

July 10, 1973

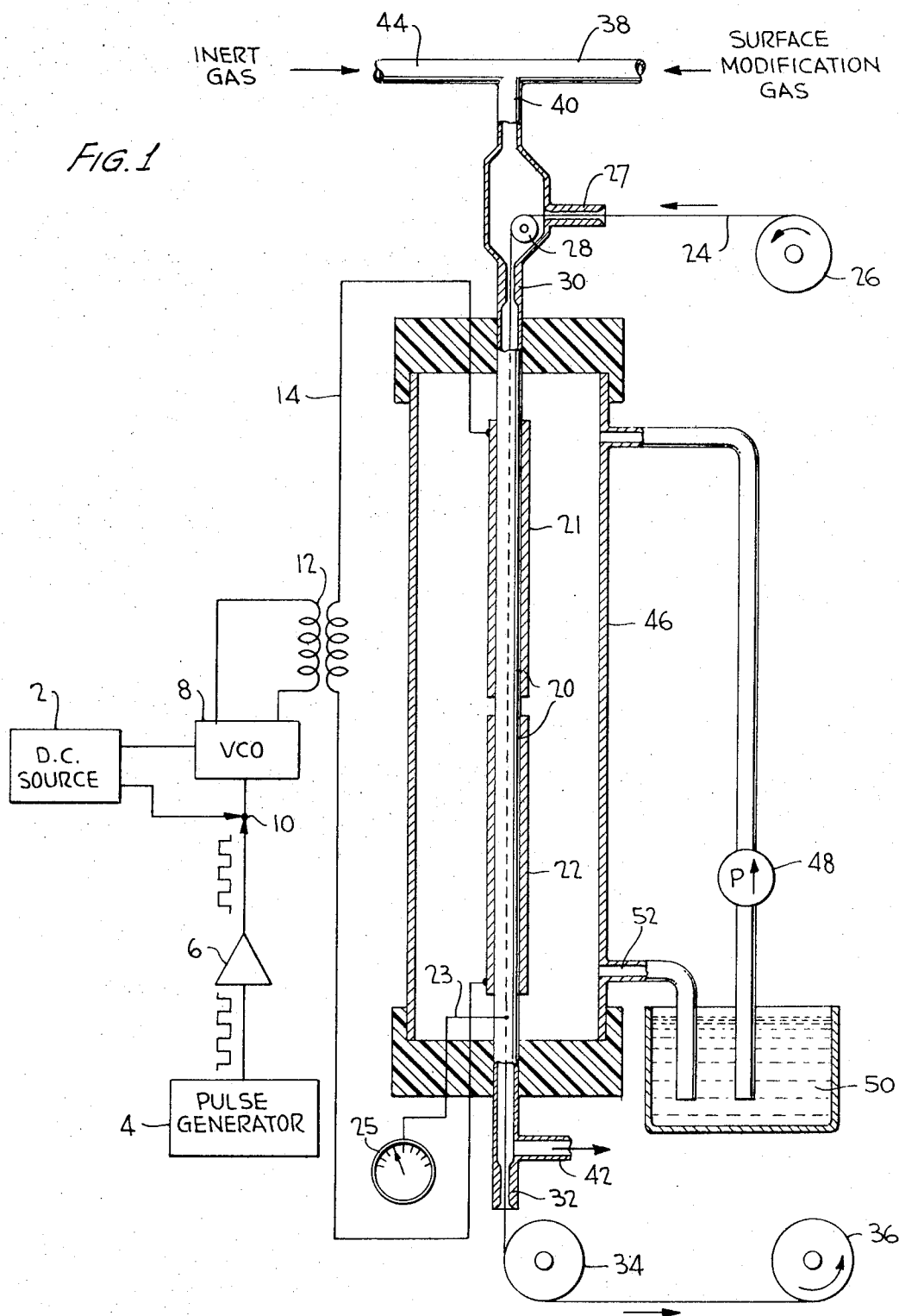
K. C. HOU

3,745,104

SURFACE MODIFICATION OF CARBON FIBERS

Filed Dec. 17, 1970

3 Sheets-Sheet 1



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SURFACE MODIFICATION OF CARBON FIBERS

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3 Sheets-Sheet 2

FIG. 1A

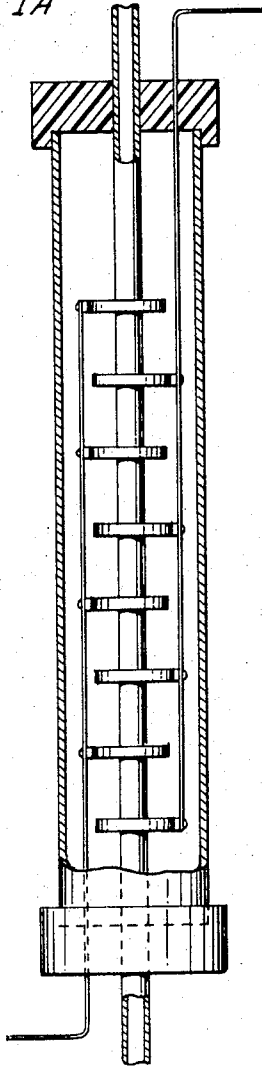


FIG. 1B

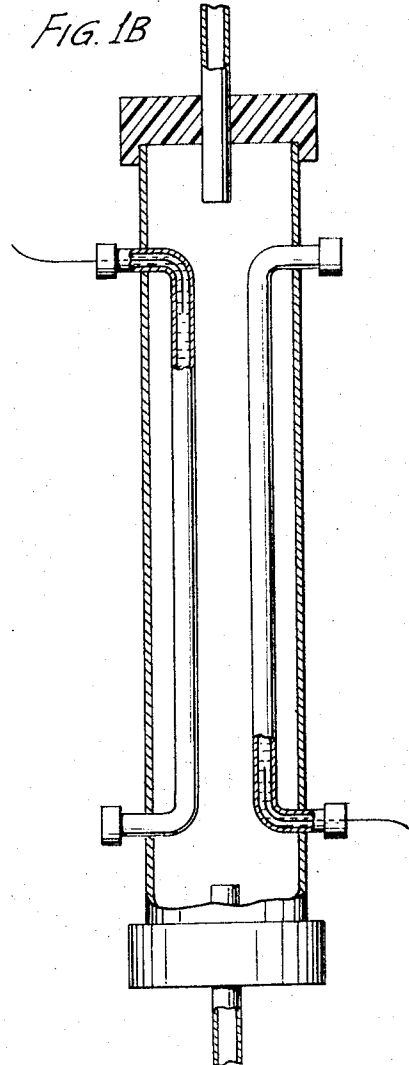
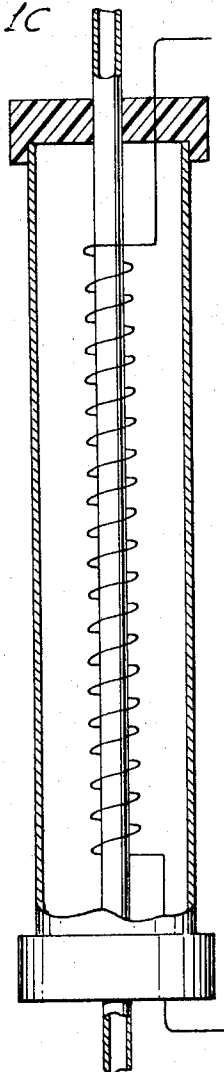


FIG. 1C



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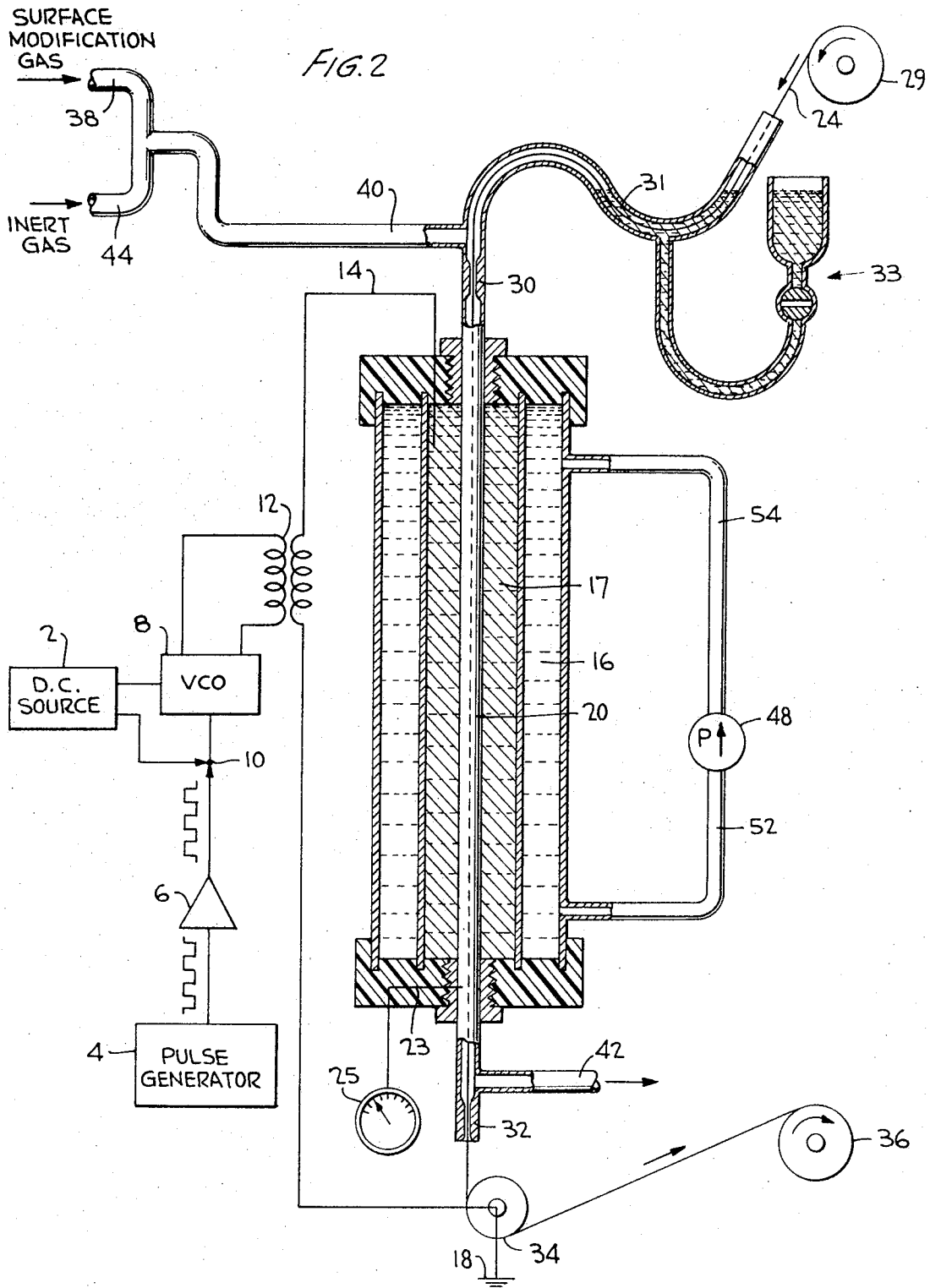
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SURFACE MODIFICATION OF CARBON FIBERS

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3 Sheets-Sheet 3



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3,745,104

SURFACE MODIFICATION OF CARBON FIBERS
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Filed Dec. 17, 1970, Ser. No. 99,169

Int. Cl. C01b 31/07

U.S. Cl. 204—164

19 Claims

ABSTRACT OF THE DISCLOSURE

A process is provided for modifying the surface characteristics of a carbonaceous fibrous material (i.e. either amorphous carbon or graphitic carbon) and to thereby facilitate enhanced adhesion between the fibrous material and a matrix material. The carbonaceous fibrous material is contacted for relatively brief residence time with an excited gas species at a moderate temperature of about 20 to 325° C. generated by applying high frequency electrical energy in pulsed form to a gaseous mixture comprising an inert gas and a surface modification gas. 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 carbon fibers. The term "carbon fibers" is used herein in its generic sense and includes graphite fibers as well as amorphous 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 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 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 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 carbon 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 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 car-

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bon fiber in order to make possible improved adhesion when present in a composite article. See, for instance, 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 (e.g. one hour or more). 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.

It is an object of the invention to provide a process for efficiently modifying the surface characteristics of carbon fibers with no substantial reduction in the single filament tensile properties.

It is an object of the invention to provide a process for improving the ability of 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 carbon fibers which may be conducted relatively rapidly at moderate temperatures and at atmospheric pressure.

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

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 modification of the surface characteristics of a carbonaceous fibrous material containing at least about 90 percent carbon by weight comprises (a) providing in a surface modification zone at a pressure of about 1 to 3 atmospheres a gaseous mixture comprising about 80 to 99.9 percent by volume of an inert gas and about 0.1 to 20 percent by volume of a surface modification gas selected from the group consisting of oxygen, carbon dioxide, nitric oxide, nitrous oxide, nitrogen dioxide, sulfur dioxide, water, and mixtures of the foregoing, (b) applying high frequency electrical power in pulsed form to said gaseous mixture sufficient to establish an excited gas species within said surface modification zone while maintaining the temperature of said zone at about 20 to 325° C., and (c) contacting said carbonaceous fibrous material while present in said surface modification zone with said excited gas species until the ability of said carbonaceous fibrous material to bond to a matrix material is beneficially enhanced.

The resulting carbon fibers may be incorporated in a resinous matrix material to form a composite article exhibiting enhanced interlaminar shear strength.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic illustration of a representative apparatus arrangement for modifying the surface characteristics of a carbonaceous fibrous material in accordance with the present process.

FIGS. 1A and 1B are schematic illustrations of alternative means for capacitively exciting the gaseous mixture in the surface modification zone of FIG. 1.

FIG. 1C is a schematic illustration of means for inductively exciting the gaseous mixture in the surface modification zone of FIG. 1.

FIG. 2 is a schematic illustration of a further representative apparatus arrangement for modifying the surface characteristics of a carbonaceous fibrous material in accordance with the present process wherein a mercury pool surrounds the surface modification zone.

DESCRIPTION OF PREFERRED EMBODIMENTS

The starting material

The fibers which are surface modified in accordance with the present process are carbonaceous and contain at least about 90 percent carbon by weight. Such carbon fibers may exhibit either an amorphous carbon or a predominantly graphitic carbon X-ray diffraction pattern. In a preferred embodiment of the process the carbonaceous fibers 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 carbonaceous fibrous material may be provided as either a continuous or a discontinuous length. In a preferred embodiment of the process the carbonaceous fibrous material is a continuous length which may be 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 carbonaceous fibrous material 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 carbonaceous fibrous material is one or more continuous multifilament yarn. When a plurality of multifilament yarns are surface treated simultaneously, they may be continuously passed through the heating zone while in parallel and in the form of a flat ribbon.

The 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 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 at a more highly elevated temperature, e.g. 900 to 1000° C., or more, until a carbonaceous fibrous material is formed. If the thermally stabilized material is heated to a maximum temperature of 2000 to 3100° C. (preferably 2400 to 3100° C.) in an inert atmosphere, substantial amounts of graphitic carbon are commonly detected in the resulting carbon fiber, otherwise the carbon fiber will commonly exhibit an essentially amorphous X-ray diffraction pattern.

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 fibrous material capable of undergoing carbonization 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 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 poly-

benzimidazole 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 about 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 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. pre-oxidized) on a continuous basis in accordance with the teachings of U.S. Ser. No. 749,957, filed Aug. 5, 1968, of Dagobert E. Stutez, 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, commonly 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; 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 an inert gaseous 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 carbonaceous starting material may be varied as will be apparent to those skilled in the art. It is essential that the apparatus selected to 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 or 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 or 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 gaseous mixture

Within the surface modification zone is provided a gaseous mixture comprising about 80 to 99.9 percent by volume (preferably 90 to 99 percent by volume) of an inert gas and about 0.1 to 20 percent by volume (preferably 1 to 10 percent by volume) of a surface modification gas (described hereafter).

Suitable inert gases for inclusion in the gaseous mixture include nitrogen, helium, argon, neon, krypton, and xenon, and mixtures of the foregoing. The preferred inert gases are monoatomic, e.g. helium, argon, neon, krypton, and xenon since these tend to undergo excitation more readily. The particularly preferred monoatomic inert gases for use in the process are helium and argon. The relatively high current costs of neon, krypton, and xenon militates against their selection. When present in the gaseous mixture, the inert gas undergoes excitation upon application of the high frequency electrical power in pulsed form (described hereafter) and aids in the generation of an excited gas species of the surface modification gas. In the absence of the appreciable presence of the inert gas in the gaseous mixture, the desired surface modification is not accomplished because of the inability to achieve the requisite degree of excitation while maintaining moderate surface modification conditions, e.g. temperature.

Suitable surface modification gases for use in the process are oxygen, carbon dioxide, nitric oxide, nitrous oxide, nitrogen dioxide, sulfur dioxide, and water. The preferred surface modification gases for use in the process are oxygen and carbon dioxide.

Provided the requisite minimum concentrations of the inert gas and surface modification gas are present in the gaseous mixture, remainder of the gaseous mixture by volume may be composed of other gases which do not appreciably interfere with the desired surface modification.

The gaseous mixture may be conveniently provided in the surface modification zone at substantially atmospheric pressure, thus avoiding the necessity to operate under reduced pressure conditions and the concomitant disadvantages associated therewith. Alternatively, the gaseous mixture may be provided in the surface modification zone at superatmospheric pressures. The gaseous mixture is commonly provided in the surface modification zone at a pressure of about 1 to 3 atmospheres.

The gaseous mixture may be premixed prior to introduction into the surface modification zone (described hereafter), or alternatively formed in the surface modification zone upon the introduction of separate gas streams. It is recommended that the gaseous mixture within the surface modification zone be either intermittently or continuously replenished (e.g. by the continuous introduction of a fresh gas supply).

The surface treatment

The modification of the surface characteristics of the carbonaceous fibrous material is accomplished by contacting the fibrous material while present in the surface modification zone with an excited gas species formed through the application of pulsed high frequency electrical power to the gaseous mixture. The carbonaceous fibrous material may be statically suspended or otherwise positioned within the surface modification zone. In a preferred embodiment of the process a continuous length of the carbonaceous fibrous material is continuously passed, e.g. in the direction of its length, through the excited gas species present in the surface modification zone. For instance, a rotating feed roll may be provided at the entrance end of the surface modification zone, and a rotating take-up roll may be provided at the exit end of the surface modification zone.

The surface modification zone may be bounded by walls constructed of either a conductive or a non-conductive material. For instance, a tubular chamber constructed of transparent glass may be conveniently selected to define the bounds of the zone. In such an arrangement a continuous length of carbonaceous fibrous material may be axially suspended therein with free access of its surface to the excited gas species provided.

The excited gas species required to produce the requisite surface modification may be formed by inductively or capacitively coupling pulsed high frequency electrical power to the gaseous mixture. A combination of inductive and capacitive coupling may also be utilized. As shown in FIG. 1 (described in detail hereafter), the gaseous mixture within the surface modification zone may be capacitively excited. Representative alternative apparatus arrangements wherein capacitive coupling also may be utilized are shown in FIG. 1A, FIG. 1B, FIG. 2 (described in detail hereafter). In FIG. 1A the pulsed high frequency electrical power is applied to metallic rings which are oriented perpendicularly to the axis of an elongated surface modification zone and effectively surround the same. In FIG. 1B the pulsed high frequency electrical power is applied to a pair of mercury filled tubes oriented parallel to the axis of an elongated surface modification zone and positioned within the same. In FIG. 1C pulsed high frequency electrical power is inductively applied to an elongated surface modification zone through the use of a single coil which completely surrounds the same.

The term "pulsed" electrical power or electrical power "in pulsed form" as used herein is defined as pulses or bursts of high frequency electrical energy, e.g. pulsed RF energy. The power may be an A.C. signal having an amplitude of about 500 v. to 10 kv. peak-to-peak and a frequency of about 0.5 kHz. to 2500 mHz. (preferably 1.0 kHz. to 30 mHz.). The pulses may be from about 0.1 microsecond to 10 milliseconds duration (preferably 10 to 1000 microseconds). The pulse repetition rate may be from about 0.1 kHz. to 20 mHz. (preferably about 1.0 to 100 kHz.). The pulsed electrical power may be provided in accordance with techniques known to those skilled in the electrical arts, e.g. by gating a high frequency oscillator or klystron on and off to generate "bursts" of high frequency energy. The exact dimensions of the surface modification zone will influence the power requirement as will be apparent to those skilled in the art.

The high frequency electrical power in pulsed form is applied to the gaseous mixture in sufficient quantity to establish the surface modifying excited gas species while maintaining the temperature of the surface modification zone at about 20 to 325° C., and preferably at about 100 to 200° C. If desired, the maintenance of the desired temperature may be aided by immersion of the surface modification zone in a low dielectric liquid bath, such as silicon oil.

The carbonaceous fibrous material is contacted with the excited gas species present within the surface modification zone until its ability to bond to a matrix material is beneficially enhanced. Unlike many prior art surface modification techniques, the residence time required in the present process is relatively brief. For instance, residence times of about 0.2 to 20 minutes may be conveniently selected, and preferably residence times of about 1 to 4 minutes.

The surface modification process of the present invention offers the advantage of altering the surface characteristics of the carbonaceous fibrous material to the substantial exclusion of adversely influencing its single filament tensile properties of the same, i.e. tensile strength and Young's modulus.

The theory whereby the surface of a 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 attributable to a combination of physical and chemical interactions between the excited gas species and the carbonaceous fibrous material.

The surface modification imparted to the carbonaceous fibrous material through the use of the present process exhibits 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 carbonaceous fibers, and a resinous matrix material. Accordingly, carbon fiber reinforced composite materials which incorporate fibers treated as heretofore described exhibit enhanced shear 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 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.

A representative apparatus arrangement for carrying out the surface modification process of the invention is illustrated in FIG. 1. With reference to FIG. 1, the power unit includes a conventional variable D.C. power supply 2, a conventional pulse generator 4 having a variable pulse repetition rate and a variable pulse width, a conventional signal amplifier 6, and a variable frequency oscillator 8. The output signal from the pulse generator 4 is applied to the oscillator 8 by way of the signal amplifier 6. Both a variable positive D.C. voltage and a fixed negative bias voltage from the power supply 2 are applied to the oscillator 8.

The power supply 2 may be any conventional variable D.C. power supply, e.g. a "Kepco" Model 615B, 0-600 volt and negative 150 volt power supply. The pulse generator 4 may be any conventional pulse generator of variable pulse repetition rate, e.g. a Hewlett Packard Model 3300A pulse generator, which provides pulses having a variable pulse repetition rate and either a constant or a selectable variable pulse width or duration. The amplifier 6 may be any conventional amplifier having an odd number of stages which amplifies and inverts the pulses from the pulse generator 4 and provides positive output pulses. The oscillator 8 may be any conventional variable high frequency oscillator which preferably generates an output signal in the radio frequency range above 1.0 kHz., and which is capable of being gated or pulsed on and off to provide "bursts" of high frequency energy. In a preferred operation of the power unit this is accomplished by "cutting off" the oscillator by applying a negative 150 volt bias to the control grid of an oscillator tube (not shown) by way of an input terminal 10 and by periodically applying positive pulses to the input terminal 10 and thus the control grid of sufficient amplitude to drive the oscillator tube into conduction.

In operation, the pulse generator 4 generates a series of negative going pulses, the pulse repetition rate and/or the pulse width of which may be varied to thereby vary the reoccurrence rate and/or the duration of the pulses. The signal from the pulse generator 4 is amplified and inverted by the amplifier 6 and the positive pulses from the amplifier 6 are applied to the oscillator 8. In the absence of a pulse from the amplifier 6, the oscillator 8 is cut off and does not provide an output signal. However, when a pulse from the pulse generator 4 is applied to the oscillator 8 by way of the amplifier 6, the oscillator 8 breaks into high frequency oscillations and provides an output signal for the duration of the applied pulse. The resultant pulsed high frequency signal may be coupled to the surface modification zone 20 through a conventional high frequency step-up coil 12, the primary winding of which may be utilized for both signal coupling and as a portion of the oscillator tank circuit. Lead 14 connects the coil 12 to coaxial electrode 21. Coaxial electrode 21 consists of a 10 inch length of copper tubing having an outer diameter of $\frac{1}{2}$ inch and an inner diameter of $\frac{7}{16}$ inch. Situated in series with coaxial electrode 21 is a like coaxial electrode 22.

The amplitude of the output signal from the oscillator 8 may be varied by varying the voltage directly applied to the oscillator 8 from the power supply 2. The frequency of the output signal from the oscillator 8 may, of course, be varied in any suitable conventional manner, e.g. by varying the reactive value of an electrical component in a tank circuit (not shown). In addition, the relationship between the "on" time and the "off" time of the output signal and the duration of the pulses of high frequency energy may be varied by adjusting the pulse repetition rate and/or width of the output pulses from the pulse generator 4. The pulse unit is thus capable of supplying bursts of electrical energy of a variable high frequency, the bursts occurring at a selectable burst repetition rate and having a variable burst width or duration.

Another representative pulsing unit which may be used to provide the pulsed high frequency signal to excite the gas mixture in the surface modification zone is a Lepel Model No. T-5-3 high frequency power unit capable of delivering up to a 10 kv. signal at a frequency of up to 30 mHz. pulsed by a grid pulse modulator Model 1414 available from Pulse Tronics Engineering Co.

By providing a pulsed frequency signal as described above, excessive heat buildup within the surface modification zone 20 may be prevented through variation of the pulse repetition rate, the pulse width or duration, or both of these parameters. The heat generated within the surface modification zone during the application of pulsed high frequency signal is allowed to dissipate to a great extent during the off period of the oscillator, i.e. between pulses of high frequency energy.

Since the signal amplitude, frequency, duration and repetition rate required for carrying out the process depend upon the diameter and length of the surface modification zone, such parameters may vary widely. The temperature inside the surface modification zone 20 may be sensed by a thermocouple 23 and a visual temperature indication may be provided at meter 25. The temperature within the zone 20 may thus be easily regulated by visually monitoring the meter 25 and adjusting the pulse repetition rate and/or the pulse width of the high frequency signal. The intensity of the excitation is controlled by the amplitude and duration of the pulses, the pulse repetition rate, the space gap between the electrodes, and the total length of the surface modification zone.

With a surface modification zone or chamber 20 of approximately 22 inches in length and $\frac{7}{16}$ inch in diameter, the process may be conveniently practiced utilizing a pulsed high frequency output signal from the oscillator 8 in the radio frequency range above 1.0 kHz., the particularly preferred range being from 1.0 kHz. to 30 mHz. The signal may be pulsed at a repetition rate of from

about 1.0 to about 1000 kHz. (10 to 100 kHz. being preferred) while the pulse width may be from 0.1 to 1000 microseconds, (1.0 to 500 microseconds being preferred). The amplitude of the pulsed high frequency signal may be from 500 v. to 10 kv. (1 to 5 kv. being preferred).

The following examples are given as specific illustrations of the process 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

Reference is made to the apparatus of FIG. 1.

A high strength-high modulus continuous filament carbonaceous yarn derived from an acrylonitrile homopolymer in accordance with the procedures described in U.S. Ser. Nos. 749,957, filed Aug. 5, 1968, and 777,275, filed Nov. 20, 1968 (now abandoned) was selected as the starting material. 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 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 50 million p.s.i.

The carbonaceous yarn 24 was unwound from rotating feed roll 26 into neck 27, around pulley 28, through surface modification zone 20 via annular guides 30 and 32, around pulley 34, and was ultimately taken up upon rotating uptake roll 36. The carbonaceous yarn 24 passed through surface modification zone 20 while axially suspended therein at a rate of 12 inches per minute.

The surface modification zone 20 was defined by tubular glass of about $\frac{1}{16}$ inch diameter and about 22 inches in length. Oxygen was continuously introduced as the surface modification gas via inlet tubes 38 and 40. Helium was introduced as the inert gas via inlet tubes 44 and 40 at a rate of 3000 cc. per minute. Oxygen was present in the gaseous mixture in a concentration of about 0.5 percent by weight. Off gases were exited via exit tube 42. A 3000 v. peak-to-peak A.C. signal having a frequency of 13.56 mHz. was applied to coaxial electrode 21 in pulses of 500 microseconds duration at a p.r.r. (pulse repetition rate) of 100 kHz. An excited gas species was established throughout the length of the surface modification zone 20. The yarn 24 was in contact with the excited gas species for a residence time of about 2 minutes. Throughout the surface modification treatment the temperature within zone 20 was maintained at approximately 200° C. as measured by thermocouple 23 and indicated on meter 25. The yarn following surface treatment exhibited a single filament tenacity of 13 grams per denier, and a single filament Young's modulus of 50 million p.s.i.

A composite article was next formed employing the surface modified yarn sample as a reinforcing medium in a resinous matrix. The composite article was a rectangular bar consisting of about 65 percent by volume of the yarn and having dimensions of $\frac{1}{8}$ inch x $\frac{1}{4}$ inch x 5 inches. The composite article was formed by impregnation of the yarn in a liquid epoxy resin-hardener mixture at 50° 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 at about 100 p.s.i. pressure. 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 epoxy resin and 88 parts by weight of anhydride curing agent.

The composite article was found to exhibit a horizontal interlaminar shear strength of 7000 p.s.i.

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

For comparative purposes a composite article was formed as heretofore described employing an identical carbonaceous yarn without subjecting the same to any form of surface modification. The average horizontal interlaminar shear strength of the composite article was only 3600 p.s.i.

EXAMPLE II

Example I is repeated with the exception that carbon dioxide is substituted for oxygen as the surface modification gas.

Substantially similar results are achieved.

EXAMPLE III

Example I is repeated with the exception that nitrogen dioxide is substituted for oxygen as the surface modification gas.

Substantially similar results are achieved.

EXAMPLE IV

Example I is repeated with the exception that sulfur dioxide is substituted for oxygen as the surface modification gas.

Substantially similar results are achieved.

EXAMPLE V

Example I is repeated with the exception that the continuous filament carbonaceous yarn undergoing surface modification was derived from a cellulosic precursor and was commercially available from the Union Carbide Company under the designation of Thorneil 50. The yarn had a carbon content in excess of 99 percent by weight and exhibited a predominantly graphitic X-ray diffraction pattern. The yarn consisted of a 2 ply 1440 fil bundle having a total denier of about 700.

When incorporated in a composite article (as described), the surface treated yarn exhibited a horizontal interlaminar shear strength of 7000 p.s.i. When the untreated yarn was employed in the formation of a composite article, a horizontal interlaminar shear strength of only 3600 p.s.i. was exhibited.

EXAMPLE VI

Reference is made to the apparatus of FIG. 2 in which like numerals designate similar components to those previously described in connection with FIG. 1.

A carbonaceous multifilament yarn 24 identical to that employed in Example I is continuously unwound from feed roll 29 and passed through mercury seal 31 supplied from reservoir 33.

The carbonaceous yarn is passed through surface modification zone 20 at a rate of 16 inches per minute. Oxygen is introduced as the surface modification gas via inlet tubes 38 and 40. Helium is introduced as the inert gas via inlet tubes 44 and 40 at a rate of 2000 cc. per minute. Oxygen was present in the gaseous mixture in a concentration of about 1 percent by weight.

The gaseous mixture in the surface modification zone 20 was excited by means of the capacitance between mercury jacket 17 encircling the electrically grounded carbonaceous yarn.

A Pulse Tronics generator is used to control a Lepel Model T-5-3 high frequency signal generator to provide a 3000 v. peak-to-peak A.C. signal at a frequency of 10 mHz. in pulses of 500 microseconds duration at a p.r.r. of 10 kHz. An excited gas species is established throughout the length of the surface modification zone 20. The yarn 24 is in contact with the excited gas species for a residence time of about 1 minute. Throughout the surface modification treatment the temperature within zone 20 is maintained at approximately 250° C. as measured by thermocouple 23 and indicated on meter 25.

Substantially similar surface modification results are achieved.

The nature, scope, utility, and effectiveness of the present invention have been described and specifically exemplified in the foregoing specification. However, it should be understood that these examples are not intended to be limiting and that the scope of the invention to be protected is particularly pointed out in the appended claims.

I claim:

1. A process for the modification of the surface characteristics of a carbonaceous fibrous material containing at least about 90 percent carbon by weight comprising:

- (a) providing in a surface modification zone at a pressure of about 1 to 3 atmospheres a gaseous mixture comprising about 80 to 99.9 percent by volume of an inert gas and about 0.1 to 20 percent by volume of a surface modification gas selected from the group consisting of oxygen, carbon dioxide, nitric oxide, nitrous oxide, nitrogen dioxide, sulfur dioxide, water, and mixtures of the foregoing,
- (b) applying high frequency electrical power in pulsed form to said gaseous mixture sufficient to establish an excited gas species within said surface modification zone while maintaining the temperature of said zone at about 20 to 325° C., and
- (c) contacting said carbonaceous fibrous material while present in said surface modification zone with said excited gas species until the ability of said carbonaceous fibrous material to bond to a matrix material is beneficially enhanced.

2. A process according to claim 1 wherein said carbonaceous fibrous material includes a substantial quantity of graphitic carbon.

3. A process according to claim 1 wherein said inert gas is a monoatomic gas.

4. A process according to claim 3 wherein said monoatomic inert gas is selected from the group consisting of argon, helium, and mixtures of the foregoing.

5. A process according to claim 1 wherein said surface modification gas is oxygen.

6. A process according to claim 1 wherein said surface modification gas is carbon dioxide.

7. A process according to claim 1 wherein said surface modification gas is nitrogen dioxide.

8. A process according to claim 1 wherein said gaseous mixture is provided at substantially atmospheric pressure.

9. A process according to claim 1 wherein said electrical power in pulsed form applied to said gaseous mixture is of the radio frequency range from about 1.0 kHz. to 30 mHz.

10. A process for the modification of the surface characteristics of a carbonaceous fibrous material containing at least about 90 percent carbon by weight and exhibiting a predominantly graphitic X-ray diffraction pattern comprising:

- (a) providing in a surface modification zone at a pressure of about 1 to 3 atmospheres a gaseous mixture comprising about 80 to 99.9 percent by volume of an inert gas selected from the group consisting of argon, helium, and mixtures of the foregoing and about 0.1 to 20 percent by volume of a surface modification gas

selected from the group consisting of oxygen, carbon dioxide, nitric oxide, nitrous oxide, nitrogen dioxide, sulfur dioxide, water, and mixtures of the foregoing,

- (b) applying an A.C. signal having an amplitude of from about 500 v. to 10 kv. peak-to-peak and a frequency of from about 0.5 kHz. to 2500 mHz. to said gaseous mixture in pulses of from about 0.1 microsecond to 10 milliseconds duration at a pulse repetition rate of about 0.1 kHz. to 20 mHz. sufficient to form an excited gas species within said surface modification zone while maintaining the temperature in said zone at about 20 to 325° C., and
- (c) continuously passing a continuous length of said carbonaceous fibrous material through said excited gas species of said surface modification zone for a residence time of about 0.2 to 20 minutes thereby beneficially enhancing the ability of said carbonaceous fibrous material to bond to a matrix material.

11. A process according to claim 10 wherein said carbonaceous fibrous material contains at least about 99 percent carbon by weight.

12. A process according to claim 10 wherein said inert gas is argon.

13. A process according to claim 10 wherein said inert gas is helium.

14. A process according to claim 10 wherein said surface modification gas is oxygen.

15. A process according to claim 10 wherein said surface modification gas is carbon dioxide.

16. A process according to claim 10 wherein said surface modification gas is nitrogen dioxide.

17. A process according to claim 10 wherein said gaseous mixture is provided at substantially atmospheric pressure.

18. A process according to claim 10 wherein said A.C. signal has an amplitude from about 500 v. to 10 kv., has a frequency of about 1.0 kHz. to 30 mHz., and is pulsed at a pulse repetition rate of about 1 to 100 kHz., and pulse duration of about 10 to 1000 microseconds.

19. A process according to claim 10 wherein said inert gas and said surface modification gas are continuously introduced into said surface modification zone.

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U.S. Cl. X.R.

8—19; 204—165; 423—447, 460