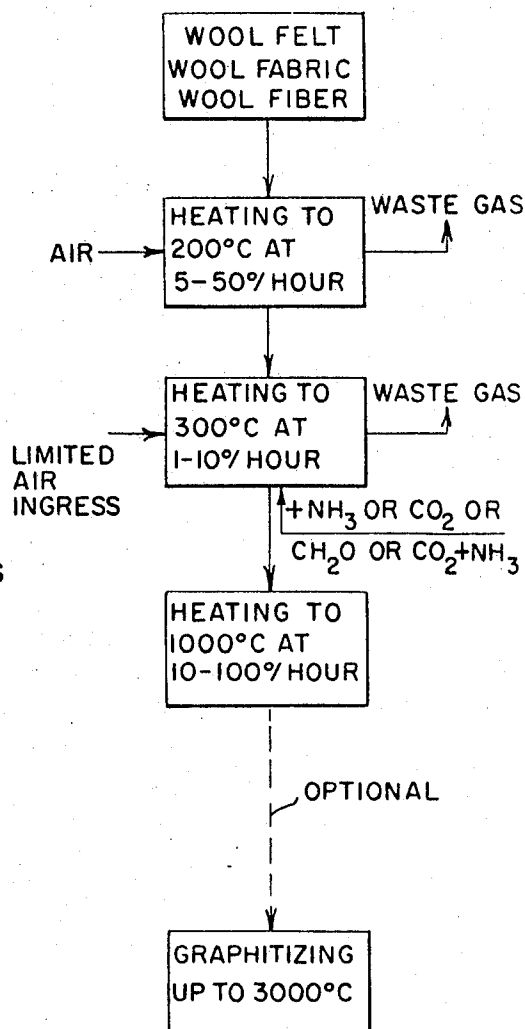


Fig. 2

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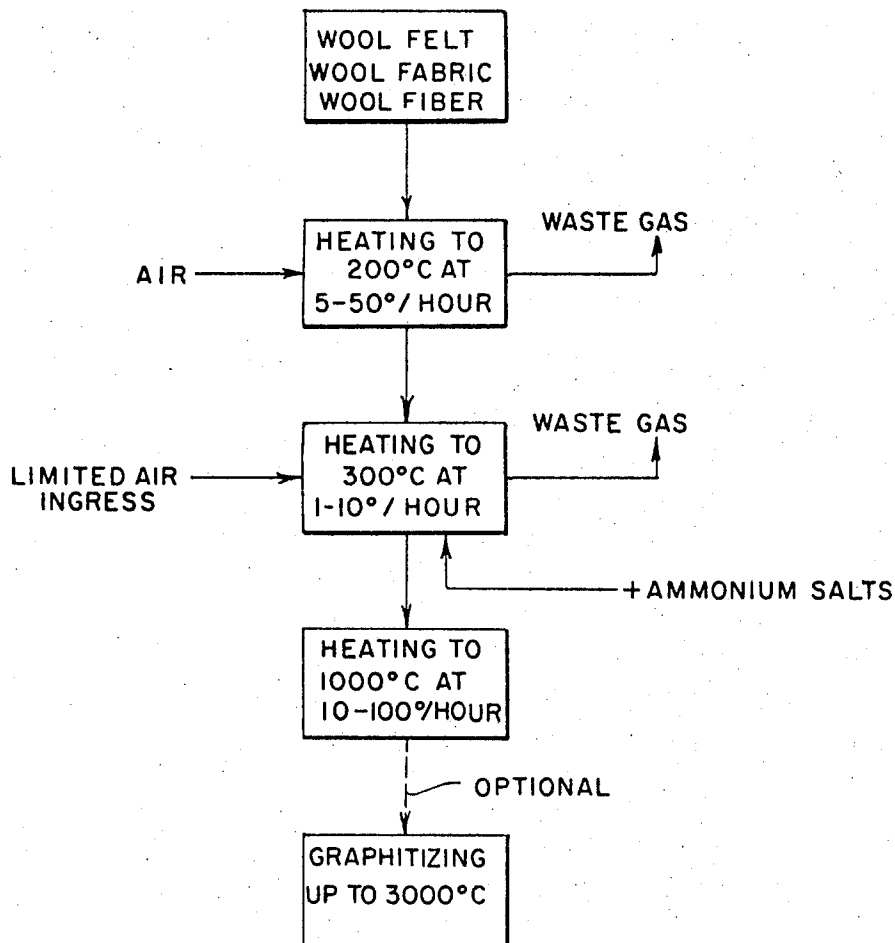


Fig. 3

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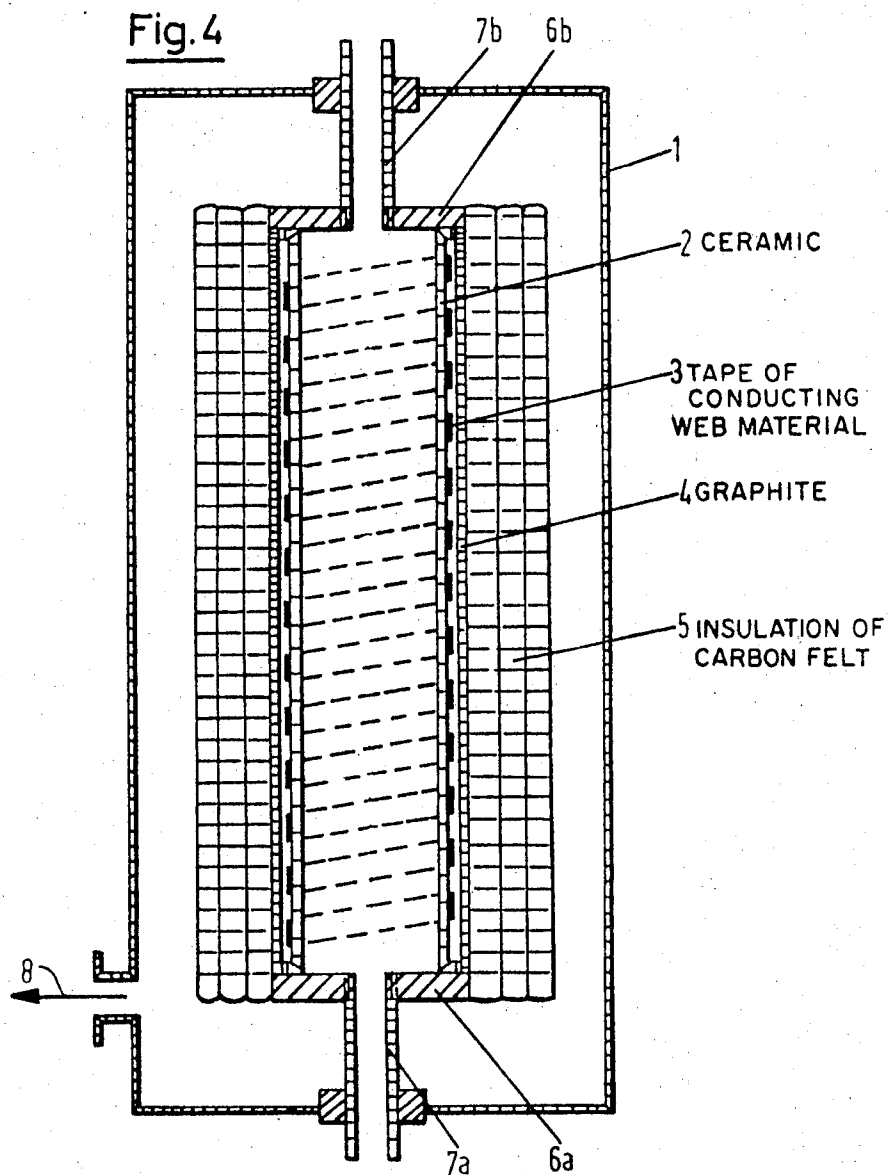
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METHOD OF CARBONIZING ANIMAL FIBER MATERIALS

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Fig. 4



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METHOD OF CARBONIZING ANIMAL FIBER MATERIALS

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15 Claims. (Cl. 23—209.1)

Our invention relates to a method of carbonizing or partially carbonizing a wool-containing material, the term "wool" being herein used to designate sheep wool as well as other fibrous substance of animal origin.

It is known to carbonize or graphitize a fiber-containing material whose fibrous constituents consist of cellulose or regenerated cellulose.

If an attempt were made to subject wool-containing material to heat treatment similar to those known for carbonizing fibrous cellulose materials, various difficulties would be encountered. The wool-containing share of the material would become deformed at the elevated temperatures and thus lose its original fibrous structure. This seems to have been one of the reasons why heretofore the carbonizing process has been limited to cellulose materials.

It is an object of our invention to provide a method of producing a carbonized, partially carbonized or fully graphitized product from a starting material which contains wool or other animal fiber, and to preserve in the resulting carbonized product essentially the cohesion, elasticity or pliability of the starting material.

Referring to web or felt material of animal fiber, particularly wool felt, to be used as starting material, it is another more specific object of the invention to afford producing a felt-like web structure of carbon which still remains well bendable without breaking and which can be fabricated with substantially the same ease as the starting web material but, due to carbonization, is applicable as a carbon or graphite product, for example as an electrical and thermal insulating material at high temperatures such as up to 3000° C. or more.

To achieve these results, and in accordance with our invention, we subject the animal-fiber containing material to a carbonizing heat treatment at a temperature up to about 1000° C. in the—at least temporary—presence of fiber-structure preserving substance. We have found that the presence of air in the carbonizing furnace has this effect if it is kept in motion or circulation within the furnace, and no fresh air is added. According to another feature of the invention, a fiber preserving substance such as formaldehyde, ammonia, carbon dioxide or mixtures thereof may be applied to the wool-containing material during the carbonizing process.

According to another feature of the invention, we carbonize the wool-containing material in continuously consecutive temperature stages of respectively different rates of temperature change and progressively reduced air supply, the last stage up to about 1000° C. being carried out under exclusion of air. Preferably, this graduated process is performed in air up to about 200° C. with a temperature increase of 5 to 50° C. per hour, then up to about 300° C. with a reduced air supply at a rate of 1 to 10° C. per hour, and thereafter concluded up to about 1000° C. under air exclusion at a rate of 10 to 100° C. per hour.

It has been found that in material carbonized according to the invention, the sulphur links or bridges in the wool fibers are largely, or to an essential extent, preserved.

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This is the reason for the preservation of the elasticity or pliability in the resulting product.

The carbonized material obtained by the novel method can further be graphitized with the consequence of affording additional possibilities of use. For example, when the bunch or web of the animal-fibrous material is carbonized in the above-described manner and thereafter graphitized, the material permits producing, among other things, a bendable heating conductor applicable for very high temperatures such as in the range of 1500 to 1700° C., or even up to 3000° C. In this case, too, the material produced by the ultimate graphitizing from the wool-containing starting material is still well bendable and thus can be readily brought into the particular shape required for a heating conductor or for other purposes.

Products made according to the invention can also be employed for all other purposes of carbon and graphite materials. In addition, since such products are flexible or bendable, the field of application, heretofore often limited by lack of flexibility or pliability, is considerably widened.

For further explanation, reference will be made to specific examples described hereinafter, as well as to the accompanying drawing in which:

FIGS. 1, 2 and 3 are respective flow sheets relating to different embodiments of the process according to the invention; and

FIG. 4 shows in section a vacuum furnace equipped with a heater and with insulating structure, both consisting of material produced according to the invention.

Example 1

A piece of a soft, 8 mm. thick wool felt of about 500 x 600 mm., spread flat, is placed into a dryer cabinet having a venting outlet. The dryer cabinet is first heated up to 240° C., the increase in temperature being about 10° C. per hour. Thereafter the cabinet is further heated up to 300° C. but at a slower rate, namely at a temperature increase of 5° C. per hour. During heating of the cabinet from 240° C. to 300° C. and in intervals of about three hours, an amount of 500 g. ammonium carbonate is each time placed into the cabinet beneath the piece of wool felt. Under the effect of heat, the ammonium compound converts to a gas mixture of ammonia and carbon dioxide having a partial pressure varying between about 5 and 760 torr (mm. Hg). The smoke gases evolving during the thermal treatment of the wool felt are continuously exhausted through the venting outlet.

After the temperature of 300° C. is reached, the already partially carbonized wool felt is taken out of the dryer cabinet, embedded in carbon powder (soot or aquadag) within a graphite casing, and then heated in a shaft furnace up to about 1000° C. At first the temperature is increased only slowly. Commencing with 300° C. the temperature increase is about 4° C. per hour, from 600° C. the temperature is raised about 10° C. per hour, and from 900° C. about 20° C. per hour. After complete coking, the furnace and its contents are permitted to cool, the graphite casing with the material is removed, and the material is cleaned of the adhering embedding material.

In tests made in this manner, the specimen was found to have shrunk to about 470 x 360 mm. However, the original fiber structure was clearly recognizable. The elasticity was preserved to such an extent that the specimen could be wound upon a round rod of about 20 mm. diameter. The electrical resistance value, measured perpendicularly to the surface of the specimen, was 8 to 11·10⁵ ohm mm.²/m.; measured in the direction of the web, the resistance was 5 to 10·10³ ohm mm.²/m. The coefficient of thermal conductance was lower than 10⁻² kcal./m. hour ° C.

The properties of wool felt processed in this manner make it suitable for use as heat insulating material, for example.

Example 2

50 g. raw shorn (virgin) wool are kept for three hours at 85° C. in an aqueous solution of 6% formaldehyde and 2% sodium bisulfite and then well washed and dried at room temperature. The wool thus treated is placed into a tubular furnace and heated at a temperature increasing 15° C. per hour up to 200° C. During heating, a current of air is sucked through the wool at a rate of about 21 liters per minute. Thereafter the increase in temperature is reduced to 3° C. per hour and the air flow to 0.1 liter per minute. After reaching a temperature of 300° C., the wool is taken out of the furnace and further processed as described in Example 1.

The carbonized ultimate product obtained by this process exhibited the fiber structure of the original virgin wool. The elasticity or pliability of the starting material was largely preserved. For example the carbonized product could be twisted to threads of yarn.

Another specimen of shorn wool treated for 48 hours at 50° C. in an aqueous solution of 6% formaldehyde and 10% sodium hydrosulfite and thereafter processed in the manner described above, exhibited the same results with respect to mechanical properties.

Example 3

A specimen web of 100 x 500 mm. size woven from wool carded yarn and consisting of 80% of pure shorn sheep wool, was placed upon a tunnel-shaped insert into a dryer cabinet and then heated at a temperature increasing 20° C. per hour up to 200° C., then at the rate of 7° C. per hour up to 300° C. During this heat treatment, when the temperature of 240° C. was reached, ammonia gas was introduced into the dryer cabinet at a partial pressure between 50 and 200 torr. The ammonia gas atmosphere was maintained until the temperature of 300° C. was reached.

The further processing corresponded to the one described in Example 1. The ultimate exhibited good tear strength and was elastic. Its "square" resistance, that is the resistance value of a square of any edge length, was 5 ohm.

During a subsequently performed graphitizing process up to 2700° C., this square resistance was reduced to 1 ohm.

Graphitized material thus produced is particularly well applicable as a heating conductor, preferably in tape form, as well as for various other purposes.

The sulphur content of the latter specimen was analyzed prior to, and after, the thermal treatment. It was found that the sulphur content of the starting material was 3.03% by weight and had declined to 2.28% after the thermal treatment. This slight reduction in sulphur content is still negligible as regards preservation of elasticity or pliability of the ultimate material.

Further modes of performing the process of the invention will be described with reference to the drawings.

According to the process represented by the flow sheet in FIG. 1 the starting material (for example wool felt, wool fabric or raw animal wool) is immersed in an aqueous solution of formaldehyde in the presence of a reduction agent, such as sodium bisulfite, and thereafter dried in air. Thereafter the material is heated with access of air to a temperature of 200° C. at a rate of 5 to 50° C./hour, and the evolving vapors and gases are continuously withdrawn. Thereafter the material is further heated with a reduced ingress of air, up to 300° C. at a rate of 1 to 10° C./hour, the evolving waste gases being likewise withdrawn continuously. The further heating up to 1000° C. is applied at a rate of 10 to 100° C./hour under exclusion of air.

According to the process represented diagrammatically in FIG. 2, the starting material is first heated up to 3000°

C. in the manner described above with reference to FIG. 1. However, during the processing period between 200 and 300° C. a substance or mixture, such as formaldehyde, ammonia and/or carbon dioxide, in gaseous constitution is supplied, resulting in a partial pressure of these gases between about 5 and 760 torr. The subsequent heating up to 100° C. corresponds to the processing stage described above with reference to FIG. 1.

According to the process represented in FIG. 3, the thermal treatment is carried out in the same manner as described in the foregoing, except that an ammonia compound or a mixture of ammonium compounds is directly added during the heating period between 200 and 300° C. for the purpose of supplying ammonia and, as the case may be, also carbon dioxide.

The material resulting from the processes exemplified by FIGS. 1, 2 and 3 may be additionally subjected to graphitizing under exclusion of air in the known manner at temperatures up to 3000° C.

The vacuum furnace illustrated in FIG. 4 represents an example in which animal fiber material processed according to the invention is employed for two different purposes. The furnace comprises a vacuum-tight jacket 1 of sheet metal which surrounds a cylindrical heater body composed of a ceramic carrier tube 2 and a helical conductor tape 3 mounted on the outer cylindrical surface of the ceramic tube 2. The conductor tape 3 consists of a fabric processed according to the invention and graphitized at temperatures up to about 2700° C. The fiber structure and the pliability of the fibrous material are preserved in the tape so that it could be wound about the ceramic tube 2. The resistance value of the tape 3 was reduced during the graphitizing process to such an extent that the graphitized material became suitable and advantageous for use as a heating resistor. Shoved over the heater body 2, 3 is a cylindrical tube 4 of graphite which is heat insulated by a surrounding material 5 constituted by several concentric layers. This insulating material 5 consists of carbonized wool felt made by a method according to the invention.

The ceramic tube is closed at both ends by respective ring-shaped cover plates 6a and 6b. The end of a cylindrical duct 7a, 7b is joined with each ring-shaped cover plate. The other end of each duct passes through the wall of the vacuum-tight jacket 1 and is heat-insulated therefrom by an insulating sealing member of annular shape.

The cylindrical conduits 7a and 7b thus form a connection between the interior of the ceramic tube 2 and the vicinity of the furnace and may be used for supplying and removing of the material to be heated in the furnace.

A free space remains between the vacuum-tight jacket 1 and the heater body of the furnace. During operation of the furnace the heat transfer through this interspace can be reduced by evacuating it through a nipple 8 of jacket 1.

We claim:

1. The process of carbonizing animal fiber material, which comprises subjecting the animal fiber material to carbonizing heat treatment in several consecutive stages of gradually increasing temperature up to about 1000° C., permitting access of air to the material during the first stage, and reducing such access during the subsequent stages down to exclusion of air in the last stage, whereby the resulting carbonized material substantially retains mechanical fiber characteristics of the starting material.

2. The process of carbonizing animal fiber material, which comprises heating the animal fiber material in air up to about 200° C. at a rate of 5 to 50° C. per hour, then further heating the material with a limited air supply up to about 300° C. at a rate of 1 to 10° C. per hour, and thereafter continuing the heating of the material under exclusion of air up to about 1000° C. at a rate of 10 to 100° C. per hour.

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3. The process of carbonizing animal fiber material, which comprises heating the animal fiber material at a gradually increasing temperature up to about 1000° C., and applying to the material during the heating period with proteinaceous fiber preserving substance.

4. The process of carbonizing animal fiber material, which comprises heating the animal fiber material at a gradually increasing temperature up to about 1000° C., and applying to the material during the heating period at least one substance from the group consisting of formaldehyde, ammonia, carbon dioxide and mixtures thereof, whereby the resulting carbonized material substantially retains mechanical fiber characteristics of the starting material.

5. The process of carbonizing animal fiber material, which comprises subjecting the animal fiber material to carbonizing heat treatment in several consecutive stages of gradually increasing temperature up to about 1000° C., permitting access of air to the material during the first stage, reducing such access during the subsequent stages down to exclusion of air in the last stage, and applying to the material during the heat treatment at least one substance from the group consisting of formaldehyde, ammonia, carbon dioxide and mixtures thereof.

6. The process, according to claim 2, which comprises applying to the material during heating at a temperature above 200° C. at least one gaseous substance from the group consisting of formaldehyde, ammonia, carbon dioxide and mixtures thereof.

7. The process according to claim 6, which comprises adding said substance at a temperature between about 240° C. and about 300° C. at a partial pressure of 5 to 760 torr.

8. The process according to claim 1, which comprises adding to the animal fiber material an ammonium compound, whereby said heat treatment causes said compound to evolve gaseous ammonia.

9. The process of carbonizing animal fiber material, which comprises impregnating the animal fiber material with formaldehyde, then subjecting the impregnated material to carbonizing heat treatment in several consecutive stages of gradually increasing temperature up to about 1000° C., permitting access of air to the material during the first stage, and reducing such access during the subsequent stages down to exclusion of air in the last stage.

10. The process of carbonizing animal fiber material, which comprises immersing the animal fiber material in an aqueous solution of formaldehyde, drying the material, then subjecting the dried material to carbonizing heat treatment in several consecutive stages of gradually increasing temperature up to about 1000° C., permitting

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access of air to the material during the first stage, and reducing such access during the subsequent stages down to exclusion of air in the last stage.

11. The process according to claim 10, wherein said aqueous solution of formaldehyde contains an addition of bisulfite reaction agent.

12. The process according to claim 10, wherein said aqueous solution of formaldehyde contains an addition of sodium bisulfite.

13. The process according to claim 1, which comprises exhausting, up to a temperature at least of about 300° C., the vapors and gases evolving from the material being carbonized.

14. The process of carbonizing animal fiber material, which comprises subjecting the animal fiber material to carbonizing heat treatment in several consecutive stages of gradually increasing temperature up to about 1000° C., permitting access of air to the material during the first stage, reducing such access during the subsequent stages down to exclusion of air in the last stage, and thereafter graphitizing the material under exclusion of air at temperatures above 1000° C. up to about 3000° C.

15. The process of carbonizing animal fiber material, which comprises heating the animal fiber material at a gradually increasing temperature up to about 1000° C., applying to the material during the heating period at least one substance from the group consisting of formaldehyde, ammonia, carbon dioxide and mixtures thereof, and thereafter graphitizing the material under exclusion of air at temperatures above 1000° C., up to about 3000° C.

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