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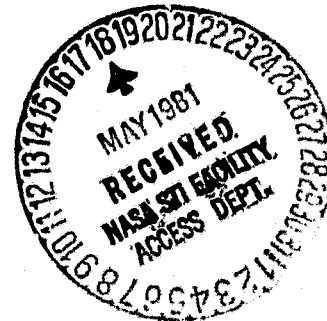
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PROCESS FOR THE MANUFACTURE OF CARBON OR GRAPHITE FIBERS
West German Patent Disclosure [Offenlegungsschrift] No. 2,220,614

D. Overhoff, E. Winkler and D. Mueller

Translation of "Verfahren zur Herstellung von Kohlenstoff-
oder Graphitfasern," Deutsches Patentamt: Offenlegungsschrift
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Sigri Elektrographit GmbH, 8901 Meitingen, W. Germany; In-
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16. Abstract Patent for a process by which carbon or graphite fibers are manufactured by heating polyacrylonitrile fiber materials in various solutions and gases, characterized in that the materials are heated to a temperature of from 150 to 300°C in a solution containing one or more acids from the group of carbonic acids, sulfonic acids, and/or phenols.			
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PROCESS FOR THE MANUFACTURE OF CARBON OR GRAPHITE FIBERS

West German Patent Disclosure [Offenlegungsschrift] No. 2,220,614

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The invention concerns a process for the manufacture of /1* carbon or graphite fibers from fibrous polyacrylonitrile polymer or polyacrylonitrile polymer mixtures by heating the acrylonitrile fiber material first in a solution which promotes the cyclization of lateral nitrile groups, and subsequently in an atmosphere containing oxidizing gases, to a temperature of between 200 and 400°C, and in an inert or reducing atmosphere to ca. 1000°C, with (if required) further heating to ca. 2500°C.

Under U.S. Patent No. 2,913,802 it is known that heating in air to a temperature of ca. 200°C can convert fiber material consisting of acrylonitrile polymers or copolymers into a thermally stable state especially suitable for the manufacture of carbon and graphite fibers. The change in state is based upon interlacing reactions between adjacent molecule strands and cyclization reactions of the side nitrile groups; the speed of these reactions is primarily determined by the diffusion rate of the oxygen entering the fibers. The treatment times necessary to complete the reaction involve many hours, depending on fiber diameter. Thus, for instance, at 220°C /2 under the action of oxygen it takes 20 hours for a complete interlacing of polyacrylonitrile or copolymer fibers with copolymerizable monovinyl compounds like methyl acrylate, vinyl acetate or vinyl chloride, at a fiber diameter of 20 µm.

Attempts to increase reaction speed with higher temperatures

* Numbers in the margin indicate pagination in the foreign text.

did not yield satisfactory results, since under these conditions the heat developing from the interlacing and cyclization reactions could not be completely drawn off. The fibers, overheated in places, are brittle, have low strength, and are unsuitable for such applications as the reinforcement of plastics.

Under U.S. Patent No. 3,497,318 it is also known how to treat polyacrylonitrile fibers with oxide compounds of transition metals at a temperature of preferably 85°C, with especially good results from oxides of titanium, vanadium, chromium, molybdenum, manganese, tungsten, cobalt, platinum and palladium, as well as potassium permanganate and potassium perchromate. The time necessary for complete cross-linking of the molecule strands here is only 5 to 30 min. Since the dissolved, vaporized or suspended (in a liquid) catalyst only contacts the fiber surface, the interlacing reaction is accelerated catalytically almost exclusively on the surface, while the interlacing inside the fibers is increased by the unremoved reaction heat. This process, too, can hardly avoid the local overheating that diminishes fiber flexibility.

Finally, under German Patent Disclosure No, 1,929,849 it is known how to treat polyacrylonitrile fibers first at a temperature between 150 and 250 °C with one or more Lewis acids, and then oxidize them at temperatures of 175 to 350 °C. The advantage of this process is in the temperature of the cyclization and interlacing reactions, decreasing the heat gradations and making possible greater reaction speeds without hurting the fibers. However, because of the ultimate diffusion speed of Lewis acids and oxygen, one cannot go below certain minimum times for complete interlacing, depending on fiber diameter.

A further disadvantage of the cyclization treatment of polyacrylonitrile fibers with Lewis acids lies in the fact that the cations of the Lewis acids used, such as titanium tetrachloride, stannous tetrachloride, boron trifluoride or ferric trichloride,

remain in the fibers, having ill effects on the characteristics of the carbon or graphite fibers produced with this process. The effect of the cations is based first upon the formation of carbides by reactions with the fiber carbon, thus reducing strength and flexibility in particular, and then also upon material characteristics of the cations, such as a catalytic increase /4 in the oxidation rate or an increase in the absorption cross-section for thermic neutrons, especially by inclusions of boron.

Under British Patent No. 1,253,827, finally, it is known how to avoid exothermic pyrolysis reactions during carbonization of polyacrylonitrile at least in part by adding up to 15 wt% of carbon acids, phenols or amides to acryl solutions. In the polymerization of such solutions one gets acid copolymers or polymers with included free acids, which are converted after the usual method of spinning into carbon fibers, without the appearance of strong exothermic reactions.

The addition of acids to the raw materials rules out the use of commercial polyacrylonitrile fibers of known and consistent quality as the starting material for the production of carbon fibers. To meet the relatively low need for carbon fibers, rather, smaller polymerization and spinning plants must be built, which generally have lower reproducibility than large plants in continuous operation. Since the characteristics of carbon fibers are largely determined by the quality of the raw material, the use of inconsistent fiber material yields products that can be evaluated technically only to a limited extent.

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The invention is based upon the goal of producing carbon or graphite fibers with high strength and stiffness from regular commercial fibrous polyacrylonitrile or polyacrylonitrile polymer mixtures, and of avoiding harmful exothermic reactions in the thermic stabilization of the original fibers without adding metal cations. Another goal of the invention is to reduce the time needed for the thermic stabilization and carbonization of the

original fibers.

The goal is reached under the invention by heating acrylonitrile fiber material to a temperature of 150 to 300°C in a solution containing one or more acids from the carbon, sulfonic or phenol groups.

The invention is based on the knowledge that at high temperatures in a suitable solvent, dissolved organic acids from the carbonic acid, sulfonic acid and phenol groups diffuse into acrylonitrile fibers drawn through the solution, catalytically accelerate the cyclization of lateral nitrile groups, and make possible a higher heating rate in the interlacing phase without damaging the fibers with local overheating. The original molecular orientation of the fibers is largely preserved by the cyclization that occurs before interlacing, so that one gets carbon or graphite fibers with great strength and stiffness without additional high-temperature stretching treatments.

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Suitable raw materials for the production of carbon or graphite fibers under the invention are acrylonitrile copolymers, and especially copolymers with a content of up to 15% of one or several monovinyl units like styrene, vinyl pyridine, vinyl chloride, vinylidene chloride, acrylic acid methyl ester, methacrylate and vinyl acetate. The acrylonitrile material is spun under known processes, e.g. the dry or wet spinning process, and the resulting fiber material is then washed, dried and stretched, under a preferred version of the invention, to at least 5 times the original length, in order to improve molecular orientation and raise fiber strength to at least 5 p/dex. Stretching can be carried out in known ways in water, steam, glycerine or air. To improve handling it is advantageous to provide the fiber material with a twist, e.g. 5 - 40 rpm.

The following acids are especially suitable as cyclization catalysts:

Acids: formic acid
 nitroformic acid
 acetic acid
 nitroacetic acid
 oxalic acid
 "seminitrile" of malonic acid
 "seminitrile" of succinic acid
 maleic acid anhydride
 furan carbonic acid
 benzoic acid
 nitrobenzoic acid
 dinitrobenzoic acid
 nitrophenylacetic acid
 phthalic acid

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Sulfonic Acids: benzenesulfonic acid
 toluenesulfonic acid
 styrenesulfonic acid
 pyridinesulfonic acid

Phenols; nitrophenols
 nitrocresols
 picric acid
 quinones
 quinhydrone

The efficacy of the acids is determined mainly by the strength of the acid and the temperature applied, which can advantageously be 150 - 300 °C. Suitable solvents for the aforementioned acids, which also favor their diffusion by swelling the fibers, are nitro-compounds, especially nitrobenzene, as well as ethers and esters, such as nitroanisole or diphenylether.

The acrylonitrile fiber material is preferably moved continuously through one or more sequential acid baths at different

temperatures. The time for which the material remains is determined by the acid concentration, which is preferably 0.5 to 10 wt%, and the bath temperature, where the soaking time is shortened by higher acid concentrations and higher temperatures. Pretreatment can also be performed, at least in part, in an atmosphere containing acid vapors. According to the invention acrylonitrile fibers prestretched to at least five times their initial length are preferred. Material that is not prestretched is advantageously stretched during acid treatment by applying a tensile stress.

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Cyclization is followed by an oxidation treatment, in which gas mixtures with air or oxygen, e.g. oxygen-nitrogen mixtures, or gases containing other oxidizing agents, such as nitrogen with bromine or chlorine additions, are conducted through a tube-shaped furnace through which the stabilized acrylonitrile material is continuously moved. The furnace temperature is raised in the oxidation stage to a maximum of 900°C; oxidation time is ca. 5 to 20 min.

The latticed and thermally stabilized fiber material is subsequently carbonized by heating to temperatures of ca. 1000°C in a reducing or inert atmosphere, and if required is graphitized by further heating to temperatures over 2000°C.

The advantages of the process under the invention consist particularly in the fact that commercial acrylonitrile fiber materials yield high-quality carbon or graphite with no foreign elements; production times are shortened and the equipment necessary for control and regulation is reduced. The carbon and graphite fibers produced under the invention present high uniformity and excellent mechanical characteristics, such as tear strength and modulus of elasticity, and are especially well suited as reinforcement fibers for mechanically and thermally heavily-stressed structural components.

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The invention is further explained in the following examples.

Example 1

A strand of an acrylonitrile polymer consisting of 95 wt% acrylonitrile and 5% acrylic acid methyl ester with an individual titer of 2 dtex and a tear strength of 5 p/dtex was continuously drawn through a solution of 1% benzoic acid in diphenyl ether at 230°C, and after resting ca. 2 hours in air was oxidized at a temperature of 250°C for a duration of 20 minutes. Subsequently the stabilized fiber material was carbonized by heating to 1000°C in a nitrogen stream.

The strength of the resulting carbon fiber was 21,000 kp/cm²; the modulus of elasticity was $1.9 \cdot 10^6$ kp/cm².

Example 2

The same material as in Example 1 was cyclized in a 1% solution of p-toluenesulfonic acid in nitroanisole under the conditions as in Example 1, and then, after washing with acetone, was drawn through a tube furnace with a temperature gradient of ca. 200°C/hr., through which oxygen was conducted at the same time; subsequently it was put through a second furnace with a temperature that rose continuously from 300 to 1000°C. The time spent by the fibers in the /10 furnaces was 25 and 35 minutes, respectively.

The carbon fibers, which presented a breaking strength of 22,000 kp/cm², and a modulus of elasticity of $2.0 \cdot 10^6$ kp/cm², were then graphitized by heating to ca. 2800°C in an argon atmosphere. The strength of the graphite fibers was 19,000 kp/cm²; their modulus of elasticity was $3.7 \cdot 10^6$ kp/cm².

Example 3

Fibers from an acrylonitrile mixture of 97 wt% acrylonitrile and 3% acrylic acid methyl ester were stretched wet to 5 times

their original length. The breaking strength was 4.5 p/dtex; the breaking stretch was 15%. The fibers were heated for 30 min. in a boiling solution of 2 wt% furanocarbonic acid in nitrobenzene, drawn from the bath through wringer rollers, washed with acetone, dried and then heated 15 min. in air at 280°C. The subsequently carbonized fibers presented the following mechanical characteristics: breaking strength 20,000 kp/cm²; modulus of elasticity $2.5 \cdot 10^6$ kp/cm².

Example 4

The fiber material described in Example 3 was first drawn through a trough containing an 8% solution of nitroacetic acid in nitrobenzene, and then exposed to nitrobenzene vapor at ca. 210°C. /11 The times of exposure were 10 and 20 minutes, respectively. Cyclization was followed by an oxidation treatment in air at 300°C and an exposure time of 15 min., and by carbonization through heating in nitrogen to 1150°C.

The strength of the resulting carbon fibers was 23,000 kp/cm²; modulus of elasticity $2.0 \cdot 10^6$ kp/cm².

Example 5

The same material as in Examples 3 and 4 was treated in a first stage at a temperature of 150°C with a 5% solution of picric acid in nitrobenzene and then in a second stage with the same solution at a temperature of 210°C; the exposure times were 5 and 40 minutes, respectively. In the second stage a tensile stress of ca. 0.1 p/dtex was applied to the fibers. They were then heated in 15 minutes from 250 to 350°C and subsequently carbonized as in Example 2.

The resulting carbon fibers had the following characteristics: breaking strength 25,000 kg/cm², modulus of elasticity $2.3 \cdot 10^6$ kp/cm².

1. Process to manufacture carbon or graphite fibers from fibrous polyacrylonitrile or polyacrylonitrile polymer mixtures by heating the acrylonitrile fiber material in a solution that promotes the cyclization of lateral nitrile groups, and subsequently in an atmosphere containing oxidizing gases to a temperature of between 200 and 400 °C and in an inert or reducing atmosphere to ca. 1000°C, with (in some cases) further heating to ca. 2500°C; characterized in that acrylonitrile fiber material is heated to a temperature of from 150 to 300°C in a solution containing one or more acids from the group of carbonic acids, sulfonic acids, phenols.

2. Process as in Claim 1, characterized in that acrylonitrile fiber material is continuously moved through a hot bath containing acid and then through an atmosphere containing acid vapors.

3. Process as in Claims 1 and 2, characterized in that the acid content of the solution is 0.5 to 10 wt%.

4. Process as in Claims 1 to 3, characterized in that nitrobenzene is used as the solvent for the solution. /13

5. Process as in Claims 1 to 4, characterized in that the acrylonitrile fiber material is stretched during the acid treatment by applying a tensile stress.

6. Process as in Claims 1 to 5, characterized in that the acrylonitrile fiber material is stretched to at least 5 times its initial length.