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Druin et al.

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[54] **ELECTROLYTIC PROCESS FOR THE SURFACE MODIFICATION OF HIGH MODULUS CARBON FIBERS**

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[51] **Int. Cl.**..... **C01d 7/34,** B01k 1/00

[58] **Field of Search** 204/130, 132, 211, 206

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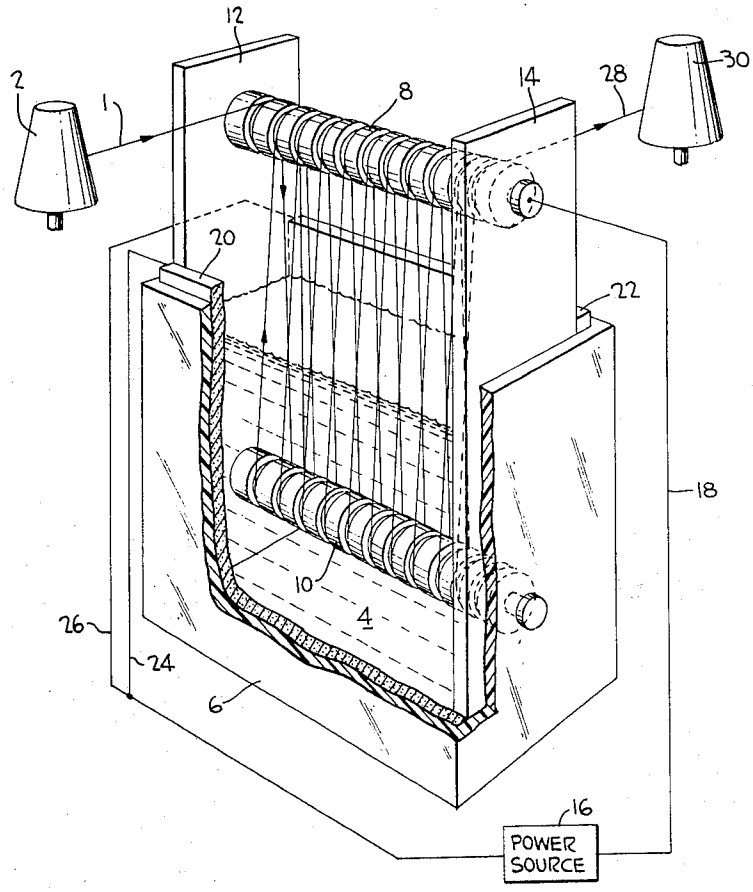
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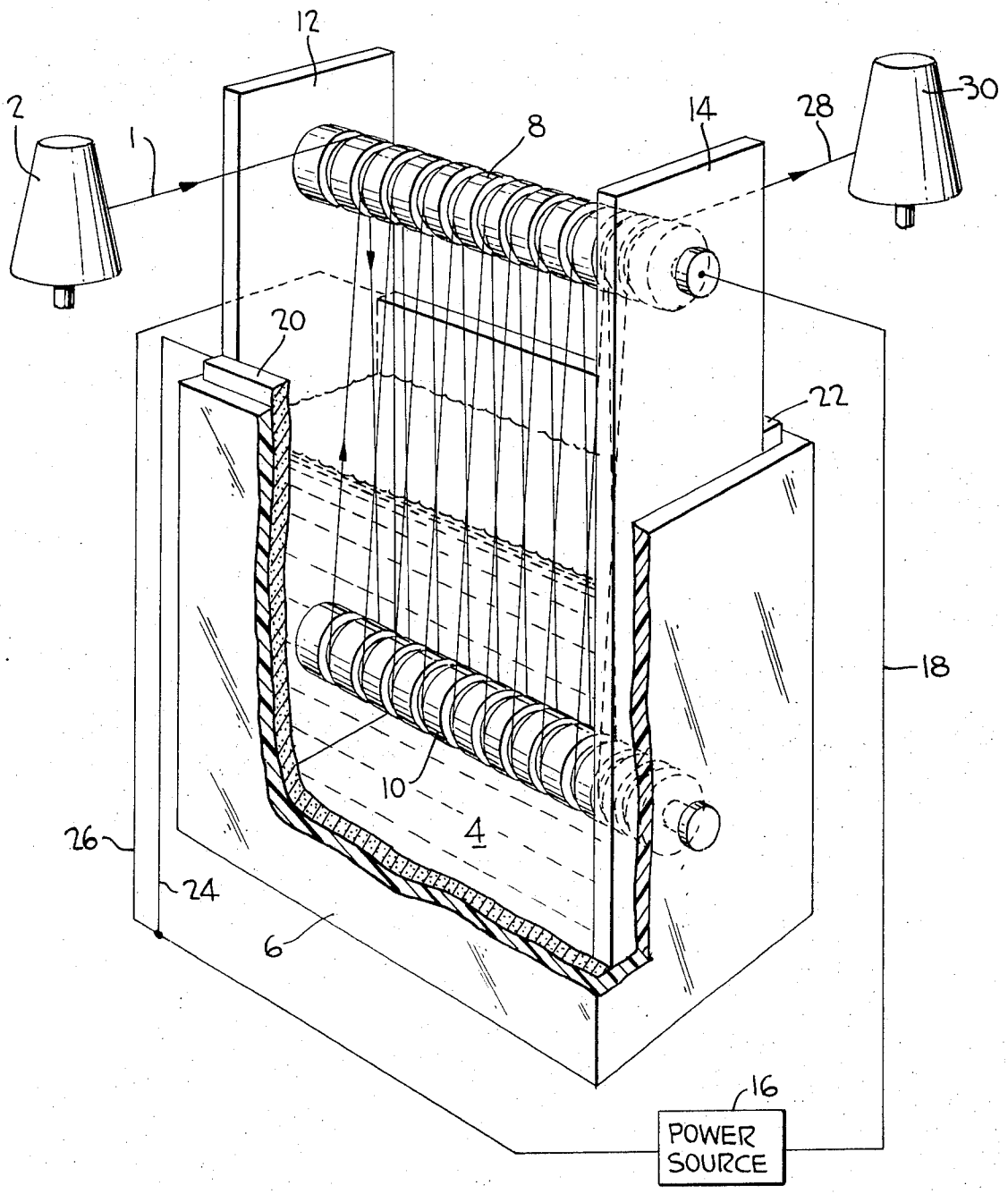
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[57] **ABSTRACT**

An improved electrolytic process is provided for modifying the surface characteristics of an electrically conductive high modulus graphitic carbonaceous fibrous material (i.e., exhibiting a mean single filament Young's modulus of at least about 60 million psi) and to thereby facilitate enhanced adhesion between the fibrous material and a resinous matrix material. The electrolytic process is carried out upon immersion of the fibrous material in an aqueous electrolytic solution of sodium hypochlorite (as defined) provided at a moderate temperature for a relatively brief residence time (i.e., about 2 to 10 minutes) while subjected to a relatively low current density (i.e., about 2.5 to 12 milliamps per square centimeter of surface area of fibrous material), and thereafter washing the same. Composite articles of enhanced interlaminar shear strength may be formed by incorporating the fibers modified in accordance with the present process in a resinous matrix material.

16 Claims, 1 Drawing Figure




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POWER SOURCE

ELECTROLYTIC PROCESS FOR THE SURFACE MODIFICATION OF HIGH MODULUS CARBON FIBERS

BACKGROUND OF THE INVENTION

In the search for high performance materials, considerable interest has been focused upon carbon fibers. Graphite fibers or graphitic carbonaceous fibers are defined herein as fibers which consist essentially of carbon and have a predominant x-ray diffraction pattern characteristic of graphite. Amorphous carbon fibers, on the other hand, are defined as fibers in which the bulk of the fiber weight can be attributed to carbon and which exhibit an essentially amorphous x-ray diffraction pattern. Graphitic carbonaceous fibers generally have a higher Young's modulus than do amorphous carbon fibers and in addition are more highly electrically and thermally conductive.

Industrial high performance materials of the future are projected to make substantial utilization of fiber reinforced composites, and graphitic carbonaceous fibers theoretically have among the best properties of any fiber for use as high strength reinforcement. Among these desirable properties are corrosion and high temperature resistance, low density, high tensile strength, and high modulus. Graphite is one of the very few known materials whose tensile strength increases with temperature. Uses for graphitic carbonaceous fiber reinforced composites include recreational equipment such as golf club shafts, aerospace structural components, rocket motor casings, deep submergence vessels ablative materials for heat shields on re-entry vehicles, etc.

In the prior art numerous materials have been proposed for use as possible matrices in which graphitic carbonaceous fibers may be incorporated to provide reinforcement and produce a composite article. The matrix material which is selected is commonly a thermosetting resinous material and is commonly selected because of its ability to also withstand highly elevated temperatures.

While it has been possible in the past to provide graphitic carbonaceous fibers of highly desirable strength and modulus characteristics, difficulties have arisen when one attempts to gain the full advantage of such properties in the resulting fiber reinforced composite article. Such inability to capitalize upon the superior single filament properties of the reinforcing fiber has been traced to inadequate adhesion between the fiber and the matrix in the resulting composite article.

Various techniques have been proposed in the past for modifying the fiber properties of a previously formed carbon fiber in order to make possible improved adhesion when present in a composite article. See, for instance, U.S. Pat. No. **3,476,703** to Nicholas J. Wadsworth and William Watt wherein it is taught to heat a carbon fiber normally within the range of 350°. to 850°C. (e.g., 500° to 600°C.) in a gaseous oxidizing atmosphere such as air for an appreciable period of time. Other atmospheres contemplated for use in the process include an oxygen rich atmosphere, pure oxygen, or an atmosphere containing an oxide of nitrogen from which free oxygen becomes available such as nitrous oxide and nitrogen dioxide. Such hot gas techniques while effectively improving bonding characteristics have been found, however, commonly to have a tendency to concomitantly decrease the carbon fiber

single filament properties which ultimately produces a composite article exhibiting a diminished tensile strength.

More recently, various liquid oxidative surface treatments for carbon fibers have been proposed. Illustrative examples of representative nonelectrolytic treatments utilizing an aqueous sodium hypochlorite solution are disclosed in British Pat. No. 1,238,308, and German Pat. Nos. 2,112,455 and 2,147,419. Illustrative examples of electrolytic liquid oxidative surface treatments are disclosed in British Pat. No. 1,257,022, Belgian Patent No. 747,631, and German Pat. No. 2,048,916. The nonelectrolytic treatments identified above commonly employ elevated processing temperatures, extended treatment times, and relatively unstable solutions with which the carbon fibers are treated. The electrolytic treatments identified above commonly employ highly elevated current densities and relatively unstable solutions with which the carbon fibers are treated. It has been recognized by those skilled in the art that high modulus graphitic carbonaceous fibers have proven to be more difficult to surface treat than low modulus carbon fibers.

It is an object of the invention to provide an improved electrolytic process for efficiently modifying the surface characteristics of high modulus graphitic carbonaceous fibers.

It is an object of the invention to provide an improved electrolytic process for enhancing the ability of high modulus graphitic carbonaceous fibers to bond to a resinous matrix material.

It is an object of the invention to provide an improved electrolytic process for modifying the surface characteristics of high modulus graphitic carbonaceous fibers which may be conducted relatively rapidly at relatively low current densities.

It is an object of the invention to provide an improved electrolytic liquid phase oxidation process for modifying the surface characteristics of high modulus graphitic carbonaceous fibers in the absence of any substantial diminution in the tensile properties thereof.

It is an object of the invention to provide an improved electrolytic liquid phase oxidation process for modifying the surface characteristics of high modulus graphitic carbonaceous fibers wherein the fibers are treated with an aqueous solution of sodium hypochlorite.

It is an object of the invention to provide composite articles exhibiting an improved interlaminar shear strength reinforced with high modulus carbon fibers.

These and other objects, as well as the scope, nature, and utilization of the invention will be apparent from the following detailed description and appended claims.

SUMMARY OF THE INVENTION

It has been found that an improved electrolytic process for enhancing the ability of an electrically conductive carbonaceous fibrous material containing at least about 90 percent carbon by weight and exhibiting a mean single filament Young's modulus of at least about 60 million psi and a predominantly graphitic x-ray diffraction pattern to bond to a resinous matrix material comprises:

a. immersing the fibrous material in an aqueous electrolytic solution of sodium hypochlorite having a

pH of about 8 to 12 and an active chlorine concentration of about 1 to 7 percent by weight,

b. providing a cathode in contact with the aqueous electrolytic solution and in a spaced relationship to the immersed fibrous material,

c. applying electrical current to the fibrous material while immersed in the aqueous electrolytic solution of sodium hypochlorite at a current density of about 2.5 to 12 milliamps per square centimeter of surface area of the immersed fibrous material for a residence time of about 2 to 10 minutes with the fibrous material serving as an anode,

d. washing the resulting carbonaceous fibrous material to remove residual aqueous electrolytic solution adhering to the same, and

e. drying the same.

The resulting high modulus graphitic carbonaceous fibers may be incorporated in a matrix material to form a composite article exhibiting an enhanced interlaminar shear strength.

DESCRIPTION OF DRAWING

The drawing is a schematic presentation of an apparatus arrangement capable of carrying out the improved process of the present invention on a continuous basis.

DESCRIPTION OF PREFERRED EMBODIMENTS

The Starting Material

The graphitic carbonaceous fibrous materials which are modified in accordance with the present process contain at least about 90 percent carbon by weight and exhibit a predominantly graphitic carbon x-ray diffraction pattern. In a preferred embodiment of the process the graphitic carbonaceous fibrous materials which undergo surface treatment contain at least about 95 percent carbon by weight, and at least about 99 percent carbon by weight in a particularly preferred embodiment of the process.

The fibers which are modified in accordance with the present process additionally exhibit a relatively high mean single filament Young's modulus of at least about 60 million psi, e.g., about 60 to 90 million psi, and preferably a mean single filament Young's modulus of about 70 to 90 million psi. Additionally, the fibers commonly exhibit a single filament tensile strength of at least about 250,000 psi, e.g., about 300,000 to 400,000 psi. The Young's modulus of the fiber may be determined, for instance, by the procedure of ASTM Designation D-2101-64T.

The graphitic carbonaceous fibrous materials may be present as a continuous length and may be provided in a variety of physical configurations so long as substantial access to the fiber surface is possible during the surface modification treatment described hereafter. For instance, the graphitic carbonaceous fibrous materials may assume the configuration of a continuous length of a multifilament yarn, tape, tow, strand, cable, or similar fibrous assemblage. In a preferred embodiment of the process the graphitic carbonaceous fibrous material is one or more continuous multifilament yarn or tow.

The graphitic carbonaceous fibrous material which is treated in the present process optionally may be provided with a twist of about 0.1 to 5 tpi (turns per inch), and preferably about 0.3 to 1.0 tpi, may be imparted to a multifilament yarn. Also, a false twist may be used instead of or in addition to a real twist. Alternatively, one may select continuous bundles of fibrous material which possess essentially no twist.

The graphitic carbonaceous fibers which serve as the starting material in the present process may be formed in accordance with a variety of techniques as will be apparent to those skilled in the art. For instance, organic polymeric fibrous materials which are capable of undergoing thermal stabilization may be initially stabilized by treatment in an appropriate atmosphere at a moderate temperature (e.g., 200° to 400°C.), and subsequently heated in an inert atmosphere to a more highly elevated temperature, e.g., **1,500°** to **2,000°**C., or more, until a graphitic carbonaceous fibrous material is formed. The higher the temperature the greater the amount of graphitic carbon produced within the same.

The exact temperature and atmosphere utilized during the initial stabilization of an organic polymeric fibrous material commonly vary with the composition of the precursor as will be apparent to those skilled in the art. During the subsequent carbonization reaction elements present in the fibrous material other than carbon (e.g., oxygen and hydrogen) are substantially expelled. Suitable organic polymeric fibrous materials from which the fibrous material capable of undergoing carbonization and graphitization may be derived include an acrylic polymer, a cellulosic polymer, a polyamide, a polybenzimidazole, polyvinyl alcohol, etc. As discussed hereafter, acrylic polymeric materials are particularly suited for use as precursors in the formation of graphitic carbonaceous fibrous materials. Illustrative examples of suitable cellulosic materials include the natural and regenerated forms of cellulose, e.g., rayon. Illustrative examples of suitable polyamide materials include the aromatic polyamides, such as nylon 6T, which is formed by the condensation of hexamethylenediamine and terephthalic acid. An illustrative example of a suitable polybenzimidazole is poly-2,2'-m-phenylene-5,5-bibenzimidazole.

A fibrous acrylic polymeric material prior to stabilization may be formed primarily of recurring acrylonitrile units. For instance, the acrylic polymer should contain not less than about 85 mole percent of recurring acrylonitrile units with not more than about 15 mole percent of a monovinyl compound which is copolymerizable with acrylonitrile such as styrene, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, vinylidene chloride, vinyl pyridine, and the like, or a plurality of such monovinyl compounds.

During the formation of a preferred carbonaceous fibrous material for use in the present process multifilament bundles of an acrylic fibrous material may be initially stabilized in an oxygen-containing atmosphere (i.e., preoxidized) on a continuous basis in accordance with the teachings of U.S. Ser. No. 749,957, filed Aug. 5, 1968, of Dagobert E. Stuetz, which is assigned to the same assignee as the present invention and is herein incorporated by reference. More specifically, the acrylic fibrous material should be either an acrylonitrile homopolymer or an acrylonitrile copolymer which contains no more than about 5 mole percent of one or more monovinyl comonomers copolymerized with acrylonitrile. In a particularly preferred embodiment of the process the fibrous material is derived from an acrylonitrile homopolymer. The stabilized acrylic fibrous material which is preoxidized in an oxygen-containing atmosphere is black in appearance, contains a bound oxygen

content of at least about 7 percent by weight as determined by the Unterzaucher analysis, retains its original fibrous configuration essentially intact, and is non-burning when subjected to an ordinary match flame. Another preferred stabilization technique is disclosed in commonly assigned U.S. Pat. No. 3,508,874 of Richard N. Rulison. A preferred carbonization and graphitization technique is disclosed in commonly asssigned U.S. Serial No. 244,990, filed Apr. 17, 1972 of Charles M. Clarke which is herein incorporated by reference.

In accordance with a particularly preferred carbonization and graphitization technique a continuous length of stabilized acrylic fibrous material which is non-burning when subjected to an ordinary match flame and derived from an acrylic fibrous material selected from the group consisting of an acrylonitrile homopolymer and acrylonitrile copolymers which contain at least about 85 mole percent of acrylonitrile units and up to about 15 mole percent of one or more monovinyl units copolymerized therewith is converted to a graphitic fibrous material while preserving the original fibrous configuration essentially intact while passing through a carbonization/graphitization heating zone containing an inert gaseous atmosphere and a temperature gradient in which the fibrous material is raised within a period of about 20 to about 300 seconds from about 800°C. to a temperature of about 1,600°C. to form a continuous length of carbonized fibrous material, and in which the carbonized fibrous material is subsequently raised from about 1,600°C. to a maximum temperature of at least about 2,400°C. within a period of about 3 to 300 seconds where it is maintained for about 10 seconds to about 200 seconds to form a continuous length of graphitic fibrous material.

The equipment utilized to produce the heating zone used to produce the graphitic carbonaceous starting material may be varied as will be apparent to those skilled in the art. It is essential that the apparatus selected be capable of producing the required temperature while excluding the presence of an oxidizing atmosphere.

In a preferred technique the continuous length of fibrous material undergoing carbonization is heated by use of an induction furnace. In such a procedure the fibrous material may be passed in the direction of its length through a hollow graphite tube or other susceptor which is situated within the windings of an induction coil. By varying the length of the graphite tube, the length of the induction coil, and the rate at which the fibrous material is passed through the graphite tube, many apparatus arrangements capable of producing carbonization and graphitization may be selected. For large scale production, it is of course preferred that relatively long tubes or susceptors be used so that the fibrous material may be passed through the same at a more rapid rate while being carbonized and graphitized. The temperature gradient of a given apparatus may be determined by conventional optical pyrometer measurements as will be apparent to those skilled in the art. The fibrous material because of its small mass and relatively large surface area instantaneously assumes essentially the same temperature as that of the zone through which it is continuously passed.

The Surface Treatment

The graphitic carbonaceous fibrous material (heretofore described) is subjected to a relatively brief electrolytic treatment while immersed in an aqueous solution of sodium hypochlorite as described in detail hereafter, and the resulting fibrous material is washed and dried. During the electrolytic treatment the graphitic carbonaceous fibrous material serves as an anode. A cathode is provided in contact with the aqueous solution of sodium hypochlorite and in a spaced relationship to the immersed graphitic carbonaceous fibrous material.

The aqueous solution of sodium hypochlorite in which the graphitic carbonaceous fibrous material is immersed during the electrolytic treatment has a pH of about 8 to 12, preferably 10.5 to 11.5 (e.g., about 11), and an active chlorine concentration (i.e., an available chlorine concentration) of about 1 to 7 percent by weight, preferably about 3 to 7 percent by weight, and most preferably about 5.025 to 5.4 percent by weight (e.g., 5.25 percent by weight). The active chlorine concentration for a given solution of sodium hypochlorite may be determined by titration with sodium thiosulfate after addition of excess KI. Commercially available liquid bleach meeting the above prerequisites may be selected for use in the present process, and is sometimes designated as soda bleach liquor or simply as household bleach solution. Such a solution may be formed, inter alia, by passage of chlorine through a dilute caustic soda solution in either a batch or continuous operation in accordance with techniques known in the art. The sodium hypochlorite solution utilized in the process of the present invention is considerably more stable than common laundry grade commercial bleach solutions which contain 12 to 15 percent active chlorine. For optimum stability a sodium hypochlorite solution having a pH of about 11 is selected. As the electrolytic treatment progresses, active chlorine is consumed and the pH of the solution decreases. The active chlorine concentration of the solution may accordingly be replenished either continuously or intermittantly so that the active chlorine concentration and the pH are substantially maintained at the desired level throughout the electrolytic treatment. For instance, the active chlorine concentration may be conveniently replenished by feeding fresh aqueous electrolytic solution and withdrawing a portion of the spent solution. The active chlorine concentration should not fall below about 1 percent by weight, preferably should not fall below about 3 percent by weight, and most preferably should not fall below about 5.025 percent by weight during any substantial portion of the electrolytic treatment. The pH of the solution preferably should not fall below about 8, and most preferably should not fall below about 10.5 during any substantial portion of the electrolytic treatment.

During the process of the present invention an electrical current is applied to the graphitic carbonaceous fibrous material while immersed in the aqueous electrolytic solution of sodium hypochlorite at a relatively low current density of about 2.5 to 12 milliamps per square centimeter of surface area of said immersed fibrous material, and preferably a current density of about 4 to 12 milliamps per square centimeter of surface area of said immersed fibrous material. At current densities much below about 2.5 milliamps the desired surface treatment has been found to be inordinately slow. At current densities much above about 12 milliamps the rate of the desired surface modification is not appreciably increased and a significant fire hazard results because of the formation of hydrogen at the cathode via overvoltage. The surface area of the graphitic

carbonaceous fibrous material undergoing treatment may be determined by the aid of BET analysis, or any other conventional technique. For instance, the specific surface area of graphitic carbonaceous fibrous material may be determined by BET analysis and multiplied by the number of grams of fibrous material immersed in the aqueous electrolytic solution.

The solution preferably is provided at the mild temperature of about 20° to 35°C. when contacted with the graphitic carbonaceous fibrous material, and most preferably is provided at room temperature (i.e., at about 25°C.). More highly elevated temperatures have been found to lead to process instability.

The improved electrolytic process of the present invention surprisingly produces the desired surface modification of the graphitic carbonaceous fibrous material in the brief residence time of about 2 to 10 minutes in spite of the relatively mild current density utilized. The exact residence time for optimum results will vary somewhat with the Young's modulus of the graphitic carbonaceous fibrous material undergoing treatment. Generally, the higher the mean Young's modulus above about 60 million psi the longer the residence time employed for optimum results. Commonly residence times of about 2 to 6 minutes are utilized with a graphitic carbonaceous fibrous material having a mean Young's modulus of 60 to 90 million psi. For instance, a residence time of about 2 minutes may be selected while operating at a current density of about 12 milliamps per square centimeter of surface area of said immersed fibrous material, and a residence time of about 5 to 6 minutes may be selected while operating at a current density of about 4 milliamps per square centimeter of surface area of said immersed fibrous material.

During the electrolytic treatment in the aqueous solution of sodium hypochlorite adequate solution is provided so that the fibrous material is completely immersed in the same.

The electrolytic surface modification process of the present invention may be carried out on either a batch or a continuous basis. For instance, an electrical contact may be secured to the graphitic carbonaceous fibrous material and the fibrous material immersed in a suitable aqueous solution of sodium hypochlorite in which a cathode is also provided. Preferably the process is carried out on a continuous basis with a continuous length of the fibrous material being continuously passed through the aqueous solution of sodium hypochlorite. In such an embodiment the continuous length of fibrous material may pass over one or more electrical contact (e.g., idler or driven rollers) through which a current of an appropriate current density is supplied.

Following the surface modification treatment heretofore described the resulting graphitic carbonaceous fibrous material is washed so as to remove residual quantities of the sodium hypochlorite solution adhering to the same. The washing may be carried out in any convenient manner and should be as exhaustive as possible since residual sodium hypochlorite if left on the fiber will adversely influence the properties of a composite incorporating the same. In a preferred wash technique the washing is conducted by initially contacting the resulting graphitic carbonaceous fibrous material with a solution of a dilute acid, and by subsequently rinsing the same with water. The acid serves to neutralize any adhering residue and to aid in its expeditious removal. For instance, dilute mineral acids such as hydrochloric acid, sulfuric acid, etc. may be employed. Also, acetic acid may be conveniently selected. The washing may be carried out on a static or a continuous basis wherein a continuous length of the fibrous material is passed through one or more wash solutions.

Following washing and prior to utilization as fibrous reinforcement in a composite article, the surface modified carbonaceous fibrous material is dried to remove any adhering wash solution. Such drying may be simply conducted by placing the same in a circulating air oven provided at about 70° to 250°C.

The theory whereby the high modulus carbonaceous fibrous material heretofore defined may be beneficially surface modified under the relatively mild electrolytic surface treatment conditions and brief residence times disclosed herein is considered complex and incapable of simple explanation. Additionally, the ability of one to produce the desired surface modification utilizing the conditions heretofore recited is considered to be most surprising when compared with the considerably more severe electrolytic surface modification conditions employed by others in the prior art.

The surface modification imparted to the graphitic carbonaceous fibrous material through the use of the present process has been found to exhibit an appreciable life which is not diminished to any substantial degree even after the passage of 30, or more days. Also, the single filament tensile properties of the carbonaceous fibrous material are not adversely influenced by the surface modification treatment of the present invention, and the surface of the resulting fibrous material is substantially free of pitting.

The surface treatment of the present process makes possible improved adhesive bonding between the graphitic carbonaceous fibers, and a resinous matrix material. Accordingly, carbon fiber reinforced composite materials which incorporate fibers treated as heretofore described exhibit an enhanced interlaminar shear strength, flexural strength, compressive strength, etc. The resinous matrix material employed in the formation of such composite materials is commonly a polar thermosettng resin such as an epoxy, a polyimide, a polyester, a phenolic, etc., or a thermoplastic resin. The graphitic carbonaceous fibrous material is commonly provided in such resulting composite materials in either an aligned or random fashion in a concentration of about 20 to 70 percent by volume.

The following examples are given as specific illustrations of the invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples.

EXAMPLE I

A high strength-high modulus continuous filament graphitic carbonaceous yarn derived from an acrylonitrile homopolymer was selected as the starting material for use in the present process. The graphitic carbonaceous yarn was provided as a continuous length and consisted of 25 ends twisted in a yarn bundle at a rate of 0.5 turn per inch. Each end consisted of about 385 continuous filaments, each having a denier per filament of about 0.9. The graphitic carbonaceous yarn was formed by heating the acrylonitrile homopolymer fibers in air at a temperature of about 270°C. for about 175 minutes, and by subsequently heating the resulting stabilized yarn in a circulating nitrogen atmosphere to a maximum temperature of about 2,650°C. in accor-

dance with the teachings of commonly assigned U.S. Ser. No. 244,990, filed Apr. 17, 1972, of Charles M. Clarke which is herein incorporated by reference.

The yarn prior to surface treatment in accordance with the present process exhibited a carbon content of about 99 percent by weight, a mean single filament Young's modulus of about 76 million psi, a density of 1.925 grams/cc., and a mean single filament tenacity of about 318,000 psi. The yarn exhibited a predominantly graphitic x-ray diffraction pattern.

The yarn **1** was supplied by feed bobbin **2** and continuously was passed in the directon of its length through the apparatus illustrated in the drawing wherein it was immersed in an aqueous solution of sodium hypochlorite **4.** The yarn was wrapped about grooved graphite roller **8** and grooved polyvinylchloride roller **10** as it passed through the apparatus. The rollers **8** and **10** were mounted on supports **12** and **14** provided in a polymethylmethacrylate vessel **6.** The aqueous solution of sodium hypochlorite **4** was provided at room temperature (i.e., at about 25°C.), had a pH of 11, and an active chlorine concentration of 5.25 percent by weight. The aqueous solution of sodium hypochlorite was obtained under the designation of Clorox household bleach solution. While immersed in aqueous solution for a residence time of about 9 minutes, a DC current was applied to the yarn via contact with graphite roller **8** at a current density of 2.7 milliamps (i.e., 0.0027 amps) per square centimeter of surface area of the immersed yarn. The graphite roller **8** was connected to power source **16** by electrical lead **18.** The cathode consisted of a pair of graphite plates **20** and **22** which were also immersed in the sodium hypochlorite solution **4** and were connected to the power source **16** by electrical leads **24** and **26.** The resulting surface treated yarn **28** was taken up on rotating bobbin **30.** At the conclusion of the surface treatment the aqueous solution exhibited a pH of 9.6 and an active chlorine concentration of 4.6 percent by weight.

Following the immersion in the aqueous solution of sodium hypochlorite, the yarn was washed by (a) immersing the same in flowing tap water for 15 minutes, (b) contacting the same with a 2 percent hydrochloric acid solution provided in distilled water for about 1 minute, and (c) rinsing the same with deionized water for **15** minutes. The yarn was next dried in a forced air circulating oven at 70°C. for approximately 16 hours. The tensile properties of the resulting fibers were substantially unchanged. More specifically, the mean single filament Young's modulus of the surface treated yarn was 75 million psi, and the mean single filament tenacity was unchanged.

A composite article was next formed employing the surface modified yarn as a reinforcing media in an epoxy resin matrix. The composite article was a rectangular bar consisting of about 59.7 percent by volume of the yarn and having dimensions of ⅛ inch × ¼ inch × 5 inches. The composite article was formed by impregnation of the yarn in a liquid epoxy resinhardner mixture at 80°C., followed by unidirectional layup of the required quantity of the impregnated yarn in a steel mold, and compression molding of the layup for 2 hours at 93°C., and 2.5 hours at 200°C. in a heated platen press. The mold was cooled slowly to room temperature, and the composite article was removed from the mold cavity and cut to size for testing. The resinous matrix material used in the formation of the composite article was provided as a solventless system which contained 100 parts by weight of epoxy resin and about 87 parts by weight of anhydride curing agent.

The resulting composite article exhibited a horizontal interlaminar shear strength of 8,540 psi, a flexural strength of 128,000 psi, and a flexural modulus of 34,000,000 psi.

The horizontal interlaminar shear strength was determined by short beam testing of the fiber reinforced composite according to the procedure of ASTM D2344-65T as modified for straight bar testing at a 4 : 1 span to depth ratio. The flexural strength of the fiber reinforced composite was determined by four point bending according to the procedure of ASTM D2344 at a 3.2 : 1 span to depth ratio. The modulus was also determined by four point bending.

For comparative purposes Example I was repeated with the exception that the high strength-high modulus continuous filament grpahitic carbonaceous yarn underwent no form of surface modification prior to incorporation in the composite article. The resulting composite article exhibited a horizontal interlaminar shear strength of only 3150 psi, a flexural strength of 121,000 psi, and a flexural modulus of 35,200,000 psi.

EXAMPLE II

Example I was repeated with the exception that the high strengthhigh modulus continuous filament graphitic carbonaceous yarn was surface modified while immersed in the aqueous solution of sodium hypochlorite for a time of about 5.5 minutes at a current density of 3.6 milliamps (i.e., 0.0036 amps) per square centimeter of surface area of the immersed yarn. At the conclusion of the surface treatment the aqueous solution exhibited a pH of 9.44 and an active chlorine concentration of 4.19 percent by weight. The resulting composite article exhibited a horizontal interlaminar shear strength of 9340 psi, a flexural strength of 121,000 psi, and a flexural modulus of 37,500,000 psi.

EXAMPLE III

Example I was repeated with the exception that the high strengthhigh modulus continuous filament graphitic carbonaceous yarn was surface modified while immersed in the aqueous solution of sodium hypochlorite for a residence time of 5.5 minutes at a current density of about 4 milliamps (i.e., about 0.004 amps) per square centimeter of surface area of the immersed yarn. At the conclusion of the surface treatment the aqueous solution exhibited a pH of 9.44 and an active chlorine concentration of 4.12 percent by weight. The resulting article exhibited a horizontal interlaminar shear strength of 10,500 psi, a flexural strength of 117,000 psi, and a flexural modulus of 34,000,000 psi.

Although the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations are to be considered within the purview and scope of the claims appended hereto.

We claim:

1. An improved electrolytic process for enhancing the ability of an electrically conductive carbonaceous fibrous material containing at least about 90 percent carbon by weight and exhibiting a mean single filament Young's modulus of at least about 60 million psi and a

predominantly graphitic x-ray diffraction pattern to bond to a resinous matrix material comprising:

a. immersing said fibrous material in an aqueous electrolytic solution of sodium hypochlorite having a pH of about 8 to 12 and an active chlorine concentration of about 1 to 7 percent by weight,

b. providing a cathode in contact with said aqueous electrolytic solution and in a spaced relationship to said immersed fibrous material,

c. applying electrical current to said fibrous material while immersed in said aqueous electrolytic solution of sodium hypochlorite at a current density of about 2.5 to 12 milliamps per square centimeter of surface area of said immersed fibrous material for a residence time of about 2 to 10 minutes with said fibrous material serving as an anode,

d. washing the resulting carbonaceous fibrous material to remove residual aqueous electrolytic solution adhering to the same, and

e. drying the same.

2. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material in accordance with claim **1** wherein said carbonaceous fibrous material contains at least about 95 percent carbon by weight.

3. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material in accordance with claim **1** wherein said carbonaceous fibrous material exhibits a mean single filament Young's modulus of about 60 to 90 million psi.

4. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material in accordance with claim **1** wherein said carbonaceous fibrous material is continuously passed through said aqueous electrolytic solution in the direction of its length.

5. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material in accordance with claim **1** wherein said aqueous electrolytic solution of sodium hypochlorite has an active chlorine concentration of about 3 to 7 percent by weight.

6. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material in accordance with claim **1** wherein said aqueous solution of sodium hypochlorite has a pH of about 10.5 to 11.5 and an active chlorine concentration of about 5.025 to 5.4 percent by weight.

7. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material according to claim **1** wherein said aqueous electrolytic solution is provided at a temperature of about 20° to 35°C.

8. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material according to claim **1** wherein said electrical current is applied to said fibrous material for about 2 to 6 minutes.

9. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix according to claim **1** wherein said washing is conducted by initially contacting said resulting carbonaceous fibrous material with a solution of a dilute acid, and by subsequently rinsing the same with water.

10. An improved process for enhancing the ability of a carbonaceous fibrous material containing at least about 95 percent carbon by weight and exhibiting a mean single filament Young's modulus of about 60 to 90 million psi and a predominantly graphitic x-ray diffraction pattern to bond to a resinous matrix material comprising:

a. immersing said fibrous material in an aqueous electrolytic solution of sodium hypochlorite provided at about 20° to 35°C. having a pH of about 10.5 to 11.5 and an active chlorine concentration of about 5.025 to 5.4 percent by weight,

b. providing a cathode in contact with said aqueous electrolytic solution and in a spaced relationship to said immersed fibrous material,

c. applying electrical current to said fibrous material while immersed in said aqueous electrolytic solution of sodium hypochlorite at a current density of about 4 to 12 milliamps per square centimeter of surface area of said immersed fibrous material for a residence time of about 2 to 6 minutes with said fibrous material serving as an anode,

d. washing the resulting carbonaceous fibrous material to remove residual aqueous electrolytic solution adhering to the same, and

e. drying the same.

11. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material in accordance with claim **10** wherein said carbonaceous fibrous material is continuously passed through said aqueous electrolytic solution in the direction of its length.

12. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material in accordance with claim **10** wherein said electrolytic aqueous solution of sodium hypochlorite is provided at about 25°C.

13. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material in accordance with claim **10** wherein said washing is conducted by initially contacting said resulting carbonaceous fibrous material with a solution of a dilute acid, and by sebsequently rinsing the same with water.

14. An improved process for enhancing the ability of a carbonaceous fibrous material containing at least about 95 percent carbon by weight and exhibiting a mean single filament Young's modulus of about 70 to 90 million psi and a predominantly graphitic x-ray diffraction pattern to bond to a resinous matrix material comprising:

a. immersing said fibrous material in an aqueous solution of sodium hypochlorite provided at about 25°C. having a pH of about 11 and an active chlorine concentration of about 5.025 to 5.4 percent by weight,

b. providing a cathode in contact with said aqueous electrolytic solution and in a spaced relationship to said immersed fibrous material,

c. applying electrical current to said fibrous material while immersed in said aqueous electrolytic solution of sodium hypochlorite at a current density of about 4 milliamps per square centimeter of surface area of said immersed fibrous material for a residence time of about 5 to 6 minutes with said fibrous material serving as an anode,

d. washing the resulting carbonaceous fibrous material to remove residual aqueous electrolytic solution adhering to the same, and

e. drying the same.

15. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material in accordance with claim **14** wherein said carbonaceous fibrous material is continuously passed through said aqueous electrolytic solution in the direction of its length.

16. A composite article exhibiting enhanced interlaminar shear strength comprising a resinous matrix material having incorporated therein a carbonaceous fibrous material having its surface characteristics modified in accordance with the process of claim **1.**

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