Oct. 23, 1973

K. C. HOU

SURFACE TREATMENT OF PREVIOUSLY GRAPHITIZED CARBONACEOUS

3,767,774

Filed Aug. 12, 1971

2 Sheets-Sheet 1

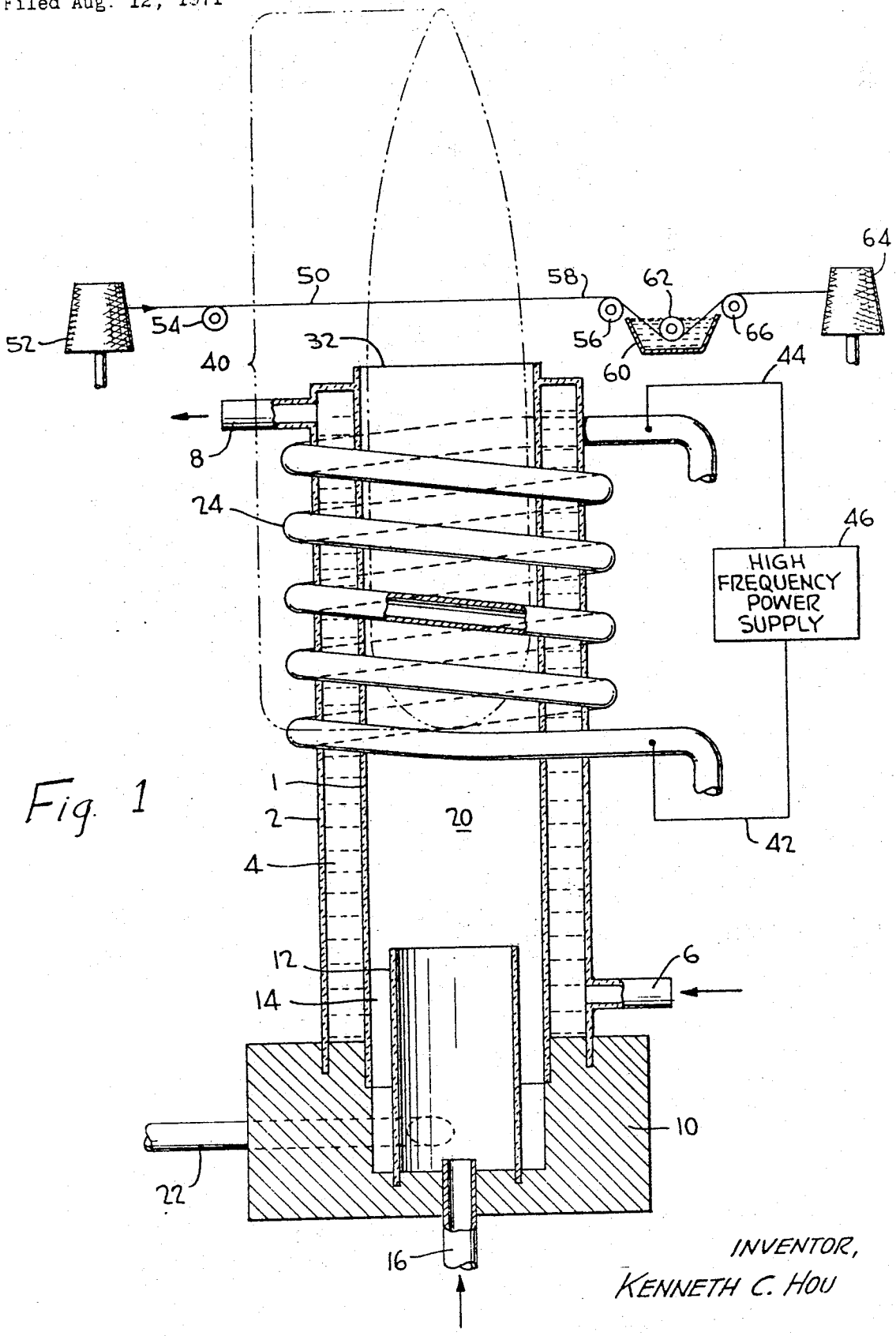



Fig. 1

INVENTOR,
KENNETH C. HOU

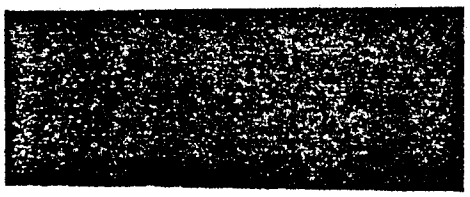
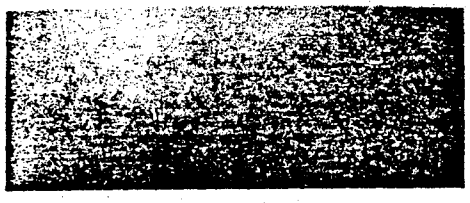
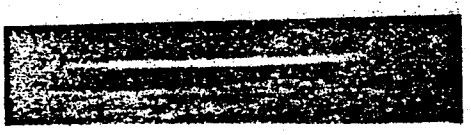


FIG. 2





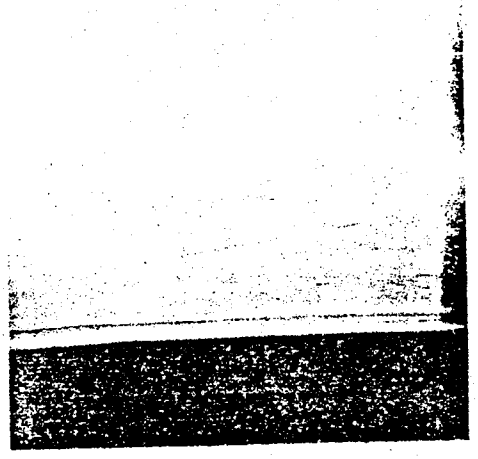


FIG. 3

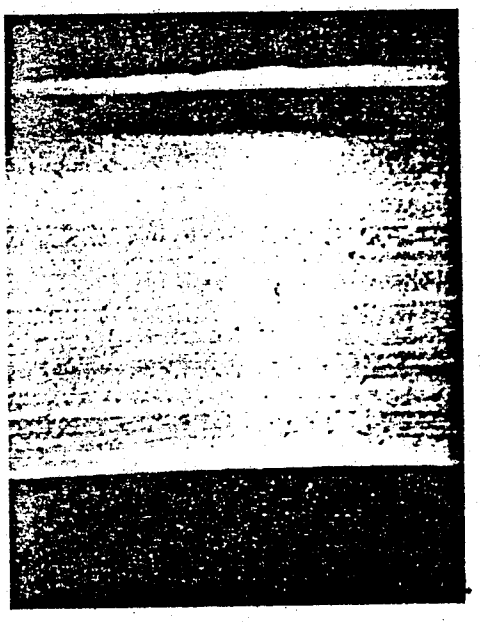


FIG. 4

INVENTOR
KENNETH C. HOU

United States Patent Office 3,767,774 Patented Oct. 23, 1973



3,767,774

# SURFACE TREATMENT OF PREVIOUSLY GRAPHITIZED CARBONACEOUS FIBERS

Kenneth C. Hou, Whippany, N.J., assignor to Celanese Corporation, New York, N.Y.

Filed Aug. 12, 1971, Ser. No. 171,233
Int. Cl. C01b 31/07
U.S. Cl. 423—447 10 Claims

## ABSTRACT OF THE DISCLOSURE

An improved process is provided for modifying the surface characteristics of a predominantly graphitic carbonaceous fibrous material thereby to facilitate enhanced adhesion between the fibrous material and a matrix material. The fibrous material is continuously passed for an exteremely brief residence time transversely through the tip of an inert gas thermal plasma present in an open atmosphere. 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.

## BACKGROUND OF THE INVENTION

In the search for high performance materials, considerable interest has been focused upon graphitic carbon fibers. Graphite 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. Graphite 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 carbon 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 carbon fiber reinforced composites include aerospace structural components, rocket motor casings, deep-submergence vessels and ablative materials for heat shields on re-entry vehicles.

In the prior art numerous materials have been proposed for use as possible matrices in which graphitic carbon 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 carbon fibers of highly desirable strength and modulus characteristics, difficulties have arisen when one attempts to gain the full advantages of such properties in the resulting carbon 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 and British Pat. No. 1,180,441



to Nicholas J. Wadsworth and William Watt wherein it is taught to heat a carbon fiber normally within the range of 350° C. to 850° C. (e.g. 500 to 600° C.) in an oxidizing atmosphere such as air for an appreciable period of time. Other atmospheres comtemplated 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. Improved carbon fiber surface modification processes are disclosed in commonly assigned U.S. Ser. Nos. 65,454 and 65,456, filed Aug. 20, 1970; and U.S. Ser. No. 99,169, filed Dec. 17, 1970.

It is an object of the invention to provide a continuous process for rapidly and efficiently modifying the surface characteristics of graphitic carbon fibers.

It is an object of the invention to provide an improved process for improving the ability of graphitic carbon fibers to bond to a resinous matrix material.

It is an object of the invention to provide a process for modifying the surface characteristics of graphitic carbon fibers which eliminates the need for extended treatment periods.

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

It is a further object of the invention to provide an improved process for improving the ability of graphitic carbon fibers to bond to a resinous matrix material in the absence of any substantial diminution of single filament tensile properties.

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 a process for the surface treatment of a predominantly graphitic carbonaceous fibrous material comprises:

(a) electrically inducing heating of a stream of inert gas present within a laterally enclosed zone to a thermal plasma state of at least about one atmosphere pressure wherein from about 5 to about 50 percent of the gas is in an ionized state, and wherein the tip of the thermal plasma exhibits a temperature of about 4,000 to 12,000° K. and extends beyond the confines of the laterally enclosed zone into an open atmosphere, and

(b) continuously passing in the direction of its length a continuous length of a previously graphitized carbonaceous fibrous material containing at least about 95 percent carbon by weight and exhibiting a predominantly graphitic X-ray diffraction pattern transversely through the tip of the resulting thermal plasma present in the open atmosphere for a residence time of about 0.4 to 3.5 seconds wherein the previously graphitized carbonaceous fibrous material is heated to a maximum temperature of about 1500 to 2200° C. and the surface characteristics thereof are beneficially modified and rendered capable of enhanced adhesion with a matrix material.

## DESCRIPTION OF DRAWINGS

FIG. 1 is a plan view partially cut away of a representative apparatus suitable for use in carrying out the process of the present invention.

FIG. 2 is a photograph made with the aid of a scanning electron microscope at a magnification of 6000× of a portion of a graphitic carbon filament which has not undergone surface modification.

FIG. 3 is a photograph made with the aid of a scanning electron microscope at a magnification of 6000× of a

portion of a similar graphitic carbon filament which has been surface treated in accordance with the present invention.

FIG. 4 is a photograph made with the aid of a scanning electron microscope at a magnification of 5700× of a portion of a similar graphitic carbon filament which has undergone excessive surface modification and the single filament tensile properties thereof substantially diminished.

## DESCRIPTION OF PREFERRED EMBODIMENTS

### The starting material

The carbonaceous fibers which are modified in accordance with the process of the present invention contain at least about 95 percent carbon by weight and exhibit a predominantly graphitic X-ray diffraction pattern. In a preferred embodiment of the process the graphitized carbonaceous fibers which undergo surface treatment contain at least about 99 percent carbon by weight.

The graphitized carbonaceous fibrous materials are provided in a continuous length in any one of a variety of physical configurations provided substantial access to the fiber surface is possible during the surface modification treatment described hereafter. For instance, the 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 fibrous material is one or more continuous multifilament yarn. When a plurality of multifilament yarns are surface treated simultaneously (as described hereafter), they may be continuously passed through the treatment zone while in parallel and in the form of a flat ribbon.

The previously graphitized carbonaceous fibrous material which is treated in the present process optionally may be provided with a twist which tends to improve the handling characteristics. For instance, a twist of about 0.1 to 5 t.p.i., and preferably about 0.3 to 1.0 t.p.i., 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 graphitized carbonanceous 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 at a more highly elevated temperature until a carbonized and graphitized fibrous material is formed. For instance, the thermally stabilized material may be carbonized by heating in an inert atmosphere at a temperature of about 900 to 1000° C. and subsequently heated to a maximum temperature of 2000 to 3100° C. (preferably 2400 to 3100° C.) in an inert atmosphere for a sufficient residence time to produce substantial amounts of graphitic carbon.

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 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 graphitized carbonaceous fibrous materials 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 graphitized 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 mol percent of recurring acrylonitrile units with not more than 15 mol 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 graphitized 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 is 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 mol 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.

In preferred techniques for forming the starting material for the present process a stabilized acrylic fibrous material is carbonized and graphitized while passing through a temperature gradient present in a heating zone in accordance with the procedures described in commonly assigned U.S. Ser. Nos. 777,275, filed Nov. 20, 1968 of Charles M. Clarke, now abandoned; 17,780, filed Mar. 9, 1970 of Charles M. Clarke, Michael J. Ram, and John P. Riggs, now U.S. Pat. No. 3,677,705; and 17,832, filed Mar. 9, 1970 of Charles M. Clarke, Michael J. Ram, and Arnold J. Rosenthal. Each of these disclosures 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 mol percent of acrylonitrile units and up to about 15 mol-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 1600° C. to form a continuous length of carbonized fibrous material, and in which the carbonized fibrous material is subsequently raised from about 1600° C. to a maximum temperature of at least about 2400° 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 graphitized 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 and graphitization 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 substantially the same temperature as that of the carbonization/graphitization heating zone through which it is continuously passed.

## The surface treatment

During the surface treatment process of the present invention, a stream of inert gas present in a laterally enclosed zone is heated via electrical induction of a thermal plasma state of at least about one atmosphere pressure (e.g. 1 to 3 atmospheres pressure) wherein from about 5 to about 50 percent of the gas is in an ionized state, and wherein the tip, i.e. the tail, of the thermal plasma extends beyond the confines of the laterally enclosed zone into an open atmosphere. The percent of the gas in an ionized state may be determined by spectroscopic measurements, as will be apparent to those skilled in the art.

Preferred inert gases for use in the process are monoatomic, e.g. argon, helium, neon, zenon, and radon. Particularly preferred monoatomic inert gases are argon and helium. A diatomic inert gas such as nitrogen may alternatively be utilized in the process. More electrical power is required, however, when the inert gas is diatomic.

In a preferred embodiment of the process the stream of inert gas is introduced into the laterally enclosed zone from at least two different locations. One portion of the stream is introduced tangentially to the inner peripheral regions of the zone (e.g. the inner wall of a cylindrical zone) and a second portion of the stream is introduced longitudinally along the central region of the zone. The spiral flow present within the gas stream accordingly creates a thermal pinch effect or a vortex stabilization effect wherein the thermal plasma state is positioned within the central portion of the zone in the substantial absence of contact with the periphery of the laterally enclosed zone. The periphery of the laterally enclosed zone may therefore be formed from conventional materials, such as a quartz tube. A cooling medium may also circulate within the wall of the zone.

The temperature of the gas throughout the thermal plasma commonly ranges from about 4,000 to 20,000° K. Accordingly, the thermal plasma state is substantially different than conventional plasmas (e.g. glow discharges) which are encountered in neon lights, etc., due to the extremely high temperatures in the former because of the higher pressure of the gas present and the higher degree of ionization.

The tip or tail of the thermal plasma which extends into an open atmosphere commonly measures about 0.5 to 8 inches, or more, in length and preferably about 2 to 4 inches in length. The tip of the thermal plasma is commonly at a lesser temperature than the base of the same positioned within the laterally enclosed zone and is provided at a temperature of about 4,000 to 12,000° K. If, desired, the configuration of the tip of the thermal plasma may be modified by the use of a deflector. The length of the thermal plasma tip also may be modified by adjusting the flow rate of the inert gas.

The thermal plasma utilized in the present process is created by an electrodeless discharge technique. In accordance with this technique the thermal plasma state is achieved by heating the gas to ionization temperature by means of electrical induction created preferably by a surrounding coil carrying radio frequency (e.g. 0.5 kHz. to 2500 mHz., and preferably 1 to 30 mHz.) current of 3 to 100 kw. The thermal plasma may be initiated by temporarily inserting a conductor such as a metallic wire or graphite rod into the radio frequency field whereby the field is concentrated at the tip of the conductor and the breakdown potential of the inert gas stream lowered. A finite zone is established within the reactor wherein the inert gas exists in the thermal plasma state. By adjusting and maintaining the flow rate of the inert gas, the input of power, and the size of the zone wherein the gas exists, the thermal plasma state may be effectively controlled. The length of the thermal plasma is also influenced to a substantial degree by the length of the surrounding coil. If desired, the magnetic field may be strengthened through the permanent positioning of a metallic sheet within the magnetic field created by the radio frequency power.

Once an inert gas thermal plasma state is created with the tip thereof which exhibits a temperature of about 4,000 to 12,000° K. extending into an open atmosphere, the continuous length of previously graphitized carbonaceous fibrous material may be continuously passed in the direction of its length transversely through the same for a residence time of about 0.4 to 3.5 seconds, and more preferably for a residence time of about 1 to 2 seconds. When the fibrous material is provided as a relatively more compact assemblage of a plurality of fibers, then longer residence times within the range indicated advantageously may be employed. Also, graphitic carbon fibrous materials having an extremely high Young's modulus tend to require longer residence times. While present within the tip of the thermal plasma, the fibrous material is heated to a maximum temperature of about 1500 to 2200° C., and more preferably to a maximum temperature of about 1600 to 2000° C. The maximum temperature imparted to the fibrous material may be varied depending upon the exact portion of the plasma tip which is transversed. The portion of the tip closest to the laterally enclosed zone will tend to heat the fibrous material to a higher maximum temperature. The temperature of the fibrous material may be determined by optical pyrometer techniques which are well known in the art.

If desired, the basic process of the invention may be optionally modified through the introduction of a minor quantity of an additive, such as oxygen, into the inert gas stream which is inductively converted to a thermal plasma state. Alternatively, inorganic powders, such as boron nitride or boron carbide, can be introduced into the inert gas stream, and ultimately deposited upon the surface of the fibrous material undergoing treatment.

The theory whereby the surface of a previously graphitized carbonaceous fibrous material is modified in the present process is considered complex and incapable of simple explanation. It is believed, however, that the resulting modification is induced by a combination of physical and chemical interactions between the ionized inert gas, molecular oxygen provided by the open atmosphere, and the fibrous material.

The surface treatment of the present process is accomplished in the absence of any substantial diminution of the single filament tensile properties of the fibrous material. More specifically, the single filament tensile properties (i.e. tensile strength and Young's modulus) are substan-

tially identical following the surface treatment to those properties exhibited prior to the surface treatment. A comparison of fibers of FIGS. 2 (control) and 3 (surface treated in accordance with the present process) indicates that the appearance of the fibrous material following the surface treatment is substantially unchanged, with only a very shallow pitting of the fiber surface being observable. Both FIGS. 2 and 3 show a finely textured surface on the lobes of the fiber; however, the troughs between the lobes of the fiber of FIG. 3 appear to be slightly rougher in texture. FIG. 4 indicates the appearance of a fiber which has undergone an excessive and undersirable surface treatment and is excessively pitted.

The surface modification imparted to the previously 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.

The surface treatment of the present process makes possible improved adhesive bonding between the resulting fibrous material, and a resinous matrix material. Accordingly, graphite fiber reinforced composite materials which incorporate fibers treated as heretofore described exhibit enhanced shear strength, flexural strength, compressive strength, etc. The resinous matrix material employed in the formation of such composite materials is commonly a polar thermosetting resin such as an epoxy, a polyimide, a polyester, a phenolic, etc. The graphitized 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.

In each example a continuous length of previously graphitized carbonaceous continuous multifilament yarn containing in excess of 99 percent carbon by weight was subjected to the surface treatment of the present invention utilizing the apparatus of FIG. 1.

The apparatus wherein the surface modification treatment was conducted includes a vertical quartz tube **1** having a length of 6 inches, an inner diameter of 1½ inches, and a wall thickness of 1/16 inch. A larger concentric quartz tube **2** having an internal diameter of 2¼ inches and a wall thickness of 1/16 inch is provided outside quartz tube **1** and forms a wall cavity **4** wherein a water cooling medium is continuously circulated. The cooling medium enters inlet **6** and exits at outlet **8**. The lower ends of quartz tubes **1** and **2** are mounted in steel base **10**. Also mounted in steel base **10** is a relatively short section of cylindrical Pyrex glass tubing **12** having a length of 2 inches, an inner diameter of 1 inch and a wall thickness of 1/16 inch which is provided with perforations (not shown) to aid in the mixing of the inert gas. An annular space **14** is accordingly provided between the inner wall of quartz tube **1** and the outer wall of Pyrex glass tubing **12**. Gas inlet tube **16** passes through base **10** and is directed longitudinally along the central region of the zone **20** defined by quartz tube **1**. Gas inlet tube **22** also is situated within base **10** and communicates tangentially with annular space **14**.

A hollow copper induction coil **24** having an outer diameter of ¼ inch and a wall thickness of 1/32 inch is wound about and in contact with the outer wall of quartz tube **2**. The continuous coil has 5 turns which are each separated by ⅜ inch. Water is continuously circulated through hollow copper induction coil **24**.

Argon gas is introduced through inlet tube **22** tangentially into annular space **14** at a rate of 20 ft.$^3$/hr. This gas accordingly passes spirally along the internal walls of quartz tube **1** (the inner peripheral region of zone **20**). Argon gas is introduced through inlet tube **16** at a rate of 15 ft.$^3$/hr. which is directed along the central region of zone **20** after passing through Pyrex glass tubing **12**. The pressure of the gas stream passing upwardly through zone **20** is slightly in excess of 1 atmosphere. Quartz tube **1** is open to the air atmosphere at **32**.

A thermal plasma **40** is electrically induced within the zone **20** following the temporary insertion of a metallic wire (not shown) through opening **32** wherein about 5 to 15 percent of the argon gas is in an ionized state. Radio frequency power is applied to the copper induction coil **24** via leads **42** and **44** and high frequency power supply **46**. The power supply **46** consists of a Lepel Model No. T–10–3–MC–E–S high frequency power unit capable of delivering up to a 10 kW signal at a frequency of up to 8 mHz. A 10 kv. peak-to-peak A.C. signal having a frequency of 5 mHz. is applied.

The thermal plasma **40** has a total length of about 6 inches, and a maximum width of 1¼ inches. Approximately 3 inches of the thermal plasma **40** extend beyond the open end **32** of vertical quartz tube **1** into the air atmosphere. The temperature of the gas within the thermal plasma ranges from about 4,000° K. at the extreme tip to about 8,000° K. at the area surrounded by coil **24**. The temperature of the gas within the tip portion of the thermal plasma present within the air atmosphere ranges from about 4,000 to 6,000° K.

The previously graphitized carbonaceous yarn **50** is next continuously unwound from feed bobbin **52**, and is continuously passed in the direction of its length through the tip of the thermal plasma **40** which is present in the air atmosphere. The yarn speed and exact portion of the thermal plasma transversed are varied to produce the surface treatment residence times, and maximum yarn temperatures indicated. The position of the yarn within the tip of the thermal plasma 40 is governed by the locations of rollers **54** and **56**.

The resulting surface treated yarn **58** is next passed through liquid resin bath **60** consisting of a liquid epoxy resin-hardener mixture at ambient temperature (i.e. 25° C.) by the aid of immersed roller **62**, and the resin impregnated surface treated yarn is taken up on bobbin **64** with the aid of roller **66**. The liquid resin system was provided as a solventless system which contained 100 parts by weight epoxy resin and about 87 parts by weight of anhydride curing agent.

Composite articles were next formed employing the resin impregnated surface modified yarn. The composite articles were rectangular bars consisting of about 50 percent by volume of the yarn and having dimensions of ⅛ inch x ¼ inch x 5 inches. The composite articles were formed by unidirectional layup of the required quantity of impregnated yarn in a steel mold and compression molding the layup for 2 hours at 95° C., and 3 hours at 200° C. in a heated platen press at about 100 p.s.i. pressure. The mold was cooled slowly and the composite article was removed from the mold cavity and cut to size for testing.

The horizontal interlaminar shear strengths reported were determined by short beam testing of the graphite 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.

## EXAMPLE I

The graphitic carbonaceous yarn undergoing treatment was derived from acrylonitrile homopolymer yarn in accordance with procedures described in United States Ser. Nos. 749,957, filed Aug. 5, 1968 and 777,957 filed Nov. 20, 1968. The yarn consisted of a 1600 fil. bundle having a total denier of about 1000, had a carbon content in excess of 99 percent by weight, exhibited a predomininantly graphitic X-ray diffraction pattern, a single filament tenacity of about 13 grams per denier and a single filament Young's modulus of about 50 million p.s.i.

The following data summarizes the surface treatment

conditions employed and the composite properties achieved.

| Sample | Sample distance from enclosed zone (inches) | Maximum yarn temperature (° C.) | Residence time in tip of thermal plasma (secs.) | Interlaminar shear strength of composite (p.s.i.) |
|---|---|---|---|---|
| A | 1 | 1,750 | 2.3 | 9,750 |
| B | 1 | 1,750 | 2.3 | 8,100 |
| C | 0.8 | 1,800 | 1.2 | 9,620 |
| D | 0.8 | 1,800 | 1.2 | 10,400 |

For comparative purposes a composite article was formed as heretofore described employing an identical graphitized carbonaceous yarn without subjecting the same to any form of surface modification. The average horizontal interlaminar shear strength of the composite article was only 3000 p.s.i.

## EXAMPLE II

The graphitic carbonaceous yarn undergoing treatment was derived from a cellulosic precursor and was commercially available from the Union Carbide Corporation under the designation Thornel 50 carbon yarn. The yarn consisted of a 720 fil. bundle having a total denier of about 350, had a carbon content in excess of 99 percent by weight, exhibited a predominantly graphitic X-ray diffraction pattern, a single filament tenacity of about 338,000 p.s.i., and a single filament Young's modulus of about 52 million p.s.i.

The following data summarizes the surface treatment conditions employed and the composite properties achieved.

| Sample | Sample distance from enclosed zone (inches) | Maximum yarn temperature (° C.) | Residence time in tip of thermal plasma (secs.) | Interlaminar shear strength of composite (p.s.i.) |
|---|---|---|---|---|
| A | 1.5 | 1,500 | 2.3 | 7,512 |
| B | 1.25 | 1,650 | 2.3 | 8,733 |
| C | 0.8 | 1,800 | 2.3 | 9,013 |
| D | 0.8 | 1,800 | 1.8 | 10,400 |
| E | 0.5 | 2,000 | 1.8 | 9,120 |
| F | 0.8 | 1,800 | 0.6 | 11,700 |
| G | 0.5 | 2,000 | 0.6 | 10,750 |
| H | 0.8 | 1,800 | 0.4 | 8,485 |

For comparative purposes a composite article was formed as heretofore described employing an identical graphitized carbonaceous yarn without subjecting the same to any form of surface modification. The average horizontal interlaminar shear strength of the composite article was only 3480 p.s.i.

## EXAMPLE III

The graphitic carbonaceous yarn undergoing treatment was derived from acrylonitrile homopolymer yarn in accordance with procedures described in United States Ser. Nos. 749,957, filed Aug. 5, 1968, and 777,957, filed Nov. 20, 1968. The yarn consisted of a 400 fil. bundle having a total denier of about 400, had a carbon content in excess of 99 percent by weight, exhibited a predominantly graphitic X-ray diffraction pattern, a single filament tenacity of about 13 grams per denier and a single filament Young's modulus of about 70 million p.s.i.

The following data summarizes the surface treatment conditions employed and the composite properties achieved.

| Sample | Sample distance from enclosed zone (inches) | Maximum yarn temperature (° C.) | Residence time in tip of thermal plasma (secs.) | Interlaminar shear strength of composite (p.s.i.) |
|---|---|---|---|---|
| A | 1 | 1,750 | 3.2 | 5,755 |
| B | 1 | 1,750 | 2.8 | 6,187 |
| C | 1 | 1,750 | 2.3 | 6,435 |
| D | 1 | 1,750 | 2.0 | 6,413 |
| E | 1 | 1,750 | 1.5 | 6,010 |



For comparative purposes a composite article was formed as heretofore described employing an identical graphitized carbonaceous yarn without subjecting the same to any form of surface modification. The average horizontal interlaminar shear strength of the composite article was only 2867 p.s.i.

In each of the above examples the single filament tensile properties of the graphitized carbonaceous yarns undergoing surface modification were substantially unimpaired as a result of the surface treatment.

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 and modifications are to be considered within the purview and scope of the claims appended hereto.

I claim:

1. A process for the surface treatment of a predominantly graphitic carbonaceous fibrous material comprising:

(a) electrically inducing heating of a stream of inert gas present within a laterally enclosed zone to a thermal plasma state of at least about one atmosphere pressure wherein from about 5 to about 50 percent of said gas is in an ionized state, and wherein the tip of said thermal plasma exhibits a temperature of about 4,000 to 12,000° K. and extends beyond the confines of said laterally enclosed zone into an open atmosphere, and

(b) continuously passing in the direction of its length a continuous length of a previously graphitized carbonaceous fibrous material containing at least about 95 percent carbon by weight and exhibiting a predominantly graphitic X-ray diffraction pattern transversely through said top of said resulting thermal plasma present in said open atmosphere for a residence time of about 0.4 to 3.5 seconds wherein said previously graphitized carbonaceous fibrous material is heated to a maximum temperature of about 1500 to 2200° C. and the surface characteristics thereof are beneficially modified and rendered capable of enhanced adhesion with a matrix material.

2. A process according to claim 1 wherein said continuous length of previously graphitized carbonaceous fibrous material contains at least about 99 percent carbon by weight and exhibits a predominantly graphitic X-ray diffraction pattern.

3. A process according to claim 1 wherein said continuous length of previously graphitized carbonaceous fibrous material is one or more continuous multifilament yarn.

4. A process according to claim 1 wherein said stream of inert gas is selected from the group consisting of nitrogen, argon, and helium.

5. A process according to claim 1 wherein said previously graphitized carbonaceous fibrous material is heated to a maximum temperature of about 1,600 to 2,000° C.

6. A process for the surface treatment of a predominantly graphitic carbonaceous fibrous material comprising:

(a) continuously introducing an inert gas tangentially to the inner peripheral regions of a laterally enclosed zone,

(b) continuously introducing an inert gas longitudinally along the central region of said laterally enclosed zone, with said inert gas being supplied within said laterally enclosed zone at a rate sufficient to establish a pressure of said gas of at least one atmosphere within said zone,

(c) continuously conducting about the outer peripheral boundaries of said laterally enclosed zone a radio frequency current sufficient to heat said inert gas to the ionization temperature thereof, thereby maintaining said inert gas in a thermal plasma state wherein from about 5 to about 50 percent of said gas is in

an ionized state, and wherein the tip of said thermal plasma exhibits a temperature of about 4,000 to 12,000° K. and extends beyond the confines of said laterally enclosed zone into an open atmosphere, and

(d) continuously passing in the direction of its length a continuous length of a previously graphitized carbonaceous fibrous material containing at least about 95 percent carbon by weight and exhibiting a predominantly graphitic X-ray diffraction pattern transversely through said tip of said resulting thermal plasma present in said open atmosphere for a residence time of about 0.4 to 3.5 seconds wherein said previously graphitized carbonaceous fibrous material is heated to a maximum temperature of about 1500 to 2200° C. and the surface characteristics thereof are beneficially modified and rendered capable of enhanced adhesion with a matrix material.

7. A process according to claim 6 wherein said continuous length of previously graphitized carbonaceous fibrous material contains at least about 99 percent carbon by weight and exhibits a predominantly graphitic X-ray diffraction pattern.

8. A process according to claim 6 wherein said continuous length of previously graphitized carbonaceous fibrous material is one or more continuous multifilament yarn.

9. A process according to claim 6 wherein said inert gas is selected from the group consisting of nitrogen, argon, and helium.



10. A process according to claim 6 wherein said previously graphitized carbonaceous fibrous material is passed transversely through said tip of said resulting thermal plasma present in said open atmosphere for a residence time of about 1 to 2 seconds wherein said previously graphitized carbonaceous fibrous material is heated to a maximum temperature of about 1600 to 2000° C.


**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 3,294,489 | 12/1966 | Millington et al. | 423—447 |
| 3,408,164 | 10/1968 | Johnson | 423—460 |
| 3,454,362 | 7/1969 | Spry | 423—447 X |
| 3,476,703 | 11/1969 | Wadsworth et al. | 260—37 |
| 3,539,295 | 11/1970 | Bam | 423—447 |

OTHER REFERENCES

Johnson: "Applied Polymer Symposia," No. 9, 229–243 (1969).

Sach et al.: "Chemical Abstracts," vol. 71, 1969, 103026h.



EDWARD J. MEROS, Primary Examiner

U.S. Cl. X.R.

106—307; 117—47; 260—37; 423—460