United States Patent [19]

Boss et al.

[11] **3,844,822**

[45] **Oct. 29, 1974**

[54] **PRODUCTION OF UNIFORMLY RESIN IMPREGNATED CARBON FIBER RIBBON**

[75] Inventors: **A. Evan Boss**, Mountainside; **Michael J. Ram**, West Orange, both of N.J.; **Thomas K. Reynolds**, Santa Monica, Calif.

[73] Assignee: **Celanese Corporation**, New York, N.Y.

[22] Filed: **Dec. 23, 1971**

[21] Appl. No.: **211,339**

[52] **U.S. Cl.**..... **117/119.6**, 117/65.2, 117/161 ZB, 117/228, 118/59, 118/70

[51] **Int. Cl.**..... **B44d 1/48**

[58] **Field of Search**..... 117/119.6, 161 ZB, 228, 117/65.2, DIG. 11; 118/59, 106; 34/116

[56] **References Cited**

UNITED STATES PATENTS

1,905,959	4/1933	Cutler et al.	118/106
2,419,922	4/1947	Tippetts	117/7
2,528,168	10/1950	Paulsen	117/65.2 X
2,838,420	6/1958	Valente	117/119.8
2,881,090	4/1959	Reidl et al.	117/161 ZB X
2,898,664	8/1959	Salen	117/7 X
3,214,324	10/1965	Peerman	117/161 ZB X
3,271,350	9/1966	Vertnik	117/161 ZB X
3,382,086	5/1968	Singleton	117/7 X
3,625,739	12/1971	Kaspar et al.	117/65.2
3,677,804	7/1972	Kalnin et al.	117/228 X
3,723,157	3/1973	Druin	117/161 ZB

FOREIGN PATENTS OR APPLICATIONS

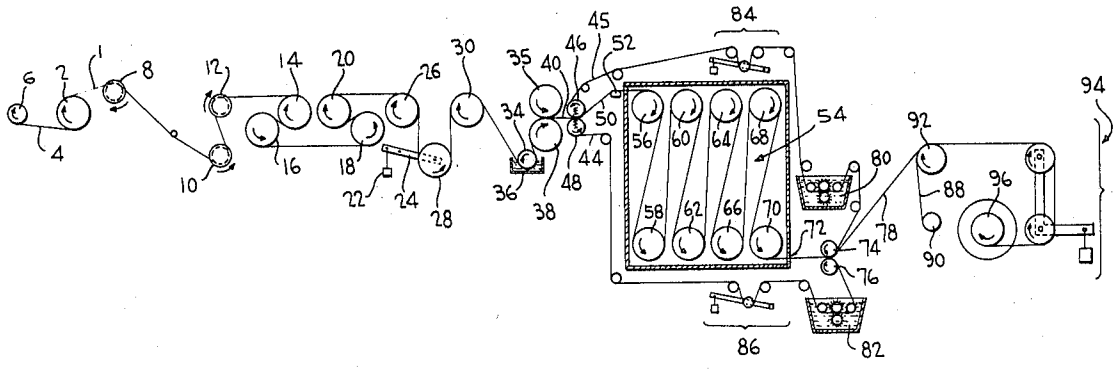
710,750	6/1965	Canada	117/65.2
525,037	5/1956	Canada	117/65.2
791,598	3/1958	Great Britain	117/228

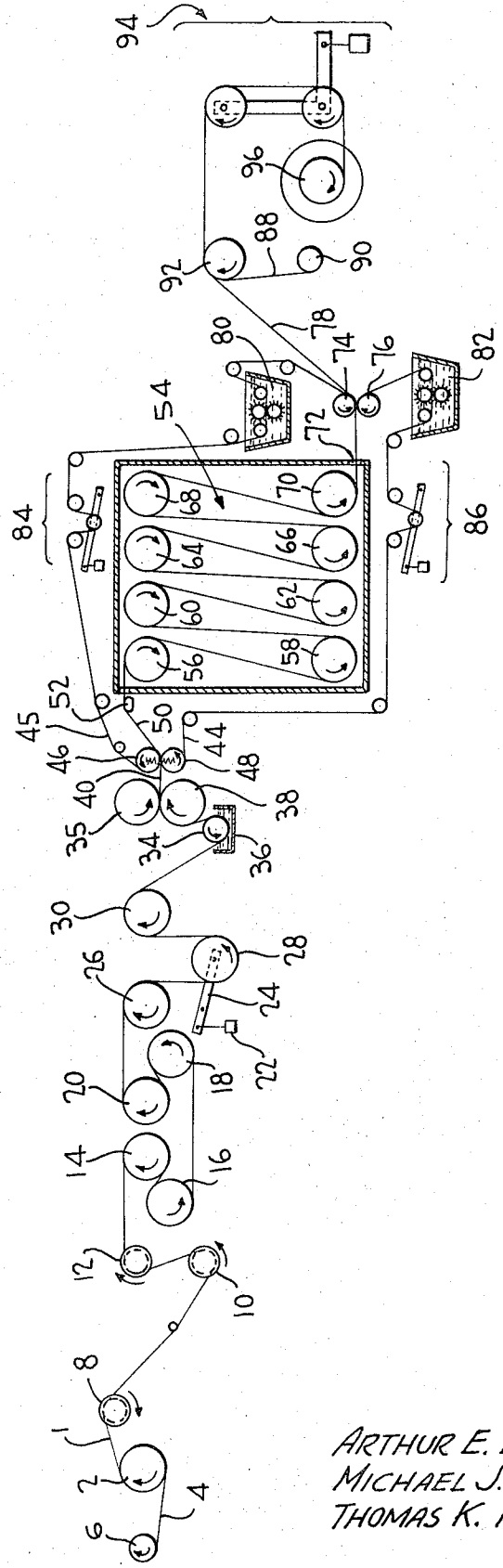
Primary Examiner—William D. Martin
Assistant Examiner—Shrive P. Beck

[57] **ABSTRACT**

An improved process is provided for the production of a continuous length of a carbon fiber ribbon which is impregnated with a tacky B-stage thermosetting resin. The fibrous ribbon undergoing treatment is resin impregnated with a neat liquid resin system of relatively high viscosity containing an A-stage thermosetting resin through the application of a force sufficient to bring the resin into intimate association with the individual fibers of the ribbon. The resin impregnated ribbon is next partially cured while continuously passing through a heating zone as described while interposed between a pair of flexible endless belts. The resulting ribbon is uniformly impregnated with a thermosetting resin of a tacky B-stage consistency and may be utilized in the formation of carbon fiber reinforced composite structures by filament winding or other suitable techniques.

19 Claims, 1 Drawing Figure





INVENTORS,
ARTHUR E. BOSS, JR.
MICHAEL J. RAM
THOMAS K. REYNOLDS

PRODUCTION OF UNIFORMLY RESIN IMPREGNATED CARBON FIBER RIBBON

BACKGROUND OF THE INVENTION

In the search for high performance materials, considerable interest has been focused upon carbon fibers. The terms "carbon" fibers or "carbonaceous" fibers are used herein in the generic sense and include graphite fibers which consist substantially 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 a predominantly 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.

As is known in the art, numerous precedures have been proposed in the past for the conversion of various organic polymeric fibrous materials to a carbonaceous form while retaining the original fibrous configuration essentially intact. Such procedures have in common the thermal treatment of the fibrous precursor in an appropriate atmosphere or atmospheres which is commonly conducted in a plurality of heating zones, or alternatively in a single heating zone wherein the fibrous material is subjected to progressively increasing temperatures. See, for instance, U.S. Pat. No. 3,539,295 to Michael J. Ram for a representative conversion process.

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.

Carbon fiber reinforced composites are commonly formed by coating or impregnating carbon fibers with an uncured or partially cured liquid thermosetting resinous material which is ultimately to serve as the matrix or continuous phase in the composite article, converting the resinous material present on the carbon fibers to a tacky consistency through partial curing and/or evaporation of solvent, molding or otherwise shaping the same into the desired configuration, and fully curing the same to form a rigid monolithic structure. Heretofore, a thermosetting resinous material has commonly been applied to the carbon fibers from a solvent system which has necessitated volatilization of the solvent during the composite formation prior to complete curing. Additionally, techniques have been proposed wherein the thermosetting resin is applied from a liquid solventless system. Whenever filament winding is utilized to shape the composite article, the resin impregnated carbon fibers bearing a partially cured resin must by necessity be provided in an appreciable length. The efficient uniform resin impregnation, handling, and partial curing of continuous lengths of carbon fibers particularly in ribbon form has been an elusive goal when employing prior art technology. Arch ovens have been employed wherein the resin impregnated ribbon is passed through a highly elongated heating zone while supported upon one surface and the solvent evaporated. The exposed surface accordingly tends to cure at a different rate than the surface in contact with the support. If the resin impregnated ribbon is unsupported over an appreciable span, roping and/or splitting of the same commonly occurs. A non-uniformly resin impregnated or nonuniformly partially cured carbon fiber ribbon is incapable of yielding a carbon fiber reinforced composite structure consistently exhibiting the required tensile properties for many end use applications.

It is an object of the invention to provide an improved process for the production of a carbon fiber ribbon which is uniformly impregnated with a thermosetting resin which has a tacky B-stage consistency and is suitable for use in the formation of carbon fiber reinforced composite structures.

It is an object of the invention to provide an improved process for production of a continuous length of a thermosetting resin impregnated carbon fiber ribbon wherein the necessity to volatilize a solvent from the resin system in contact with the ribbon is eliminated.

It is an object of the invention to provide an improved process for the production of a continuous length of a thermosetting resin impregnated carbon fiber ribbon wherein the partial curing of the resin is uniformly accomplished on a continuous basis within a limited area while preserving intimate association between resin and the carbon fiber ribbon.

It is another object of the invention to provide an improved process for the production of a carbon fiber ribbon which is uniformly impregnated with a thermosetting resin having a tacky B-stage consistency wherein the single filament tensile properties initially exhibited by the carbon fiber ribbon are substantially unimpaired.

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

SUMMARY OF THE INVENTION

It has been found that an improved process for the production of a uniformly resin impregnated ribbon of a carbonaceous fibrous material which is suitable for use in the manufacture of carbon fiber reinforced composite structures comprises:

a. continuously conveying to an impregnation zone a carbonaceous fibrous ribbon containing at least about 90 percent carbon by weight,

b. forcing a liquid solventless system having a viscosity of about 500 to 10,000 cps, comprising an A-stage thermosetting resin into intimate association with the carbonaceous fibrous ribbon while present in the impregnation zone,

c. interposing the ribbon while in intimate association with the solventless system between the outer surfaces of a pair of flexible endless belts having a width greater than that of the ribbon,

d. continuously passing the ribbon in the direction of its length while interposed between the flexible endless belts through a substantially enclosed heating zone provided with a heated gaseous atmosphere while substantially suspended therein wherein the belts and the ribbon are looped in a single wrap about each of a multiplicity of rotating parallel rollers wherein the inner surfaces of the belts are in alternating contact with the rollers as

the belts and the ribbon progress through the heating zone with the ribbon being out of contact with the rollers and wherein the thermosetting resin in intimate association with the ribbon is converted to a B-stage consistency,

e. continuously withdrawing the ribbon from the heating zone while interposed between the outer surfaces of the pair of flexible endless belts and while the thermosetting resin in intimate association with the ribbon remains in a B-stage consistency, and

f. separating the resulting resin impregnated carbonaceous fibrous ribbon from the flexible endless belts.

BRIEF DESCRIPTION OF DRAWING

The drawing is a schematic presentation of a representative apparatus arrangement capable of carrying out the process of the present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

The carbonaceous fibrous ribbon which serves as the starting material in the present process contains at least about 90 percent carbon by weight. The carbon fibers of the ribbon may exhibit either an amorphous carbon or a predominantly graphitic carbon X-ray diffraction pattern. In a preferred embodiment of the process the carbon fibers contain at least about 95 percent carbon by weight and exhibit a predominantly graphitic X-ray diffraction pattern.

The width of the carbonaceous fibrous ribbon may conveniently vary from about 0.5 to 12 inches, or more.

The carbonaceous fibrous ribbon may comprise a single flat tow of continuous carbon filaments or a plurality of substantially parallel multifilament fiber bundles which are substantially coextensive with the length of the ribbon.

In the latter embodiment the carbonaceous fiber bundles of the ribbon may be provided in a variety of physical configurations. For instance, the bundles of the ribbon may assume the configuration of continuous lengths of multifilament yarns, tows, strands, cables, or similar fibrous assemblages. The multifilament bundles are preferably lengths of a continuous multifilament yarn. The fiber bundles within the ribbon optionally may be provided with a twist which tends to improve their handling characteristics. For instance, a twist of about 0.1 to 5 tpi, and preferably about 0.3 to 1 tpi, may be imparted to each fiber bundle. Also, a false twist may be used instead of or in addition to a real twist. Alternatively, the fiber bundles may possess substantially no twist.

Multifilament fiber bundles may be provided within the ribbon in a substantially parallel manner in the substantial absence of bundle crossovers to produce a flat ribbon. The number of parallel multifilament bundles present within the carbonaceous ribbon may be varied widely, e.g., from 6 to 1,000, or more. In a preferred embodiment of the process a ribbon precursor is selected having a weft pick interlaced with substantially parallel fiber bundles in accordance with the teachings of commonly assigned U.S. Ser. No. 112,189, filed Feb. 3, 1971 of K. S. Burns, G. R. Ferment, and R. C. Waugh which is herein incorporated by reference. It is not essential, however, that the parallel fiber bundles or the filaments of a flat tow be bound by any form of weft interlacement when constructing carbon fiber tapes for resin impregnation in accordance with the present invention.

The carbonaceous ribbon which serves as the starting material in the present process may be produced 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 1,000° C., or more, until a carbonaceous fibrous material is formed. If the thermally stabilized material is heated to a maximum temperature of 2,000° to 3,100° C. (preferably 2,400° to 3,100° 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 a substantially 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 carbonaceous ribbon may be derived include an acrylic polymer, a cellulosic polymer, a polyamide, a polybenzimidazole, polyvinyl alchol, etc. Acrylic polymeric materials are particularly suited for use as precursors in the formation of the carbonaceous ribbon. 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. Preferred carbonization and graphitization techniques for use in forming the carbonaceous ribbon are 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.

The carbonaceous ribbon optionally may be surface treated in order to improve its ability to bond to a thermosetting resinous material. Conventional surface modification techniques may be selected. Preferred surface modification treatments are disclosed in commonly assigned U.S. Ser. Nos. 65,454 and 65,456, (now U.S. Pat. No. 3,723,150) filed Aug. 20, 1970 of M. L. Druin, G. R. Ferment, and N.V.P. Rao.

In the process of the present invention the carbonaceous ribbon is continuously conveyed to the impregnation zone while in a flat configuration. The ribbon may be conveyed in accordance with conventional fiber advancing techniques, and is preferably under a uniform tension across its width when it arrives at the impregnation zone.

While present in the impregnation zone, a liquid solventless system of a relatively high viscosity comprising an A-stage thermosetting resin is forced into intimate association with the individual fibers of the ribbon. The solventless system exhibits a viscosity of about 500 to 10,000 cps. and preferably a viscosity of about 1,000 to 3,000 cps, during impregnation. It has been found that such resin systems of relatively high viscosity are capable of producing a more uniformly resin impregnated ribbon.

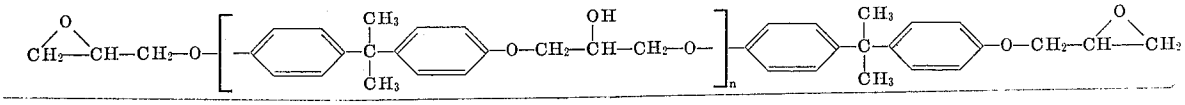
The solventless system comprising an A-stage thermosetting resin is a flowable liquid and is substantially uncured during the impregnation step. Such a material when exposed to heat hardens or sets to a rigid solid consistency designated as a C-stage thermoset resin, and may not subsequently be rendered plastic or flowable upon the reapplication of heat. The curing or hardening of the thermosetting resin is brought about by heat-promoted chemical changes which result in the formation of a compact, often cross-linked system. It is accordingly essential that thermosetting resins be molded to the desired configuration prior to the point in time when the curing reaction has progressed to the C-stage. A B-stage thermosetting resin is defined as a partially cured thermosetting resin which has neither the consistency of a flowable liquid, nor the consistency of a rigid solid. A B-stage thermosetting resin is accordingly soft and tacky in its consistency and may be readily molded. Upon the passage of time even at room temperature, a B-stage thermosetting resin will assume a C-stage consistency.

The solventless system applied in the impregnation zone may comprise the A-stage thermosetting resin, one or more curing agents for the thermosetting resin, one or more accelerators and one or more solid particulate inert fillers. Conventional solvents such as acetone which may dissolve the A-stage thermosetting resin are to be avoided, since upon evaporation such solvents tend to produce strength-reducing voids, and also lengthen the period of time required for the A-stage thermosetting resin to assume a B-stage consistency within the heating zone (described in detail hereafter). If desired, various modifiers or diluents of the reactive type may be present within the solventless system since such components form a permanent portion of the hardened thermoset resin, and it is not essential to evaporate the same during the curing reaction.

The resin employed in the solventless system may generally be selected from those thermosetting resins utilized in the production of fiber reinforced composites by prior art techniques. It is, of course, necessary that a substantially uncured thermosetting resin be selected which inherently possesses the required viscosity at the impregnation temperature or which may be modified to possess the required viscosity at the impregnation temperature by the addition of a reactive modifier or diluent. Illustrative examples of suitable thermosetting resins for use in the present process include epoxy resins, phenolic resins, polyester resins, polyimides, etc.

An epoxy resin is the preferred thermosetting resin for use in the process of the invention. The epoxy resins utilized in the present invention are most commonly prepared by the condensation of bisphenol A (4,4' isoproplidene diphenol) and epichlorohydrin. Also, other polyols, such as aliphatic glycols and novolac resins may be reacted with epichlorohydrin for the production of epoxy resins suitable for use in the present process provided the resinous products possess or can be modified to possess the requisite viscosity characteristics. Numerous reactive diluents or modifiers which are capable of increasing the flow properties of uncured epoxy resins are well known and include butyl glycidyl ether, higher molecular weight aliphatic and cycloaliphatic monoglycidyl ethers, styrene oxide, aliphatic and cycloaliphatic diglycidyl ethers, and mixtures of the above.

In a preferred embodiment of the invention epoxy resins are selected which possess terminal epoxide groups and are condensation products of bisphenol A and epichlorohydrin of the following formula:



where n varies between zero and a small number less than about 10. When n is zero, the resin is a very fluid light-colored material which is substantially the diglycidyl ether of bisphenol A. As the molecular weight increases, so generally does the viscosity of the resins. Accordingly, the particularly preferred liquid epoxy resins generally possess an n value averaging less than about 1.0. Illustrative examples by standard trade designations of particularly useful commercially available epoxy resins include: Epi-Rez 508 and Epi-Rez 510 (Celanese Coatings) ERLA 2256 (Union Carbide), ERLA 4617 (Union Carbide), and Epon (Shell) epoxy resins.

Epoxy novolac resins formed by the reacting of epichlorohydrin with phenol-formaldehyde resins are also particularly preferred thermosetting resins. An illustrative example of a highly useful resin is Epi-Rez 5155 epoxy novolac resin (Celanese Coatings).

A variety of epoxy resin curing agents may be employed in conjunction with the epoxy resin. The curing or hardening of the epoxy resin typically involves further reaction of the epoxy or hydroxyl groups to cause molecular chain growth and cross-linking. The term "curing agent" as used herein is accordingly defined to include the various hardeners of the co-reactant type. Illustrative classes of known epoxy curing agents which may be utilized include aliphatic and aromatic amines, polyamides, tertiary amines, amine adducts, acid anhydrides, acids, aldehyde condensation products, and Lewis acid type catalysts, such as boron trifluoride. The preferred epoxy curing agents for use with the epoxy resin are acid anhydrides (e.g. hexahydrophthalic acid and methylbicyclo[2.2.1]heptene-1,1-dicarboxylic anhydride isomers marketed under the designation Nadic Methyl Anhydride by the Allied Chemical Company), and aromatic amines (e.g., meta-phenylene diamine and dimethylaniline).

The solventless system comprising an A-stage thermosetting may be provided at a moderately elevated temperature during the impregnation step of the process in order to impart the required viscosity to the

same. The exact temperature selected will vary with the specific system selected as will be apparent to those skilled in the art. Resin system temperatures commonly range from about 25° to 100° C. at the time of impregnation. Those resin systems which exhibit a substantial pot life at the impregnation temperature are preferred.

The technique utilized to force the resin system into intimate association with multifilament fiber bundles of the ribbon may be varied. It is essential, however, that the impregnation technique selected results in no substantial diminution of the tensile properties of the carbonaceous bundles. In a preferred embodiment of the process the resin system is initially applied to the ribbon by briefly passing the ribbon through a vessel containing the same, and the ribbon bearing the resin system adhering to its surface is next passed between a pair of parallel nip rollers. In addition to immersion the resin initially may be satisfactorily applied by spraying, extruding, etc., prior to passage between a pair of nip rollers. One of the nip rollers optionally may be provided with a flat groove corresponding in width to the width of the ribbon, and the other nip roller provided with a substantially matching raised surface which in combination with the grooved roller provides a rectangular gap for the ribbon. The force exerted by such nip rolls causes the resin system to flow throughout the ribbon. Alternatively, the impregnation step may be accomplished through the use of poltrusion or other application technique capable of bringing out the desired impregnation.

The carbonaceous ribbon while in intimate association with the solventless system is next interposed between the outer surfaces of a pair of flexible endless belts. The belts preferably have smooth nonporous surfaces, are relatively thin so as to permit efficient heat transfer therethrough in the heating zone as described hereafter, and are capable of being readily stripped from a ribbon impregnated with a tacky thermosetting resin. The belts are capable of withstanding the temperatures employed in the subsequent heating zone, are capable of withstanding wash solvents, and may be formed from a variety of materials. Preferred endless belts are formed from fiberglass reinforced polytetrafluoroethylene sheets having a thickness of about 0.005 to 0.030 inch. Flexible endless belts alternatively may be formed from flexible metallic strips or other fiber reinforced flexible resinous materials. The width of the endless belts is greater than the width of the ribbon interposed therebetween (e.g., 0.5 to 2 inches or wider), so that the ribbon has each of its surfaces completely covered by the endless belts. The ribbon is preferably interposed substantially at the center of each belt and is aligned in parallel with the edges of the belts.

While interposed between the flexible belts, the resin impregnated ribbon is continuously passed in the direction of its length through a substantially enclosed heating zone provided with a heated gaseous atmosphere wherein the belts and the ribbon are looped in a single wrap about each of a multiplicity of rotating spaced parallel rollers wherein the inner surfaces of the belts are in alternating contact with the rollers as the belts and the ribbon progress through the heating zone. The heating zone may be relatively compact and provided with a plurality of pairs of spaced parallel rollers. As the belts and ribbon pass through the heating zone as a unitary body, the impregnated ribbon remains between the belts at a fixed location in the absence of sliding contact and is substantially suspended within the heating zone. As the belts and ribbon intermittently pass over the rotating rollers a flexing action occurs and pressure is exerted on alternating sides of the ribbon which further improves the uniformity of the resin distribution throughout the ribbon. Each side of the ribbon is uniformly heated at the same temperature while passing through the heating zone.

The nature of heated gaseous atmosphere within the heating zone may be varied. For instance, ordinary air may be employed. Alternatively, inert gases such as nitrogen may serve as the gaseous atmosphere. The gas is preferably preheated prior to introduction into the heating zone such as by passing over electrical resistance heaters. Additionally, the gas is preferably circulated within the heating zone by continuously introducing and withdrawing a portion of the same.

While present in the heating zone, the thermosetting resin in intimate association with the ribbon is converted to a tacky B-stage consistency. The temperature of the gaseous atmosphere of the heating zone, as well as the residence time during which the ribbon is within the heating zone will vary depending upon the specific thermosetting resin undergoing partial curing. Heating zone temperatures of about 75° to 175° C. are commonly selected, and preferably the temperature of the gaseous atmosphere within the heating zone is maintained at about 100° to 150° C. Satisfactory residence times in which to accomplish the desired partial curing within the heating zone commonly range from about 2 to 30 minutes, an preferably about 10 to 15 minutes.

Since the ribbon is positioned between the endless belts as it passes through the heating zone, no splitting of roping of the ribbon occurs as is common in the prior art when a resin impregnated ribbon is passed across an unsupported span. The overall dimensious of the heating zone may be substantially reduced. Additionally, any volatile components of the resin system, e.g., curing agents, are retained within the ribbon by the adjoining belts, thereby making possible uniform curing of the thermosetting resin to the desired tacky consistency. Since the endless belts have a width greater than that of the ribbon, the resin system never contacts the rotating rollers present within the heating zone.

The resulting ribbon is continuously withdrawn from the heating zone while interposed between the flexible belts prior to a point in time when the thermosetting resin is advanced to a hard non-tacky C-stage consistency. The resin in intimate association with the ribbon remains in a tacky B-stage consistency at the time of its withdrawl from the heating zone.

The resin impregnated carbonaceous ribbon is next separated from the flexible endless belts and may be collected or directly utilized in the formation of carbon fiber reinforced composite structures. The endless belts following separation from the resin impregnated ribbon may be washed with an appropriate solvent (e.g., acetone or methylene chloride) to remove any adhering resin and returned for further use.

The uniformly resin impregnated carbon fiber ribbons formed in the present process preferably contain about 35 to 55 percent partially cured thermosetting resin by volume (preferably about 40 to 45 percent by volume) and about 45 to 65 percent carbon fiber by volume (preferably about 55 to 60 percent by volume).

The resin impregnated ribbon following its separation from the endless flexible belts may be positioned upon releasable interlay, such as silicone coated release

paper, and collected by winding upon a flanged bobbin or other support where it may be stored for future use. The resulting ribbons commonly exhibit an extended shelf life at ambient conditions. For instance, epoxy impregnated ribbons commonly may be stored as long as several days at room temperature while still retaining a B-stage consistency. If stored under refrigeration (e.g. at about 0° C.), such ribbons commonly exhibit a considerably longer shelf life (e.g., up to about 90 days or more). The exact shelf life will vary with the thermosetting resin selected.

The resin impregnated ribbons produced in the present process find particular utility in the production of high performance composite structures which are highly useful in the aerospace industry. For instance, impellers, turbine blades, and similar lightweight structural components may be formed by conventional filament winding, molding, or shaping techniques.

A representative apparatus arrangement for carrying out the process of the present invention is illustrated in the drawing. Carbonaceous ribbon having a width of 2.75 inches is continuously unwound from flanged bobbin **2** which is free to rotate about its central axis. The carbonaceous ribbon consists of 300 continuous multifilament yarn bundles which are arranged in parallel with each yarn bundle containing about 400 filaments, having a twist of about 0.5 tpi, exhibiting a total denier of about 400, and a predominantly graphitic X-ray diffraction pattern. The yarn bundles are derived from an acrylonitrile homopolymer and contain in excess of 99 percent carbon by weight. An interlay **4** of Kraft paper is also continuously unwound from flanged bobbin **2** and is received by interlay takeup **6** which is rotated about its axis by a driven constant speed AC motor (not shown) having a spring-tensioned friction plate. The unwinding of carbonaceous ribbon **1** from flanged bobbin **2** is accordingly assisted by the rotation of interlay takeup **6** which exerts a pulling force on interlay **4**.

The carbonaceous ribbon **1** following unwinding from flanged bobbin **1** passes over three grooved idler rolls **8, 10,** and **12** which serve to center the ribbon, eliminate splits, and equalize yarn density across the web. Each of the grooved idler rolls **8, 10,** and **12** has groove width of 2.75 inches, a groove depth of 0.25 inch, and a diameter within the groove of 3 inches. After leaving grooved idler roller **12** the carbonaceous ribbon is wrapped about a series of four tensioning rollers **14, 16, 18,** and **20** each having a 6 inch diameter, which apply a uniform tension to the ribbon. The tension is adjusted by varying the weight **22** on dancer arm **24** as the ribbon passes about idler rolls **26, 28,** and **30** each having a diameter of 6 inches. Dancer arm **24** controls the speed of tensioning rollers **14, 16, 18,** and **20** as well as the speed of upper nip roller **35** with all five of these rollers being driven by the same variable speed motor (not shown) by means of a chain drive (not shown).

After leaving idler roller **30,** the carbonaceous ribbon passes about a driven grooved dip roller **34** which is partially immersed in vessel **36** which contains a liquid solventless system containing an A-stage thermosetting resin and a curing agent for the resin. The driven grooved dip roller **34** has groove width of 2.75 inches, a groove depth of 0.125 inch, and a diameter within the groove of 3 inches. The carbonaceous ribbon bearing a coating of the solventless system next passes between a pair of driven parallel nip rollers **35** and **38.** The nip rollers **35** and **38** serve to force the resin system comprising an A-stage thermosetting resin into intimate association with the multifilament fiber bundles of the ribbon. Dip roller **34,** vessel **36,** and nip rollers **35,** and **38** are internally heated by a recirculating ethylene glycol-water solution which aids in maintaining the solventless resin system at the desired viscosity.

The carbonaceous ribbon **40** in intimate association with the resin system comprising an A-stage thermosetting resin is next interposed between a pair flexible endless belts **44** and **45.** The endless belts **44** and **45** are non-porous, have widths of 4 inches, and are composed of polytetrafluoroethylene coated fiberglass. Spring mounted idler rollers **46** and **48** facilitate the interpositioning of the ribbon **40** between belts **44** and **45.** The impregnated carbonaceous ribbon interposed between the belts passes as a flat unitary structure **50** over compression plate **52** and into heating zone **54.**

The heating zone **54** is provided in a forced air convection oven measuring 3 × 3 × 2 feet having a top to bottom air flow. Cantilevered within the heating zone **54** are eight oven rollers **56, 58, 60, 62, 64, 66, 68,** and **70** having diameters of 6 inches which are driven by a common motor (not shown) at a constant speed. The resin impregnated ribbon while interposed been the belts and present in heating zone **54** is successively wrapped about each of oven rollers **56, 58, 60, 62, 64, 66, 68,** and **70.** The driven rollers **56, 58, 60, 62, 64, 66, 68** and **70** within the heating zone **54** are rotated at the same rate as grooved dip roller **34** and lower nip roller **38.** While passing through heating zone **54** the thermosetting resin in intimate association with the carbonaceous ribbon is advanced to a tacky B-stage consistency, and it is in this state when it exits from heating zone **54** at opening **72.**

After passing between a pair of driven exit nip rollers **74** and **76,** which are rotating at the same rate as the oven rollers, the resulting carbonaceous ribbon **78** is separated from the endless flexible belts **42** and **44.** The exit nip rollers **74** and **76** serve to isolate the tension exerted upon the ribbon within the oven from the takeup winding tension. The belts **42** and **44** pass through belt washing pans **80** and **82** containing a solvent for the resin system where any adhering resin is removed by the aid of rotating brushes. Uniform tension is maintained upon endless belts **42** and **44** by dancer arm assemblies **84** and **86.**

A releasable paper interlay **88** is continuously unwound from reel **90** and contacts the surface of idler roller **92** prior to the arrival of the resulting thermosetting resin impregnated carbonaceous ribbon **78.** The interlay **88** bearing the tacky thermosetting resin impregnated carbonaceous ribbon **78** next passes about tensioning arm **94** and is wound upon flanged bobbin **96.**

The following examples are given as more 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. Reference is made in the examples to the drawing.

EXAMPLE I

The solventless system provided in dip pan **36** contained 100 parts by weight of epoxy novolac resin formed by reacting epichlorohydrin with a phenol-formaldehyde resin, and 88 parts by weight of an anhydride curing agent. The solventless system at room tem-

perature (i.e., 25° C.) exhibited a viscosity of about 100,000 cps. Internally heated dip roller **34**, vessel **36**, and nip rollers **35** and **38** were maintained at 50° C. during the resin impregnation step at which temperature the resin system exhibited a viscosity of about 1,000 cps. The gap between nip rollers **35** and **38** was 0.008 inch.

The carbonaceous ribbon was passed through apparatus at a rate of 20 inches per minute, and was present in heating zone **54** for a residence time of 13.5 minutes which was maintained at a uniform temperature of 132° C.

The resulting carbonaceous ribbon was uniformly impregnated with the tacky B-stage epoxy resin and consisted of about 42.6 percent of volume resin, and about 57.4 percent by volume carbon fiber.

EXAMPLE II

The solventless system provided in dip pan **36** contained 100 parts by weight of epoxy resin formed by reacting bisphenol A with epichlorohydrin, and 35 parts by weight of an amine curing agent. The solventless system at room temperature (i.e., 25° C.) was substantially non-flowable. Internally heated dip roller **34**, vessel **36**, and nip rollers **35** and **38** were maintained at 78° C. during the resin impregnation step at which temperature the resin system exhibited a viscosity of about 2,000 cps. The gap between nip rollers **35** and **38** was 0.010 inch.

The carbonaceous ribbon was passed through the apparatus at a rate of 20 inches per minute, and was present in heating zone **54** for a residence time of 13.5 minutes which was maintained at a uniform temperature of 125° C.

The resulting carbonaceous ribbon was uniformly impregnated with the tacky B-stage epoxy resin and consisted of about 45 percent by volume resin, and 55 percent by volume carbon fiber.

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.

We claim:

1. An improved process for the production of a uniformly resin impregnated ribbon of a carbonaceous fibrous material which is suitable for use in the manufacture of carbon fiber reinforced composite structures comprising:

a. continuously conveying to an impregnation zone a carbonaceous fibrous ribbon containing at least about 90 percent carbon by weight,

b. forcing a liquid solventless system having a viscosity of about 500 to 10,000 cps, comprising an A-stage thermosetting resin into intimate association with said carbonaceous fibrous ribbon while present in said impregnation zone,

c. interposing said ribbon while in intimate association with said solventless system between the outer surfaces of a pair of flexible endless belts having a non porous surface and a width greater than that of said ribbon,

d. continuously passing said ribbon in the direction of its length while interposed between said flexible endless belts through a substantially enclosed heating zone provided with a heated gaseous atmosphere while substantially suspended therein wherein said belts and said ribbon are looped in a single wrap about each of a multiplicity of rotating parallel rollers wherein the inner surfaces of said belts are in alternating contact with said rollers as said belts and said ribbon progress through said heating zone with said ribbon being out of contact with said rollers and wherein said thermosetting resin in intimate association with said ribbon is converted to a B-stage consistency,

e. continuously withdrawing said ribbon from said heating zone while interposed between said outer surfaces of said pair of flexible endless belts and while said thermosetting resin in intimate association with said ribbon remains in a B-stage consistency, and

f. separating said resulting resin impregnated carbonaceous fibrous ribbon from said flexible endless belts.

2. An improved process according to claim **1** wherein said carbonaceous fibrous ribbon comprises a plurality of substantially parallel multifilament fiber bundles.

3. An improved process according to claim **1** wherein said carbonaceous fibrous ribbon is a tow.

4. An improved process according to claim **1** wherein said carbonaceous fibrous ribbon contains at least about 95 percent carbon by weight and exhibits a predominantly graphitic X-ray diffraction pattern.

5. An improved process according to claim **1** wherein said liquid solventless system comprising an A-stage thermosetting resin has a viscosity of about 1,000 to 3,000 cps.

6. An improved process according to claim **1** wherein said solventless system comprising an A-stage thermosetting resin is forced into intimate association with said carbonaceous fibrous ribbon by passing said ribbon bearing said system upon its surface through a pair of rotating parallel nip rollers.

7. An improved process according to claim **1** wherein said solventless system comprises an A-stage epoxy resin and a curing agent for said resin.

8. An improved process according to claim **7** wherein said epoxy resin is a condensation product of bisphenol A and epichlorohydrin.

9. An improved process according to claim **7** wherein said epoxy resin is an epoxy novolac resin formed by the reacting of epichlorohydrin with a phenol-formaldehyde resin.

10. An improved process according to claim **1** wherein said resulting uniformly resin impregnated carbonaceous fibrous ribbon contains about 35 to 55 percent B-stage thermosetting resin by volume, and about 45 to 65 percent carbon fiber by volume.

11. An improved process for the production of a uniformly resin impregnated ribbon of a carbonaceous fibrous material which is suitable for use in the manufacture of carbon fiber reinforced composite structures comprising:

a. continuously conveying to an impregnation zone a carbonaceous fibrous ribbon containing at least about 90 percent carbon by weight,

b. forcing a liquid solventless system having a viscosity of about 1,000 to 3,000 cps. comprising an A-stage thermosetting epoxy resin and a curing agent for said resin into intimate association with said carbonaceous fibrous ribbon while present in said impregnation zone,

c. interposing said ribbon while in intimate association with said solventless system between the outer surfaces of a pair of flexible endless belts having a non porous surface and a width greater than that of said ribbon,

d. continuously passing said ribbon in the direction of its length while interposed between said flexible endless belts through a substantially enclosed heating zone provided with a heated gaseous atmosphere at a temperature of about 75° to 175° C. while substantially suspended therein wherein said belts and said ribbon are looped in a single wrap about each of a multiplicity of rotating parallel rollers wherein the inner surfaces of said belts are in alternating contact with said rollers as said belts and said ribbon progress through said heating zone with said ribbon being out of contact with said rollers and wherein said thermosetting epoxy resin in intimate association with said ribbon is converted to a B-stage consistency,

e. continuously withdrawing said ribbon from said heating zone while interposed between said outer surfaces of said pair of flexible endless belts and while said thermosetting epoxy resin in intimate association with said ribbon remains in a B-stage consistency, and

f. separating said resulting epoxy resin impregnated carbonaceous fibrous ribbon from said flexible endless belts.

12. An improved process according to claim **11** wherein said carbonaceous fibrous ribbon comprises a plurality of substantially parallel multifilament fiber bundles.

13. An improved process according to claim **11** wherein said carbonaceous fibrous ribbon is a tow.

14. An improved process according to claim **11** wherein said carbonaceous fibrous ribbon contains at least about 95 percent carbon by weight and exhibits a predominantly graphitic X-ray diffraction pattern.

15. An improved process according to claim **11** wherein said heated gaseous atmosphere provided within said heating zone has a temperature of about 100° to 150° C.

16. An improved process according to claim **11** wherein said solventless system comprising an A-stage thermosetting epoxy resin and a curing agent for said resin is forced into intimate association with said carbonaceous fibrous ribbon by passing said ribbon bearing said system upon its surface through a pair of rotating parallel nip rollers.

17. An improved process according to claim **11** wherein said epoxy resin is a condensation product of bisphenol A and epichlorohydrin.

18. An improved process according to claim **1** wherein said epoxy resin is an epoxy novolac resin formed by the reacting of epichlorohydrin with a phenol-formaldehyde resin.

19. An improved process according to claim **11** wherein said resulting uniformly epoxy resin impregnated carbonaceous fibrous ribbon contains about 35 to 55 percent B-stage thermosetting epoxy resin by volume, and about 45 to 65 percent carbon fiber by volume.

* * * * *