

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process and an apparatus for the continuous production of metal coated filaments.

2. Description of the Prior Art

Filaments comprising semi-metals and non-metals, such as carbon, boron, silicon carbide, polyester, nylon, aramid, cotton, rayon, and the like, in the form of monofilaments, yarns, tows, mats, cloths and bonded strands are known to be useful in reinforcing metals and organic polymeric materials. Articles comprising metals or plastics reinforced with such fibers find widespread use in replacing heavier components made up of lower strength conventional materials such as aluminum, steel, titanium, vinyl polymers, nylons, polyester, etc., in aircraft, automobiles, office equipment, sporting goods, and in many other fields.

A common problem in the use of such filaments, and also glass, asbestos and others, is a seeming lack of ability to translate the properties of the high strength filaments to the material to which ultimate and intimate contact is to be made. In essence, even though a high strength filament is employed, the filaments are merely mechanically entrapped, and the resulting composite pulls apart or breaks at disappointingly low applied forces.

The problems have been overcome in part by depositing a layer or layers of metals on the individual filaments prior to incorporating them into the bonding material, e.g., metal or plastic. Metal deposition has been accomplished by vacuum deposition, e.g., nickel on fibers as described in U.S. 4,132,828; and by electroless deposition from chemical baths, e.g., nickel on graphite filaments as described in U.S. 3,894,677; and by electrodeposition, e.g., nickel electroplating on carbon fibers as described in Sara, U.S. 3,622,283 and in Sara, U.S. 3,807,996. When the metal coated filaments of such procedures are twisted or sharply bent, a very substantial quantity of the metal flakes off or falls off as a powder. When such metal coated filaments are used to reinforce either metals or polymers, the ability to resist compressive stress and tensile stress is much less than what would be expected from the rule of mixtures, and this is strongly suggestive that failure to efficiently reinforce is due to poor bonding between the filament and the metal coating.

It has now been discovered that if electroplating is selected and if an amount of voltage is selected and used in excess of that which is required to merely dissociate (reduce) the electrodepositable metal ion on the filament surface, a superior bond between filament and metal layer is produced. The strength is such that when the metal coated filament is sharply bent, the coating may fracture, but it will not peel away. Moreover, continuous lengths of such metal coated filaments can be knotted and twisted without substantial loss of the metal to flakes or powder. High voltage is believed important to provide or facilitate uniform nucleation of the electrodepositable metal on the filament, and to overcome any screening or inhibiting effect of materials absorbed on the filament surface (EP-A-88884, published 21.09.83).

Although a quantity of electricity is required to electrodeposit metal on the filament surface, an increase in voltage may cause the filaments to burn, which would interrupt a continuous process. The aforesaid Sara patent No. 3,807,966, uses a continuous process to nickel plate graphite yarn, but employs a plating current of only 2.5 amperes, and long residence times, e.g., 14 minutes, and therefore low, and conventional, voltages. In another continuous process, described in U.K. Patent No. 1,272,777, the individual fibers in a bundle of fibers are electroplated without burning them up by passing the bundle through a jet of electrolyte carrying the plating material, the bundle being maintained at a negative potential relative to the electrolyte, in the case of silver on graphite, the potential between the anode and the fibers being a conventional 3 volts.

The present invention provides an efficient apparatus to facilitate increasing the potential between anode and the continuous filament cathode, since it is a key aspect of the present process to increase the voltage to obtain superior metal coated fibers. In addition, since it permits extra electrical energy to be introduced into the system without burning up the filaments, residence time is shortened, and production rates are vastly increased over those provided by the prior art. As will be clear from the detailed description which follows, novel means are used to provide high voltage plating, strategic cooling, efficient electrolyte-filament contact and high speed filament transport in various combinations, all of which result in enhancing the production rate and quality of metal coated filaments. Such filaments find substantial utility, for example, when incorporated into thermoplastic and thermoset molding compounds for aircraft lightning protection, EMI/RFI shielding and other applications requiring electrical/thermal conductivity. They are also useful in high surface electrodes for electrolytic cells. Composites in which such filaments are aligned in a substantially parallel manner dispersed in a matrix of metal, e.g., nickel coated graphite in a lead or zinc matrix are characterized by light weight and superior resistance to compressive and tensile stress. The apparatus of this invention can also be employed to enhance the production rate and product quality when electroplating normally non-conductive continuous filaments, e.g., polyaramids or cotton, etc., if first an adherent electrically conductive inner layer is deposited, e.g., by chemical means, on the non-conductive filament.

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SUMMARY OF THE INVENTION

It is a basic object of the present invention to provide a process for producing fibers formed of a conductive semi-metallic core with metallic coatings.

It is another object of the present invention to provide a process in which the electroplating of the fibers is effected under high voltage electroplating conditions.

Further, it is an object of the present invention to provide a process and apparatus which will efficiently and rapidly coat fibers with metallic coatings and facilitate the rinsing and collecting of the finished product.

A still further object of the present invention is to provide a process for producing fibers that are evenly plated around their diameter to the extent that any deviation in thickness of the plating is less than ten percent.

It is also an object of the present invention to plate all the fibers in a tow with the same width of material, within ten percent, regardless of whether the tow width is small or large, i.e., 3K to 12 x 12K.

It is another object of the present invention to provide a process by which metallic filaments, especially metal-coated filaments, can be provided with the properties helpful to facilitate blending with organic plastic materials, and for the provision of properties desirable and necessary for weaving the metal-coated fibers into fabric or mat-like articles.

It is a further object of the invention to provide metallic filaments with lubricity.

It is another and further object of the invention to provide metal-coated high strength fibers with a minimum of random fibrils extending outwardly from the basic fiber.

It is yet another object of the invention to provide metallized filaments with a metal oxide surface layer.

It is another object of the invention to provide composites, e.g., laminates, comprising metallized filaments having a surface treated by sizing and/or oxidizing and an organic polymeric matrix.

These and other objects are obtained in accordance with the present invention by a process as defined in one of claims 1 to 24 and with an apparatus as defined in one of claims 25 to 44.

In accordance with the present invention, an apparatus is provided in which a plurality of fibers can be simultaneously plated efficiently with a metal surface and thereafter cleaned and reeled for use in a variety of end products.

The apparatus is provided generally with a pay-out assembly adapted to deliver a multiplicity of fibers to an electrolytic plating bath. The pre-treatment process includes tri-sodium phosphate cleaning, rinsing and acid wash. For plating applications wherein non-conductive fibers are to be plated, pre-treatment processes may also include roughening or abrading the fibers, followed by chemical deposition of a thin metallic interlayer. Thereafter, metal-plating is performed in a continuous process by the passage of the fibers through an electrolyte in which the plating of the fibers is carried out at high voltage conditions. Means are provided to cool the fibers during the passage from the contact roll associated with the electrolytic tank and the electrolyte bath. Preferred means, in essence, are constituted by a recycle of electrolyte at strategic positions over the contact rollers and the fiber. The process also contemplates a series of discrete electrolytic tanks associated with separate rectifiers to facilitate variable current plating. The current is varied as a function of the resistance developed by the plating on the fibers.

After the plating has been completed, the plated fibers are rinsed by water and steam treated and thereafter dried.

The firmly adherent, high voltage, metal coated fibers prepared in the apparatus and process of the present invention are extremely useful as reinforcements to provide improved fiber-resin matrix composites. In these end use applications, it is further desirable to size the surface of the metal coated fibers so that they may be more easily knitted or woven into mats or fabrics, and to provide enhanced compatibility with the matrix resins or metals they reinforce.

In accordance with this aspect of the invention, the post-treatment sizing process of the present invention is characterized by delivery of metallic filaments to a medium comprising a coupling and sizing agent, e.g., aminosilane, alone, or in further combination with a medium comprising a bulking and polymeric sizing agent, e.g., polyvinyl acetate. Further processing of the material is also contemplated by passage of the material through dispersants, fluxes, and/or an external lubricant and sizing agent, e.g., polyethylene emulsion, combined with, or after discharge from the bulking and polymeric sizing bath. This entire process is conveniently referred to as sizing. During an intermediate step or after the sizing steps are complete, the fibers can be heated to dry and set the sizing material on the fibers. Among its features, the present invention also contemplates a process to surface oxidize metallic filaments under controlled conditions, alone, or in further combination with sizing.

As a result of the high voltage electroplating process, the continuous line is provided with means for synchronization of each of the process steps with the other. The high voltage environment also includes a specially designed commutation system for the contact rollers in which fingers of unequal length are provided and by the specially designed anode arrangement comprising an anode basket, a portion of which is coated with insulation for protection from the electrolyte bath.

The rinse tanks and electrolytic tanks are specially designed for maintenance of electrolyte level and minimal accumulation of waste rinse fluid.

The special rollers developed to use in the pay-out further facilitate the effectiveness of the process.

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DESCRIPTION OF THE DRAWINGS

The invention will be more readily understood when viewed in association with the following drawings wherein:

FIGURE 1 is a schematic view of the overall process of the subject continuous electrolytic plating process except for the pay-out assembly.

FIGURE 2 is an elevational view of the pay-out section arranged specifically to simultaneously deliver a multiplicity of fibers to the electrolytic plating operation.

FIGURE 3 is a plan view of the pay-out assembly of FIGURE 2.

FIGURE 4 is a sectional elevational view of the pay-out roller assembly.

FIGURE 5 is a sectional view through line 5—5 of FIGURE 4.

FIGURE 6 is an isometric view of the wetting and tensioning rollers between the pay-out and electrolytic bath.

FIGURE 7 is a sectional elevational view of the pre-treatment tank and associated apparatus.

FIGURE 8 is an elevational view of one electrolytic tank.

FIGURE 9 is a plan view of the tank of FIGURE 8.

FIGURE 10 is a sectional elevational view through line 10—10 of FIGURE 8.

FIGURE 11 is an isometric view of the commutation fingers.

FIGURE 12 is an isometric view of one contact roller in association with the means for providing coolant to the fibers and a current carrying medium from the contact roller to the bath.

FIGURE 13 is an elevational view of a section of the electrolytic tank depicting an anode basket.

FIGURE 14 is a plan view of the means for delivering electrolyte to the fibers extending from the contact roller to the electrolytic bath.

FIGURE 15 is a detail plan view of the nozzles of the spray assembly of FIGURE 12.

FIGURE 16 is a schematic of the electrolytic coolant conductor and a contact roller.

FIGURE 17 is a sectional elevational view of a contact roller of the process assembly.

FIGURE 18 is a detail of the end cap of the roller of FIGURE 17.

FIGURE 19 is a partial detail of the opposite end of the roller of FIGURE 17.

FIGURE 20 is a partially exploded sectional elevational view of the contact mount for the anode basket.

FIGURE 21 is an isometric view of the anode basket of the subject invention.

FIGURE 22 is a view of the electrical system of the present invention.

FIGURE 23 is a sectional elevational view of the rinse tanks and associated apparatus.

FIGURE 24 is a sectional elevational view of the washing-tee of the subject invention.

FIGURE 25 is a view through line 25—25 of the washing-tee of FIGURE 24.

FIGURE 26 is a view through line 26—26 of the washing-tee of FIGURE 24.

FIGURE 27 is a drawing of the mechanism for synchronously driving the apparatus of the subject invention.

FIGURE 28 is a plan view through line 28—28 of the section of FIGURE 27.

FIGURE 29 is a side elevational view of the roller assembly in the drying section of the system.

FIGURE 30 is a sectional view of a guide roller shown through line 30—30 of FIGURE 29.

FIGURE 31 is a schematic transverse cross sectional view of a metal coated rough-surfaced filament of this invention.

FIGURE 32 is a schematic longitudinal cross sectional view of a metal coated rough-surfaced filament according to this invention.

FIGURE 33 is a schematic magnified view of a portion of FIGURE 32.

FIGURE 34 is a schematic partial sectional view of a metal coated filament-reinforced polymer matrix obtained by using this invention.

FIGURE 35 is a schematic of an apparatus for carrying out the roughening and metallic interlayer chemical deposition process of the present invention.

FIGURE 36 is a schematic transverse cross sectional view of a metal coated fiber produced by the improved process of this invention.

FIGURE 36a is a schematic longitudinal cross sectional view of a metal coated fiber produced by the improved process of this invention.

FIGURE 37 and 37a are schematic transverse and longitudinal cross sectional views of, respectively, a core fiber coated with metal not according to this invention, illustrating the non-uniform plating resulting from organic compound contamination.

FIGURE 38 is a magnified photographic view of a metal coated fiber according to this invention which has a uniform coating because a core fiber free of organic compound contamination was provided.

FIGURE 39 is a magnified coating of a fiber not according to this invention which has a non uniform coating because a core fiber contaminated with adsorbed organic compounds was provided.

FIGURE 40 is a cross-sectional elevational schematic view of the process and apparatus used to size and/or surface-oxidize metallic filaments, e.g., metal coated high strength fibers.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The process and apparatus of the present invention are directed to providing an efficient and complete means for metal-plating non-metallic and semi-metallic fibers.

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The process of the invention relies on the use of very high voltage and current to effect satisfactory plating. As a result of the high voltage and current, an apparatus has been developed that can produce high volumes of plated material under high voltage conditions.

The process of the present invention and the apparatus particularly suitable for practicing the process of the invention are described in the preferred embodiment in which the specified fiber to be plated is a carbon or graphite fiber and the plating metal is nickel. However, the process and apparatus of the present invention are suitable for virtually the entire spectrum of metal-plating of non-metallic and semi-metallic fibers.

The overall process and schematic of the apparatus except for the pay-out assembly are generally shown in FIGURE 1. The operative process includes in essence, a pay-out assembly for dispensing multiple fibers in parallel, tensioning rollers 6, a pre-treatment section 8, a plating facility 10, a rinsing station 12, a drying section 14 and take-up reels 16.

More particularly, the pre-treatment section 8 shown generally in FIGURE 1 includes a tri-sodium phosphate cleaning section 26 and an associated washing-tee 28, rinse section 30 and associated washing-tees 32 and 32A, a hydrochloric acid section 34 and associated tee 36, and rinse section 38 with associated washing-tees 40 and 40A all of which are described in FIGURE 7. The plating facility 10 is comprised of a plurality of series arranged electrolyte tanks shown illustratively in FIGURE 1 as tanks 18, 20, 22 and 24, each of which is charged with current by a separate rectifier, better seen in FIGURES 8 and 22. The rinsing section 12, shown generally in FIGURE 1 is comprised of tank and tee assemblies similar to the pre-treatment apparatus. An arrangement of cascading tanks 42 and tees 44, 44A and 44B cycle rinse solution of water and electrolyte over the fibers 2. Thereafter, clean water is passed over the fibers 2 in the rinse section 46 provided with tanks and washing-tees 48 and 48A seen more specifically in FIGURE 26. The rinsed fiber 2 is passed through section 50 wherein it is air blasted in subsection 53 and then steam-treated in section 55 to produce an oxide surface on the metal plate. The process is completed by passage of the metal plated fiber 2 through the drying unit 14 and reeling of the finished fibers on take-up reels 17 in the reeling section 16.

As seen generally in FIGURE 1, the apparatus is provided with means to convey the fibers 2 through the system rapidly without abrading the fibers 2. The combination of strategically located guide rollers 51, tension rollers 6, force imposing rollers in the drying section 14 and a synchronous drive assembly shown in FIGURE 27 rapidly conveys the fibers 2 through the apparatus without abrasion of the fibers 2.

The operation begins with the pay-out assembly 4 shown in FIGURE 2 and 3. Functionally, the fibers 2 from the pay-out assembly 4 are delivered over a guide roller 5 through the tensioning rollers 6 to the pre-treatment section 8.

As best seen in FIGURES 2 and 3, the pay-out assembly 4 is comprised of a frame 52 on which the pay-out rollers 54 are mounted. The structure of the rollers 54 is better seen in FIGURE 4 and 5 and will be described more particularly in association with FIGURES 4 and 5. The pay-out rollers 54 are mounted on the frame 52 on a rail 56 and a rail 58. The rollers 54 on rail 56 are arranged to pay-out the fibers 2 to the electroplating system while the rail 58 is an auxiliary rail adapted to mount the spare rollers 54 available to provide alternate duty. A rail 60 mounts guide roller 62 over which the fibers 2 from the pay-out rollers 54 travel to reach the tensioning rollers 6.

As best seen in FIGURE 2, the fibers 2 extend from the respective rollers 54 over individual guide roller 62 associated with a particular roller 54 to the common guide roller 5 and into the tensioning roller assembly 6. Guide bars 59 are provided to guide fibers 2 from the pay-out rollers 54 to the associated guide rollers 62.

As seen in FIGURE 3, the guide rollers 62 are aligned adjacent to each other to avoid interference between the fibers 2 as a plurality of fibers 2 are simultaneously delivered to the system to be treated and plated.

The structure of the pay-out rollers 54 is best seen in FIGURES 4 and 5. The pay-out rollers 54 are comprised essentially of a centrally disposed rod 66 having end bearings 68 and 70, and are arranged to accommodate a compressive frame 64 formed of wires 72. Practice has taught that four resilient wires 72 arranged ninety degrees from each other will form a frame 64 suitable for mounting most commercial spools of fiber. Bearing 68 is arranged to bear against either the rail 56 or the rail 58 of the pay-out assembly 4.

The rod 66 is provided with a threaded end 76 that passes through an opening in the rails 56 or 58. A conventional nut (not shown) is used to attach the pay-out roller 54 which is thus cantilever mounted with the free end bearing 70 having a sliding fit on the bar 66. Thus, if the pay-out roller frame wires 72 are compressed, the bearing 70 can move transversely on the rod 66. Further, the frame wires 72 of the roller mount 64 are provided with tapered ends 74. As a result of the taper in the frame wires 72 and the transversely movable bearing 70, the compressive frame 64 can adjust to accept fiber spools of various diameter.

The pay-out assembly 4 delivers the fibers 2 over a guide roller 5 to a wetting roller 80 and then to the tensioning rollers 6. A wetting tub 84 is provided with water which wets the fiber 2 and enables suitable and more efficient cleaning and rinsing of the fibers 2 during pre-treatment. The tensioning rollers 6 seen in FIGURE 1 are shown in more detail in FIGURE 6.

The tensioning rollers 6 comprise an assembly of five rollers 90, all of which are driven through a single continuous chain 87 by a common source such as a variable speed motor 92. Each roller 90 is mounted on a shaft 89 which also mounts a fixed gear 91 around which the chain 87 is arranged. Idler rollers 97 are also arranged to engage the chain 87. A gear 93 extending from the shaft 95 of the variable speed motor 92 drives the continuous chain 87 through a chain 101 and a gear 103 fixed to the shaft 89 of a roller 90. It is necessary that tension be provided to the fibers 2 at a location in the line upstream of the first plating contact roller. The plating contact roller and the fibers 2 must be in tight contact to facilitate the operation at the high voltage and high current levels necessary for the process. With tight contact, low resistance is provided between the fibers 2 and the contact rollers, thus the high current passing through the system circuit will not overload the fibers 2 causing destruction of the fibers. As a result, the tension roller assembly 6 is located upstream of the electroplating tanks 18, 20, 22, 24 (FIGURE 1) to provide that tension. On the other hand, the fibers should be subjected to as little drag as possible. Inherent in the fibers 2 is the tendency to separate at the surface and accumulate fuzz. The variable drive motor 92 is coupled to all five of the rollers 90 to provide variable speed for the rollers at some speed equal to or less than the speed of the fibers 2. At carefully controlled speeds the necessary tension is provided without causing fuzz to accumulate on the fibers. The apparatus and process are designed to afford a tension roller assembly 6 in which the tension rollers 90 travel at a slower speed than the fibers 2. The tension on the fibers 2 is maintained by varying the speed of the tension roller 90 in response to visual determination of the tension.

In accordance with the new and improved apparatus and process of the present invention, the fibers to be coated are first subjected to cleaning in pre-treatment section 8. Pre-treatment provides an improvement which comprises providing core fibers whose surfaces are substantially free of adsorbed organic compounds which interfere with the electrodeposition of the metal. The surface substantially free of adsorbed organic compounds can be provided by removing them from the core fiber, e.g., by solvent cleaning, by chemical cleaning, by higher temperature cleaning and the like.

The term "substantially free" as used herein and in the appended claims means a very low amount of adsorbed organic compounds, i.e., an amount which does not interfere with the plating, and contribute to a non-uniform coating. It is very difficult to remove or avoid all traces, but usually an amount of up to about five percent of the surface areas of a short length can be covered and tolerated, without serious detriment.

If one pre-cleaning treatment, the surface substantially free of adsorbed organic compounds is provided by removing substantially all of any such compounds by contacting the core fibers with a solvent for such compounds. A useful solvent is 1,1,1-trichloroethane. This can be used in a conventional degreaser. Because of the high purity requirements of the cleaned fiber, the solvent must be changed or purified frequently.

In the preferred embodiment illustrated in Figure 1, the surface free of adsorbed organic compounds is provided by removing substantially all of any such compounds by contacting the fibers with an aqueous solution of an inorganic cleaning agent, preferably an inorganic phosphorus-containing compound including but not limited to phosphates and polyphosphates, and especially preferably trisodium phosphate. Typically a solution in water of 60 g./l. of trisodium phosphate can be used and heating to a temperature of about 60°C (140°F) to boiling facilitates removal of any organic compounds when the bundles of fibers are passed through the solution. Because the inorganic cleaning agents are, in most cases, alkaline when dissolved in water, and the subsequent plating solutions are generally acidic, it is a preferred feature to neutralize the pretreated yarns or tows with a dilute inorganic acid prior to immersion in the electroplating solution. Hydrochloric and/or other mineral acids are suitable in aqueous solution.

In addition to the pre-treatment in section 8, care should be taken throughout the plating process to maintain the graphite or fiber surface free of organic compounds by excluding them from the electroplating solution, or permitting the presence therein of only organic compounds which are capable of reduction to free sulfur at the cathodic surface (the clean graphite fibers themselves). This improvement comprises, in essence, rigorously excluding conventional electroplating additives which comprise or include organic compounds — such as wetting agents, like sodium lauryl sulfate, chelating agents, and brighteners which include organic components. Saccharin, for example, is suitable as an organic grain modifying agent (brightener) because, on the cathode, saccharin has the rather unique ability to reduce to elemental sulfur.

More particularly, as illustrated in the pretreatment section 8, best seen in Figures 1 and 7, the apparatus is comprised of a trisodium phosphate cleaning section 26 followed by a rinse section 30, and an acid cleaning section 34 followed by another rinse section 38. Each of the pre-treatment sections 26, 30, 34 and 38 are provided respectively with washing-tees 28, 32—32A, 36 and 40—40A shown in detail in Figures 22—24. Each pre-treatment section 26, 30, 34 and 38 is also provided with a tank into which the discharge from the washing-tees 28, 32A, 32, 36, 40A and 40 flow. The tri-sodium phosphate cleaning section 26 and the acid cleaning section 34 have single tanks 27 and 31 respectively. The rinse sections 30 and 38 have two tanks each, 33, 41 and 39, 49 respectively. In operation the fibers 2 pass through the tees 28, 32A, 32, 36, 40A and 40 in one direction while fluid passes through in the opposite direction.

A tri-sodium phosphate cleaning solution of generally any suitable concentration can be used in the cleaning section 26. However, practice has taught the 226.8 g (eight ounces) of tri-sodium phosphate per 3.765 (1 gallon) of water at 82°C (180°F) will provide the cleaning necessary for carbon fibers. Water is used

in the rinse section 30 to remove residual tri-sodium phosphate from the fibers 2 exiting from the tri-sodium phosphate section 26.

The fibers then pass through the tee 36 in the acid cleaning section 34 as the acid solution passes counter-currently with the fibers 2. The acid suitable for pre-treatment in association with the tri-sodium phosphate cleaning is a 10% hydrochloric acid solution. Thereafter, the fibers 2 are rinsed with water in the rinse section 38 wherein water again enters through the top of the tees 40 and 40A and exists through the upstream section of the tee opening thereby passing counter-currently with the fibers 2.

As seen in Figure 7, the pre-treatment section 8 is interconnected to facilitate the pre-treatment of the fibers 2 and to avoid or minimize the accumulation of contaminated pre-treatment solution. Each pre-treatment tank is provided with a stand pipe 308 that has a basket filter 310 arranged over the opening. Discharge from the tank is pumped from each tank through the stand pipe 308 by a pump 306. A line 316 from the stand pipe 308 in the rinse tank 49 communicates with the fluid inlet of the tee 40A associated with the rinse tank 39. A line 326 is connected to the inlet of the tee 40 associated with the tank 49 and a discharge line 320 is provided for the discharge of fluid from the tank 39.

A recirculating line 314 extends from the stand pipe 308 in the tank 31 to the fluid inlet of tee 36 to recirculate the hydrochloric acid wash. An inlet line 324 is provided to deliver initial and make-up hydrochloric acid wash to the fluid side of the tee 36.

The rinse tanks 41 and 33 are provided with a line 325 to the fluid inlet of the tee 32 associated with the tank 41 and a line 316 from the stand pipe 308 in tank 41 to the inlet of the tee 32A associated with the tank 33. A discharge line 322 is provided for discharge from the tank 33.

The tri-sodium phosphate tank 27 is provided with both a recirculating line 312 from the stand pipe 308 to the inlet of the tee 28 and a line 300 to deliver initial and make-up tri-sodium phosphate to the fluid inlet of the tee 28.

A neutralizing tank 318 charged with a neutralizing agent 330, such as Dolomite, is provided in the system to receive hydrochloric acid discharge from rinse tank 39 and tri-sodium phosphate discharge from rinse tank 33.

In operation the fibers 2 pass through the tees 28, 32A, 32, 36, 40A and 40 as fluid passes from the fluid inlets of the tees out the upstream fiber entry openings of the tees. The tri-sodium phosphate wash is recycled through stand pipe 308 and recycle line 312. Residue on the fibers 2 after passage from the tee 28 is rinsed from the fibers 2 by clear water that passes through the tee 32 associated with the rinse tank 41 and discharge from the rinse tank 41 that passes through the tee 32A associated with the rinse tank 33. The fluid in the rinse tank 33 which becomes contaminated with tri-sodium phosphate is discharged to the neutralizing tank 318.

After the fibers 2 leave the rinse section 30, hydrochloric acid wash is passed over the fibers 2 in tee 36. Discharge from the tee 36 is recycled to the fluid inlet of the tee 36 through stand pipe 208 in the tank 31 and recirculating line 314. The fibers 2 leaving the tee 36 are rinsed in rinse section 38. Clear water enters the rinse section 38 through the tee 40 associated with the rinse tank 49 and flows to the rinse tank 49. The fluid from rinse tank 49 is pumped through line 316 to the fluid inlet of the tee 40A associated with the rinse tank 39 and passed over the fibers 2 into the rinse tank 39. The fluid in the rinse tank 39 becomes contaminated with hydrochloric acid and is discharged through line 320 to the neutralizing tank.

The nature of the tri-sodium phosphate and the hydrochloric acid in combination with a calcium based material such as Dolomite neutralize the waste and minimize the additional treatment required for the waste before discharge through line 328 to waste.

The pre-treated fibers 2 are next electroplated. As seen in Figure 1, a plurality of electroplating tanks 18, 20, 22 and 24 are provided in series. Under the high voltage-high current conditions of the process, the series arrangement of electroplating tank 18, 20, 22 and 24 afford means for providing discrete voltage and current to the fibers 2 as a function of the accumulation of metal-plating on the fibers 2. Thus, depending on the amount of metal-plating on the fibers 2, the plating voltage and current can be set to levels most suitable for the particular resistance developed by the fiber and metal.

The electrolytic plating tank 18 is shown in FIGURES 8, 9 and 10 and is identical in structure to the plating tanks 20, 22 and 24 shown in FIGURE 1. The tank 18 is arranged to hold a bath of electrolyte. The tank 18 has mounted therewith contact rollers 100 and anode support bars 102 which are arranged in the circuit. The contact rollers 100 receive current from the bus bar 104 and the anode support bars 102 are connected directly to a bus bar 106. Each of the plating tanks 18, 20, 22 and 24 are provided with similar but separate independent circuitry as seen in FIGURE 22. The anode support bars 102 have mounted thereon anode baskets 110 arranged to hold and transfer current to nickel or other metal-plating chips.

Each tank 18, 20, 22 and 24 is also provided with heat exchangers 114 to heat the electrolyte bath to reach the desirable initial temperature at start-up and to cool the electrolyte during the high intensity current operation.

The tank 18 is provided with a well 103 defined by a solid wall 105 in which a level control 107 is mounted and with a recirculation line 109. The recirculation line 109 includes a pump 111 and a filter 113 and functions to continuously recirculate electrolyte from the well 103 to the tank 18. Under normal operating conditions recirculated electrolyte will enter the tank 18 and cause the electrolyte in the tank to rise to a level above the wall 105 and flow into the well 103. When electrolyte has evaporated from the tank the level in the well will drop and call for make-up from the downstream rinse section 12 shown in Figure 26.

The tank 18 is also provided with a line 132 and pump 134 through which electrolyte is pumped to a manifold 128 that delivers the electrolyte to the spray nozzle 130 above the contact rollers 100.

As shown in more detail in Figure 13, the fibers 2 pass over the contact rollers 100 and around idler rollers 112 located in proximity to the bottom of the tank. The idler rollers 112 are provided in pairs around which the fibers 2 pass to move into contact with the succeeding contact rollers 100.

The rollers 100 in the tank 18 communicate with the bus bar 104 through contact member 118. The detail of the contact member 118 seen in Figure 11 shows that the contact members 118 are formed of a copper bar 120 and a plural array of phosphor bronze fingers 122 and 124 that together provide the positive contact over a sufficiently large area on the contact roller 100 to avoid creating a high resistance condition at the point of contact. The fingers 122 and 124 are resiliently mounted on the bar 120 and by the nature of the material, are urged into contact with the contact roller 100 at all times.

Thus, a high strength positive electrical contact assembly is provided for an environment wherein conventional brush contacts cannot serve well.

The high voltage-high current process of the present invention is further facilitated by means for protecting the fibers 2 during the passage between the electrolyte bath and the various contact rollers. The system includes the recirculating spray system 126 shown generally in Figures 8 and 9 through which the electrolyte is recycled from the plating tanks and sprayed through the spray nozzles 130 on the fibers 2 at contact points on the contact rollers 100.

The spray nozzles 130 are arranged with two parallel tubular arms 136 and 138 having nozzle openings 139 located on the lower surfaces thereof. As best seen in Figure 15, one tubular arm 136 of the spray nozzle 130, is arranged to direct electrolyte tangentially on the fibers 2 at the point at which the fibers 2 leave the contact roller 100. The other tubular arm 138 of the spray nozzle 130 is arranged to deliver electrolyte directly on the top of the contact roller 100 at the point at which the fiber 2 engages the contact roller 100. As previously indicated, it is vital that sufficient tension be applied on the fibers 2 to insure that the fibers 2 are maintained in a tight direct line between the contact rollers 100 and the idler rollers 112. The need for a tight line is to assure that the low contact resistance suitable for current travel is available with high conductivity through the fibers 2 from the contact rollers 100 to the electrolyte bath. The electrolyte which is recirculated over the contact rollers 100 and the fibers 2 provide a parallel resistor in the circuit and serve to cool the fibers 2.

It is known that the fibers 2 being plated have a low fusing current, such as 10 amps for a 12K tow of about 7 μ m in diameter. However, the process of the the present invention requires about 25 amps between contacts or about 125 amps per strand in each tank.

Furthermore, both contact resistance and anisotropic resistance must be overcome. The contact resistance of 12K tow of about 7 μ m on pure clean copper is about 2 ohms, thus at 45 volts twenty-two and one-half amps are required before any plating can occur. The anisotropic resistance is 1,000 times the long axis. Thus, the total contact area must be 1,000 times the tow diameter, which for 7 μ m is 8.636 mm (0.34 inches). Practice has taught that 12.7 mm (0.5 inch) of contact will properly serve the electrical requirement of the system when plating 7 μ m tow, 50.8 and 76.2 mm (2 and 3 inch) contact rollers 100 are used. It is also vital that the contact rollers 100 be located at a specified distance above the electrolyte bath to enable the system to operate at the high voltages necessary to achieve the plating of the process. In practice, it has been found that the contact rollers 100 should be located 12.7 to 25.4 mm (0.5 to 1 inch) from the electrolyte bath when voltages of 16 to 25 volts are applied. Further, it has been found that recirculation of about .75 l (2 gallons) per minute per contact roller travelling at about 0.45 to 7.6 m (1 1/2 to 25 ft)/min. will properly cool the fiber and provide a suitable parallel resistor when above 5,000 amps are passed through the system on three cells.

The electrolyte in the process is a solution constituted of 226.8—283.5 g (8—10 ounces) of metal, preferably in the form of NiCl_2 and NiSO_4 per 3.785 l (1 gallon) of solution. The pH of the solution is set at 4 to 4.5 and the temperature maintained between 62.7 and 66°C (145 and 150°F). Recirculation of the electrolyte through the spray nozzles 130 at the desired rate requires that the nozzle openings be 2.38 mm (3/32 inches) in diameter on (3.175 mm) (1/8") centres over the length of each tubular arm 136 and 138. The presence of electrolyte on the fibers is vital, but care is taken to avoid excessive electrolyte otherwise the contact rollers will become subjected to the plating occurring in the electrolyte.

The anode support bar 102 for the anode basket 110 is shown in detail in Figure 20 and is comprised of essentially three layers. A steel inner bar 150 is provided to afford structural support for the anode basket 110. A copper coating 152, such as a copper pipe, over the steel bar 150 is provided to afford the electrical properties desirable for the passage of current, and an insulator of some material, such as vinyl 154, is provided to insulate the entire anode support bar 102. At strategic locations on the bar 102, the vinyl is removed and notches 156 expose the copper coating 152 to afford electrical contact.

As best seen in Figure 21, the anode basket 110 is provided with the conventional openings 158 found in anode baskets but also has a vinyl insulated covering 162 that extends from the top of the anode basket 110 to a location below the surface of the electrolytic bath. Practice has taught that insulating the anode basket 110 10.16 to 30.48 cm (four to twelve inches) from the top will protect the anode basket 110 from destruction of the protective oxide under the high intensity current and voltage conditions experienced in the process. The conventional hooks 160 found on the anode baskets 110 are arranged to fit within the notches 156 provided on the anode support bar 102. Further, the anode basket is preferably made of

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titanium due to the nature of the high voltage environment and the electrolyte. The high voltage has been found to remove the surface of the titanium which is normally a TiO_2 layer that protects the anode basket 110 from the electrolyte.

The contact rollers 100 are shown in detail in Figures 17—19. Each contact roller 100 is located in close proximity to the electrolyte in the plating tanks and each is adapted to transmit high current through the system in a high intensity voltage environment. The contact roller 100 thus is designed for continual replacement. The contact roller 100 is provided with fixed end mounting sections 170 and 172 which holds a cylindrical copper tube 174. The cylindrical copper tube 174 is arranged to contact the commutator fingers 122—124 and deliver current through both the fibers 2 and recycled electrolyte to the electrolyte bath. The copper tube 174 is formed of conventional type L copper which must be able to carry 350 amperes. The diameter of the tubing is critical in that the diameter dictates the contact surface for the fibers 2 and the distance that the contact roller 100 will be from the electrolyte surface. As a result, the mounts 170 and 172 are fixedly arranged in alignment with each other to releasably support the tube 174 of the contact roller 100. The mount 170 is provided with a bearing support 176 through which a screw mount 178 passes. The screw mount 178 rotatably supports the copper tube 174 on a bushing support 180 and has the capacity to release the copper tube 174 upon retraction of the bushing support 180 by withdrawing the screw 178. The mount 172 includes a bushing support 182 on which a detent 184 is formed. Each copper tube 174 is provided with a notched mating slot 186 to fit around the detent 184 and effect positive attachment of the copper tube 174 to the bushing support 182 thereby obviating any uncertainty in alignment and facilitating dispatch in replacing each copper tube section 174.

The overall electrical system 188 of the process and apparatus is shown schematically in Figure 22 wherein the capacity for discrete application of voltage and current to each electrolytic tank 18, 20, 22, 24 can be seen. Conventional rectifiers 189, 191, 193 and 195 are arranged as a D.C. power source to deliver current to the respective contact rollers 100 on each electrolytic tank. Bus bars 104, 194, 196, 198 are shown for illustration extending respectively from the rectifiers 189, 191, 193 and 195 to one of the six contact rollers 100 on the electrolytic tanks 18, 20, 22 and 24. However, all six contact rollers 100 on each electrolytic tank are directly connected to the same bus bar. Bus bars 106, 202, 204 and 206 are shown extending respectively from the same rectifiers 189, 191, 193 and 195 through cables 208 to one anode support bar 102 mounted on the electrolytic tanks 18, 20, 22 and 24. Again, the respective anode bus bars contact each anode support bar 102 mounted on each electrolytic tank connected to the bus bar.

As a result of the arrangement, discrete high voltage can be delivered to each electrolytic tank 18, 20, 22, 24 as a function of the metal plating on the fibers 2 in each electrolytic tank.

Practice has taught that in volume production the voltage in the first electrolyte tank 18 should not be below 16 volts and seldom be below 24 volts. The voltage in the second tank 20 should not be below 14 volts and the voltage in the third electrolyte tank 22 should not be below 12 volts.

Illustratively, fibers 2 have been coated in a system of three rectifier-tank assemblies, rather than the four shown in Figures 1 and 22, under the following conditions wherein excellent coating has resulted:

Rectifier	189	191	193
Amps	1,400	1,400	1,400
Volts	45	26	17

The nickel metal coated fibers 2 produced under these conditions have the following properties and characteristics.

Filament shape	Round (but dependent on graphite fiber)
Diameter	8 μm
Metal Coating	Approximately 0.5 μm thick, about 50% of the total fiber weight
Density	2.50—3.00 grams/cm ³
Tensile Strength	Up to (450,000 psi) 3103 N/mm ²
Tensile Modulus	(34 M psi) $2.34 \cdot 10^9 \text{ N/mm}^2$
Electrical	0.008 ohms/cm. (12K tow)
Conductivity	0.10 ohms/1000 strands/cm.

After the nickel plating has occurred, the fully plated fibers 2 are delivered to the rinsing section 12 as seen in Figure 1.

The drag-out section 42 and rinse section 46 are arranged with tanks to accumulate the discharge from the tees 44, 44A, 44B, 48 and 48A and both neutralize the discharge for waste disposal and provide a repository for accumulation of make-up for the electrolyte tanks 18, 20, 22 and 24.

As best seen in Figure 23, the tanks in the drag-out section 42 consists of a cascading tank with separate compartments 252, 254 and 256. The cascading tank is a conventional three station cascade countercurrent rinse tank manufactured by National Plastics, Thermal Electron Division. The cascading tank automatically provides for passage of the discharge fluid from the downstream tanks to the upstream tank by passage around the overflow dams 258. The fluid accumulated in tank 256 will reach a level above the separation wall 255 between tank 256 and tank 254 and pass to tank 254. Similarly, when the level in tank 254 is greater than the level of the separation wall 251, the fluid will pass further upstream to tank 252.

The rinse section includes tanks 250 and 260. Both tanks 250 and 260 are provided with stand pipes 268 having basket filters 270 arranged at the top opening. A conveying line 261 is connected to the stand pipe 268 in tank 260 and is provided with the pump 264. The discharge from tank 260 is pumped to the tee 48A associated with tank 250 to rinse the fibers 2. The discharge from the tank 250 is delivered through line 276 to the cascading tank assembly, or alternatively through line 278 to waste disposal.

A line 271 is provided to connect the discharge in the tank 252 to the tanks 18, 20, 22 and 24 which are equipped with level control devices 107 that open solenoid valve 273 when the level in a tank 18, 20, 22 or 24 drops to a level that requires electrolyte.

During the operation, the fibers 2 pass through the tees 44B, 44A, 44, 48A and 48 and are rinsed with water. The clear water is delivered to the system through line 267 to the tee 48 and flows counter to the direction of the fibers 2 to discharge through the upstream end of the tee 48 into the tank 260. The discharge from the tank 260 is pumped to the fluid inlet of tee 48A and is discharged through the upstream end of the tee 48A into the tank 250. The fluid in the tank 250 is relatively dilute due to the previous rinse treatment of the fibers 2, thus it can be discharged through line 278 as waste or delivered to the tank 256 as needed. The tanks 256, 254 and 252 operate continuously in the recirculation mode, thereby producing a fluid that becomes increasingly rich in electrolyte. As a result, a minimum of contaminated water is generated in the system, while an electrolyte rich solution is produced for electrolyte make-up.

A tee designated 28, used in the system pre-treatment section 8 and rinse section 12 is shown in Figures 26-28. As previously indicated, the tees are designed to afford countercurrent travel of solution with the fibers 2. In practice, the tees 28 are designed with an upstream opening 210 and a downstream opening 212 for the passage of fibers 2 therethrough. The tees 28 are also provided with a dome housing 214 through which the solution such as rinse water can enter and bathe the fibers 2 as the fibers 2 pass through the tee 28. The tees 28 are also provided with a sleeve 216 that creates a pressure head which directs water in the upstream direction. In addition, the tees are designed with the opening 210 for the passage of fibers 2, at an elevation slightly below the opening 212. Thus, the path by which water escapes from the tee is from the delivery pipe 218 through the opening 210. The combination of the differential elevation in the openings 210 and 212 and the presence of the sleeve 216 located in the downstream section of the tee 28 promotes travel of the solution in a direction upstream as the fibers are moving downstream.

The apparatus of the present invention is arranged for synchronous operation as shown in Figures 27-29. A motor 222 is provided to insure that the contact rollers 100 and the guide rollers 51 rotate at the same speed to avoid abrading the fibers 2.

The motor 222 directly drives an assembly of rollers 223 arranged to effect a capstan. The rollers 223 are located in the dryer 14 and as best seen in Figure 29 cause the fiber to reverse direction six times. The reversal in direction is sufficient to impose a force on the fibers 2 that will pull the fibers through the apparatus without allowing slack.

In addition, the motor 222 is connected by a gear and chain assembly to drive each contact roller 100 and each guide roller 51 at the same speed.

In essence, the gear and chain assembly is comprised of guide drive assemblies 225, best seen in Figure 28 and contact roller drive assemblies 227. Each guide drive assembly 225 includes drive transmission gear 230 mounted on shafts 231, a gear 224 fixedly secured to the guide roller 51 and a chain 233 that engages the gears 230 and 224.

The contact roller drive assembly includes drive transmission gear 239 mounted on the shafts 231 common to the gears 230, a gear 241 fixedly secured to each contact roller 100 and a chain 243 that engages both gears 239 and each of the gears 241 on the six contact rollers 100 associated with each electrolyte tank.

As seen in Figure 30 each guide roller 51 is formed with grooves 280 having tapered sides 282 and flat surfaces 284. The diameter of the guide roller at the surface 284 is the same as the diameter of the contact rollers 100 and the capstan rollers 223, thus constant speed is experienced by the fibers 2 along the path through the apparatus.

The flat surfaces 284 afford a means by which the fibers or tows 2 spread to either facilitate drying or wetting depending on the operative effect desired.

The location of the capstan rollers 223 in the dryer 14 enhances drying. The flat surface and force applied to the fibers 2 spreads the fibers and thereby accelerates drying.

The system also includes a variable speed clutch override drive motor 219 for the take-up reels 17. The

force generated by the variable torque motor 219 provides the force to draw the fiber 2 through the system. However, the capstan rollers 223 provide a means to isolate the direct force imposed on the fibers 2 at the take-up reels 17 from the fibers 2 upstream of the capstan rollers.

The apparatus and plating process described above may be used to provide firmly adherent metal coated fibers, not only to semi-conductive fibers such as carbon or graphite fibers, but also may be employed to form firmly adherent metal coatings on non-conductive fibers.

More particularly, it has been discovered that if the surface only of filaments or a plurality of filaments comprising a rough non-conductive core is sensitized and finally rendered conductive, by chemical deposition of a thin metallic interlayer, useful materials suitable for plating in the above-described high voltage continuous apparatus and process are obtained. In accordance with this aspect of the invention metal coated filaments having non-conductive cores are obtained in which the bond between the coating and the filament is so strong that bending the fiber, as in weaving or knitting, may rupture the coating, but it will not peel away. If a smooth surface core is provided, e.g., aramid, it is necessary to roughen the surface before sensitizing the roughened surface with a salt of a noble metal, e.g., palladium. If a rough surface is normally present, e.g., cotton, then the roughening can be omitted. Next there is deposited a metal, such as nickel, silver, or copper on the rough, sensitized surface. Moreover, the surface can be electroplated, e.g., with nickel or silver using a high external voltage. In either case, there will be provided uniform, continuous, adherent, thin metal coatings on the surface of the filaments. It is believed, that high voltage provides energy sufficient to provide uniform nucleation, especially if a plurality of filaments is used. Furthermore, the high voltage provides an even distribution on each fiber. Filaments comprising thin metal coatings on the metallized cores, and yarns, cloths, felts and the like, according to this invention can be knotted or folded without the metal substantially flaking off.

According to this aspect of the present invention, continuous filaments are provided having a rough, electrically non-conductive polymeric core, the rough surface of which is sensitized to the chemical deposition of a metal, an electrically conductive metallic interlayer chemically deposited on the sensitized rough surface of said core and firmly bonded thereto, alone, or in combination with at least one thin, uniform, firmly adherent, electrically conductive layer of at least one metal electrodeposited on said interlayer. The bond strength of the coated filament is at least sufficient to provide that when the coated filament is bent the coating may fracture, but it will not peel off.

More particularly, the core filaments are generally selected from a number of organic polymeric materials, all of which will be electrically non-conductive. Included are polyolefin filaments, e.g., polypropylene, polyacrylonitrile, wool, cotton, rayon and the like. Especially contemplated are polyester filaments, such as poly(ethylene terephthalate) and polyamide filaments such as nylons, e.g., poly(caprolactam) and poly(1,6-hexamethylenediamine adipate), and the so-called aramids, which are long chain synthetic polyamides in which at least 85% of the amide linkages are attached directly to two aromatic rings. The latter are described, together with methods for their production, in the Encyclopedia of Chemical Technology, 3rd Edition, Volume 3, John Wiley, New York, 1978, pages 213—242.

Especially suitable as core materials are aramid filaments made by polycondensing diacid chlorides and diamines in amide solvents, such as dimethylacetamide and N-methylpyrrolidone. High strength such filaments can be made by solvent spinning the condensation product of p-aminobenzoyl chloride hydrochloride, the product being known as poly(p-benzamide) or PPB. Another condensation product is made from p-phenylenediamine and terephthaloyl chloride. It is known as poly(paraphenyleneterephthalamide) or PPD—T. Fibers comprising the latter are available from the DuPont Company, Wilmington, Delaware 19898 under its trademark KEVLAR 29 and 49, the latter being a hot drawn fiber. Typical bundles of filaments used in this invention will average 4 thousand filaments per yarn bundle, each of which filaments has an average 12 μ m diameter.

Referring to Figs. 31 and 32 continuous yarns and tows for use in the core 2 according to the present invention are available commercially. For example, suitable aramid fiber yarns are available from DuPont Company, under the trademark KEVLAR—29 and KEVLAR—49 and suitable polyester fiber yarns are available from DuPont Company under the trademark DACRON Polyester (Type 68). Suitable nylon polyamide yarns are available from DuPont (Type 728) for example. Cotton threads and wool fibers can be used. As mentioned above, all such fibers will be non-conductive and sensitized to chemical deposition of a metallic interlayer 332. The cotton threads and wool fibers are naturally rough; the others must be made rough.

Surface roughening is carried out in any normal way, but preferred is abrading the filaments with finely divided silica, aluminium oxide, sand, etc. In conventional filaments, e.g., those 4 to 15 μ m thick, 120 mesh (U.S. standard) abrasive will produce a suitably roughened surface. The roughened surfaces provides essential anchoring sites for interlayer 332, as shown in Fig. 33, providing an enhanced mechanical grip. In continuous production, roughening is facilitated in a fluidized bed mechanical abrader, e.g., a Cole-Parmer-type apparatus.

The roughened fibers are then treated with materials to produce a sensitized and activated surface, e.g., by continuously passing them through a stannous chloride, or stannous sulfate solution and then through a solution of a salt of a noble metal. Wetting of the roughened fibers can be facilitated in the stannous chloride solution by the addition of a small amount of a cleaning agent. The preferred noble metal salt is a water-soluble palladium salt, such as palladium chloride. Salts of gold, platinum and rhodium can

also be used. The sensitized rough surface presents outwardly a thin layer of metal which catalyzes the chemical deposition of metal from ions in the solution used to form the metal interlayer, e.g., silver metal from silver nitrate solution, then, without rinsing, into a solution of hydrazine, a hydrazine compound or a borohydride, at a high reducer to low metal ratio, to reduce silver ion to silver metal, well-bonded to the surface. The thickness of interlayer 332 builds up with time and it is sufficiently thick when conductivity (or decrease in resistance) is sufficient to permit electrodeposition in subsequent steps. This can be measured in known ways. For further details on this aspect, reference is made to the abovementioned, U.S. 3,495,940, the procedure of which does not, however, use a roughened fiber surface.

Metal layer 334 will be of an electrodepositable metal deposited by the high voltage-high current process defined above. Two layers, or even more, of metal can be applied and metal can be the same or different, as will be shown in working examples.

Roughening of the non-conductive fibers followed by chemical deposition of metallic interlayer 332 may be conducted as a separate process or it may be made a part of the continuous line plating apparatus illustrated in Figure 1, by introducing abrading section 336, sensitizing and interlayer deposition sections 338, 340, 342 and 344 shown schematically in Figure 35 into the continuous line plating apparatus shown in Figure 1, intermediate pre-treatment cleaning section 8 and electroplating section 10.

The metal coated filaments of this invention can be assembled by any conventional means into composites represented in Fig. 34 in which matrix 346 is a plastic, e.g., an epoxy resin, or the like, the matrix being reinforced by virtue of the presence of metal coated cores 2.

Shown schematically in Fig. 35 are components of a continuous processing apparatus comprising in series a filament transport section, e.g., roller 51, feeding a fluidized bed mechanical abrader means 336 in which surface roughening filament 2 is accomplished, e.g., with a slurry of 120 mesh (U.S. standard) silica. This is not used if the filament has a normally rough surface. Then after sensitization, e.g., by transporting and dipping first into tank 338 holding a SnCl_2 solution, rinsing, and then into tank 340 holding a PdCl_2 solution, and rinsing, filaments having a rough sensitized surface is passed into tank 342 holding chemical metal deposition bath containing, e.g., silver nitrate and finally, without rinsing, into reducing bath tank 338, containing, e.g., hydrazine hydrate (alkaline). A thin coating of silver is deposited, sufficient to reduce electrical resistance to the point where the filament can be used in composites or, optionally, sent to electroplating section 10, of Figure 1.

As has been mentioned above, it may be desirable to size the metal-coated fibers prepared by the process of this invention in a post-treatment sizing process. The post-treatment sizing process may be run independently, however, it is preferred to have post-treatment sizing of the metal-coated fibers performed as part of the continuous line process depicted in Figure 1, as part of the drying step 14 shown therein. The post-treatment process and apparatus, in essence, provide metallized filaments, e.g., fibers, with a sizing material or materials that impart various properties to them, such as lubricity and bulk, and enhanced compatibility with plastics, and improved resistance to moisture, e.g., when mixed with polymers.

For convenience, the following discussion will deal with metal-coated fibers, although it is to be understood that metallic filaments can be processed also.

More particularly, as shown in Figure 40, the sizing and drying apparatus and process comprise steam section 55 shown in Figure 1, sizing sections 366, heating assemblies 364, and take-up reels 17 shown in section 16 of Figure 1. As will be explained later, section 366 can comprise a single tank and one or more heating assemblies 364 can be used. Furthermore, means 55 for providing an oxidized surface, such as low pressure steam boxes, can also be included.

As seen in the FIGURE 40, in one embodiment the sizing section 366 is further comprised of a first tank 346, a second tank 348, and a third tank 350, all of which are adapted to contain sizing solutions and to facilitate the continuous flow of metal-coated fibers therethrough. Each tank 346, 348 and 350 is provided with idler rollers 352 and 354 disposed near the bottom of the tank. Rollers 352 and 354 are cylindrical and guide roller 356 is flat bottom, to facilitate tow spread and uniform sizing.

Each tank is arranged with driven contact rollers 356 and 358 located above the tank in general alignment with the idler rollers 352 and 354. Guide rollers 358 are also located at the entry of each tank.

The heating section 364 consists of means for heating the sized metal-coated fiber to dry and set the sizing solutions or emulsions to the metal-coated carbon fiber. As has been indicated, each tank can be followed by an independent heating section 364.

The drive for the assembly is provided by a motor 360, which transmits drive directly to the take-up roller 17 and a chain gear assembly comprises of chains 362, from which the power is transmitted from the capstan gear 368 to the contact roller 358.

In use the metal coated fibers 2, travel through air blast section 53 as shown in FIGURE 1 and pass through steam boxes 55, as shown in FIGURES 1 and 40, which serves to oxidize the metal coating on the fibers. The metal-coated surface-oxidized fibers 2 first preferably pass through tank 346, which is filled with a coupling/sizing agent such as aminosilane solution. After passage through the tank 346, the metal-coated fiber is essentially provided with a coupling/sizing surface that has been coupled to the metal oxide surface of the coated fiber. Thereafter, the fiber 2 is delivered to the tank 348, which contains a bulking/sizing agent such as a polyvinyl acetate solution. The polyvinyl acetate solution provides, in combination with the coupling/sizing, e.g. aminosilane coating, a bulk density for the metal-coated fibers. Alternatively, both sizing agents can be combined in a single tank. Thereafter, the fibers 2 are delivered to the tank 350, in

which a sizing/lubricating agent, e.g., polyethylene solution or emulsion is provided to afford lubricity for the fibers. Alternatively, this can be combined in a single tank with the sizing/coupling and/or sizing bulk density agent.

The sized fibers 2 are then delivered to the oven section 364, wherein drying and setting occur and the heated dried fibers 2 are forwarded to a second sizing section 366 and drying section and, finally wound on the take up rollers 17. Although dual stages are shown, for flexibility, depending on the circumstances, only a single stage may be used.

With respect to the coupling/sizing agent component, this will typically comprise a surface-reactive coupling agent. Typically, it will be a silane or a titanate. Silanes have the general formula $Y-R-Si-X_3$, wherein X represents a hydrolyzable group, e.g., alkoxy; Y is a functional organic group such as methacryloxy, epoxy, etc., and R typically is a small aliphatic linkage, $-(CH_2)_n-$, that serves to attach the functional organic group to silicon (Si) in a stable position. Illustratively, available silanes are: vinyl-triethoxysilane, vinyl-tris(beta-methoxyethoxy) silane, gamma-methacryloxypropyltrimethoxy silane, beta-(3,4-epoxy-cyclohexyl) ethyltrimethoxysilane, gamma-glycidoxypropyltrimethoxysilane, gamma-amino-propyltriethoxysilane, n-beta-(aminoethyl) gamma-aminopropyltrimethoxysilane, gamma-ureidopropyltriethoxysilane, gamma-chloropropyltrimethoxysilane, gamma-mercaptopropyltrimethoxysilane, and the like. The aminosilanes are preferred. All can be used in conventional amounts and in the usual media, as supplied, or diluted with water or an organic solvent, or even as a dry concentrate, e.g., in a fluidized bed. Typical titanates are isopropyltri(dioctylpyrophosphate) titanate, titanium di(dioctylphosphate) oxyacetate and tetraoctyloxytitanium di(dilaurylphosphite).

In practice, it has been found that aminosilane solutions of between 0.1 and 2.5 parts of gamma-amino-propyltriethoxysilane such as Dow-Corning Z-6020, or gamma-glycidoxypropyltrimethoxysilane such as Dow-Corning Z-6040, per 100 parts of water adjusted to a pH of between 3.5 and 8, e.g., by acetic acid, are particularly suitable for coupling aminosilanes to nickel- or silver-coated carbon or aramid fibers. Practice has taught that the residence time of the fiber in the solution should be at least sufficient to generate a surface having a coupled sizing. This will usually be about 0.5 seconds, but the time can be longer, e.g., at least about 5 seconds, depending on downstream residence time requirements.

With respect to the bulking/sizing agent, this can be usually an organic polymeric material conventional for this purpose. Preferably, it will be a vinyl polymer or a cellulosic dissolved in water or an organic solvent, or emulsified in water. Among the polymers suitable for use are starches, cellulosic ethers, esters and carboxylates. In addition, polyvinyl esters such as polyvinyl acetate and copolymers such as ethylene/vinyl acetate can be used, as well as polyvinyl alcohol and dispersants, such as polyvinyl pyrrolidone. It is preferred to use polyvinyl acetate. All are used in amounts established and well known to be suitable for sizing purposes.

Practice has also taught that a polyvinyl acetate solution of about 20 parts of carboxylated polyvinyl acetate late (Borden's Polyco 2142, 50% solids) per 100 parts of water provides a particularly suitable solution for contributing bulk density to the metal-plated fibers. The residence time for the fiber in the polyvinyl acetate medium should be at least sufficient to generate a sized surface, preferably at least about 5.0 seconds.

Lubricity is imparted by slip agents or lubricants comprising organic materials conventionally used.

Preferably, molecular films will be formed between the sized fibers and surfaces against which they are moved, e.g., virgin plastic pellets. Such a characteristic reduces tendency to hand-up and abrade. Illustrative lubricants are fatty alcohols, fatty acid esters, glycerol partial esters, polyesters, fatty acid amides, e.g., oleamide, metal soaps, fatty acids, e.g. stearic acid and polyolefins, especially polyethylenes, which are preferred. These can be used in the form of solutions and emulsions.

A polyethylene emulsion of 10 parts c' polyethylene (Bercen, Inc.'s Bersize S-200, 50% solids) in 100 parts by weight of water provides a particularly desirable solution to afford lubricity to the fibers. Fiber residence times sufficient to generate a lubricated surface are used. Time of at least about 5 seconds in the polyethylene medium has been found to be desirable.

The method for producing an oxidized surface on the metal coated filament comprises in general exposing the outer surface to an oxidizing medium. The metal surface, of course, will be one capable of oxidation. Chemical or atmospheric techniques, and the like, can be employed, e.g., with nickel, tin, copper, brass, and the like, and the use of heat is recommended because the rate of production of the surface oxide coating is enhanced. It is especially convenient to use air or an oxygen-containing gas as the medium for oxidation and to use steam as a source of heat. Sufficient time is provided to produce the metal oxide coating, preferably a uniform, thin, coating. In a continuous process, using steam and air, only a fraction of a second is preferred, e.g., about 0.5 seconds, although less or more time can be allowed. For best results, the filaments are dried prior to being sized.

The sized and/or oxidized metallic filaments produced in the process have been used as chopped material to mix with and blend with plastics, e.g., about about 5—50% by weight in nylon, polyesters, polycarbonates, polyolefins, polyurethanes, polystyrenes, polyepoxides, and the like, to provide composites of the fibers and a matrix of the plastic. If the filaments are woven, knitted or laid up onto the mats, laminates can be obtained. It has been found that sized metal-coated carbon fibers can more readily be blended with plastic without a great deal of difficulty due to the added bulk density of the sized chopped material. Testing has shown that composites made from 60 parts of silane sized fibers according to this invention with 40

parts, by weight, of epoxy resin and curing, are about 30% better in terms of short beam shear strength at room temperature, and at elevated moist temperature, than those made with unsized fibers.

The fibers sized and/or surface oxidized in accordance with the process of the present invention also have been woven into fabric patterns. It has been observed that the fuzz typically extending randomly from the metal-coated fiber do not interfere with the weaving after the sizing has occurred. Further, the woven material can be formed into a fabric pattern very easily by virtue of the lubricity that inheres in the sized material. Conversely, sized nickel-coated carbon graphite, or other high strength fiber, has been found to have excellent lubricity and lacks abrasiveness, facilitating weaving. Also sized fibers avoid random fibers extending from the fibers which can cause an accumulation of fuzzy materials which interfere considerably with any weaving pattern by depositing on guides in the machines, etc.

Further, the sizing materials can act as water displacement agents which reduce the tendency of composites made from the coated fibers to delaminate after being put into a plastic matrix, and exposed to moisture.

Practice has taught that a carbon fiber coated with nickel and treated with steam, e.g., distilled water steam, will provide a nickel oxide surface, dense and adherent of 1.5—5 nm (15—50 angstroms) thick, particularly compatible with aminosilane, and this is very useful to produce composites with polymers having desirable characteristics.

20 Claims

1 A process for the metal electroplating of fibers comprising:

(a) passing the fiber continuously through an electrolyte solution free of organic compounds in a tank in which a metal anode is immersed;

25 (b) passing D.C. current through the fiber to the anode by delivering said current to the fiber at a contact point immediately prior to the surface of the electrolyte tank;

(c) maintaining the voltage across the electrolyte from the fiber to the anode above 16 volts; and

(d) cooling the fiber from the point of contact to the electrolyte whereby metal from the anode migrates to the fiber and is bonded thereto, said process further comprising the steps of:

30 (a') passing the metal-coated fiber continuously through a second electrolyte solution free of organic compounds in a second tank in which a metal anode is immersed;

(b') passing D.C. current through the metal-coated fiber to the anode in the second tank by delivering said current to the fiber at a contact point immediately prior to the surface of the electrolyte in the tank;

(c') adjusting the voltage across the electrolyte from the fiber to the anode to a quantity above 14 volts as a function of resistance developed by the metal-coated fiber in the second tank; and

35 (d') cooling the fiber from the point of contact to the electrolyte whereby metal from the anode migrates to the metal-coated fiber to further coat the metal-coated fiber, said process further comprising the steps of:

40 (a'') passing the metal-coated fiber continuously from the second tank of electrolyte through a third electrolyte solution free of organic compounds in a third tank in which a metal anode is immersed;

(b'') passing D.C. current through the metal-coated fiber to the anode in the third tank by delivering said current to the fiber at a contact point immediately prior to the surface of the electrolyte in the tank;

(c'') adjusting the voltage in the third electrolyte from the fiber to the anode to a quantity above 12 volts as a function of the resistance developed by the metal-coated fiber in the third tank; and

45 (d'') cooling the fiber from the point of contact to the electrolyte whereby metal from the anode in the third tank migrates to the metal-coated fiber to further coat the metal-coated fiber.

2. A process as in Claim 1, wherein the voltage in (c) is above 24 volts.

3. A process as claimed in Claim 1, wherein the voltage in the first tank is about 45 volts and the current is about 1,400 amps; the voltage in the second tank is about 26 volts and the current is about 1,400 amps; and the voltage in the third tank is about 17 volts and the current is about 1,400 amps.

4. A process as in Claim 1, further comprising passing the metal-coated fiber obtained in step (d'') continuously through electrolyte solutions in at least one additional successive tank arranged in series, in which metal anodes are immersed, wherein D.C. current is passed through the metal-coated fiber to the anode, and conducting a further metal electroplating in each tank to further coat the metal-coated fiber.

5. A process as in Claim 1, further comprising the step of pre-treating the fiber to clean the fiber prior to delivery to the electrolyte.

6. A process as in Claim 5, wherein pre-treatment cleaning of the fibers is comprised of the step of:

(a) passing the fibers counter-currently with a solution of tri-sodium phosphate; and

(b) passing the fibers leaving the tri-sodium phosphate wash through a rinse.

7. A process as in Claim 6, wherein the pretreatment further comprises the step of passing the fibers counter-currently through a hydrochloric acid wash; and rinsing the fibers with water after the hydrochloric acid wash.

8. A process as in claim 6, wherein the tri-sodium phosphate solution is a mixture of 226.8 g (8 ounces) of tri-sodium phosphate per 3.785 l (1 gallon) of water of 82°C (180°F).

9. A process as in Claim 7, wherein the hydrochloric acid solution is a 10% hydrochloric acid solution.



parts, by weight, of epoxy resin and curing, are about 30% better in terms of short beam shear strength at room temperature, and at elevated moist temperature, than those made with unsized fibers.

The fibers sized and/or surface oxidized in accordance with the process of the present invention also have been woven into fabric patterns. It has been observed that the fuzz typically extending randomly from the metal-coated fiber do not interfere with the weaving after the sizing has occurred. Further, the woven material can be formed into a fabric pattern very easily by virtue of the lubricity that inheres in the sized material. Conversely, sized nickel-coated carbon graphite, or other high strength fiber, has been found to have excellent lubricity and lacks abrasiveness, facilitating weaving. Also sized fibers avoid random fibers extending from the fibers which can cause an accumulation of fuzzy materials which interfere considerably with any weaving pattern by depositing on guides in the machines, etc.

Further, the sizing materials can act as water displacement agents which reduce the tendency of composites made from the coated fibers to delaminate after being put into a plastic matrix, and exposed to moisture.

Practice has taught that a carbon fiber coated with nickel and treated with steam, e.g., distilled water steam, will provide a nickel oxide surface, dense and adherent of 1.5—5 nm (15—50 angstroms) thick, particularly compatible with aminosilane, and this is very useful to produce composites with polymers having desirable characteristics.

20 Claims

1 A process for the metal electroplating of fibers comprising:

(a) passing the fiber continuously through an electrolyte solution free of organic compounds in a tank in which a metal anode is immersed;

25 (b) passing D.C. current through the fiber to the anode by delivering said current to the fiber at a contact point immediately prior to the surface of the electrolyte tank;

(c) maintaining the voltage across the electrolyte from the fiber to the anode above 16 volts; and

(d) cooling the fiber from the point of contact to the electrolyte whereby metal from the anode migrates to the fiber and is bonded thereto, said process further comprising the steps of:

30 (a') passing the metal-coated fiber continuously through a second electrolyte solution free of organic compounds in a second tank in which a metal anode is immersed;

(b') passing D.C. current through the metal-coated fiber to the anode in the second tank by delivering said current to the fiber at a contact point immediately prior to the surface of the electrolyte in the tank;

(c') adjusting the voltage across the electrolyte from the fiber to the anode to a quantity above 14 volts as a function of resistance developed by the metal-coated fiber in the second tank; and

35 (d') cooling the fiber from the point of contact to the electrolyte whereby metal from the anode migrates to the metal-coated fiber to further coat the metal-coated fiber, said process further comprising the steps of:

40 (a'') passing the metal-coated fiber continuously from the second tank of electrolyte through a third electrolyte solution free of organic compounds in a third tank in which a metal anode is immersed;

(b'') passing D.C. current through the metal-coated fiber to the anode in the third tank by delivering said current to the fiber at a contact point immediately prior to the surface of the electrolyte in the tank;

(c'') adjusting the voltage in the third electrolyte from the fiber to the anode to a quantity above 12 volts as a function of the resistance developed by the metal-coated fiber in the third tank; and

45 (d'') cooling the fiber from the point of contact to the electrolyte whereby metal from the anode in the third tank migrates to the metal-coated fiber to further coat the metal-coated fiber.

2. A process as in Claim 1, wherein the voltage in (c) is above 24 volts.

3. A process as claimed in Claim 1, wherein the voltage in the first tank is about 45 volts and the current is about 1,400 amps; the voltage in the second tank is about 26 volts and the current is about 1,400 amps; 50 and the voltage in the third tank is about 17 volts and the current is about 1,400 amps.

4. A process as in Claim 1, further comprising passing the metal-coated fiber obtained in step (d'') continuously through electrolyte solutions in at least one additional successive tank arranged in series, in which metal anodes are immersed, wherein D.C. current is passed through the metal-coated fiber to the anode, and conducting a further metal electroplating in each tank to further coat the metal-coated fiber.

55 5. A process as in Claim 1, further comprising the step of pre-treating the fiber to clean the fiber prior to delivery to the electrolyte.

6. A process as in Claim 5, wherein pre-treatment cleaning of the fibers is comprised of the step of:

(a) passing the fibers counter-currently with a solution of tri-sodium phosphate; and

60 (b) passing the fibers leaving the tri-sodium phosphate wash through a rinse.

7. A process as in Claim 6, wherein the pretreatment further comprises the step of passing the fibers counter-currently through a hydrochloric acid wash; and rinsing the fibers with water after the hydrochloric acid wash.

8. A process as in claim 6, wherein the tri-sodium phosphate solution is a mixture of 226.8 g (8 ounces) of tri-sodium phosphate per 3.785 l (1 gallon) of water of 82°C (180°F).

65 9. A process as in Claim 7, wherein the hydrochloric acid solution is a 10% hydrochloric acid solution.



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10. A process as in Claim 1, wherein a plurality of fibers are passed through the system in parallel arrangement and simultaneously coated with metal.

11. A process as in Claim 10, wherein the contact of the contact point is a contact roller and further comprising the step of rotating the contact roller in the direction of the fiber.

12. A process as in Claim 1, wherein the cooling of fiber is effected by recycling electrolyte over the fiber at the point of contact.

13. A process as in claim 12, further comprising the step of spraying recycled electrolyte on the fiber at both the point of initial engagement with the contact and at the point of departure from the contact.

14. A process as in Claim 1 or 4, further comprising the step of rinsing the metal-coated fiber after the metal coating has been completed.

15. A process as in Claim 14, wherein the metal-coated fiber is rinsed with water in a flow counter-current with the flow of the fiber.

16. A process as in Claim 15, further comprising the step of steam treating the rinsed metal-coated fiber.

17. A process as in Claim 16, further comprising the step of drying the steam treated metal-coated fiber.

18. A process as in Claim 17, further comprising the step of reeling the metal-coated fiber on capstans.

19. A process as in Claim 18, wherein the capstan provides the motive force to pass the fiber through the system.

20. A process as defined in Claim 1 including cooling fiber through which electrical current is passed comprising the steps of:

(a) continuously passing the fiber over an electrical current carrying surface located above a reservoir of electrolyte to the electrolyte reservoir; and

(b) directing cooling fluid to the fiber at the point at which the fiber engages the current carrying surface and the point at which the fiber departs from the current carrying surface.

21. A process as in Claim 20, wherein the current carrying surface is a first contact roller.

22. A process as in Claim 21, wherein the cooling fluid is recirculated electrolyte from the electrolyte reservoir.

23. A process as in Claim 22, further comprising the step of directing one spray of recirculated electrolyte at the center point on the top of the contact roller and the other spray tangentially downwardly on the fiber at the point on the contact roller nearest the electrolyte reservoir.

24. A process as in Claim 21, further comprising the steps of continuously passing the fiber from the electrolyte reservoir over a second contact roller for further processing; directing coolant over the first contact roller at the point at which the fiber engages the first contact roller and tangentially downwardly at the point at which the fiber disengages from the first contact roller tangentially downwardly at the point at which the fiber engages the second contact roller and directly onto the top of the second contact at the point at which the fiber departs from the second contact roller.

25. An apparatus for metal electroplating fiber according to the process of Claim 1, comprising

(a) a D.C. rectifier;

(b) an electrolyte tank to which the rectifier delivers current;

(c) electrolyte in the electrolyte tank;

(d) a metal anode in the electrolyte;

(e) means for continuously passing fiber through the electrolyte;

(f) means for delivering D.C. current from the rectifier to the fiber at a contact immediately prior to the surface of the electrolyte in the tank;

(g) means for maintaining the voltage between the fiber and the anode above 16 volts; and

(h) means for cooling the fiber from the point of contact to the electrolyte, said apparatus further comprising:

(a') a second D.C. rectifier;

(b') a second electrolyte tank to which the second rectifier delivers current;

(c') electrolyte in the second electrolyte tank;

(d') a metal anode in the electrolyte in the second electrolyte tank;

(e') means for continuously passing metal-coated fiber from the first electrolyte tank through the second electrolyte tank;

(f') means for delivering D.C. current from a second rectifier to the fiber at a contact immediately prior to the surface of the electrolyte in the second electrolyte tank;

(g') means for maintaining voltage in the second electrolyte tank between the metal-coated fiber and the anode above 14 volts as a function of the resistance developed by the metal-coated fiber; and

(h') means for cooling the fiber from the point of contact to the electrolyte, said apparatus further comprising:

(a'') a third D.C. rectifier;

(b'') a third electrolyte tank to which the third rectifier delivers current;

(c'') electrolyte in the third electrolyte tank;

(d'') a metal anode in the electrolyte in the third electrolyte tank;

(e'') means for continuously passing the metal plated fiber from the second tank through the electrolyte in the third tank;



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(f') means for delivering D.C. current from the third rectifier to the third electrolyte tank through the metal-coated fiber at a contact immediately prior to the surface of the electrolyte in the third electrolyte tank;

(g") means for maintaining the voltage in the third electrolyte tank between the metal coated fiber and the anode above 12 volts; and

(h") means for cooling the fiber from the point of contact to the electrolyte.

26. An apparatus as in Claim 25, wherein the voltage in (g) across the fiber and the anode is above 24 volts.

27. An apparatus as in Claim 25, further comprising:

(a) four or more D.C. rectifiers;

(b) four or more electrolyte tanks to which the four or more rectifiers deliver D.C. current;

(c) electrolyte in each of the four or more electrolyte tanks;

(d) a metal anode in the electrolyte of each of the four or more electrolyte tanks;

(e) means for continuously passing metal-coated fiber to the four or more electrolyte tanks;

(f) means for delivering D.C. current from the respective rectifier to the metal-coated fiber at a contact immediately prior to the surface of the electrolyte in each of the four or more electrolyte tanks;

(g) means for maintaining the voltage in the four or more electrolyte tanks between the metal-coated fiber and the anode at a voltage determined as a function of the resistance resulting from the metal-coated fiber; and

(h) means for cooling the fiber from the point of contact to the electrolyte in each of the four or more tanks.

28. An apparatus as in Claim 25, further comprising means for pre-treating the fiber prior to delivery to the first electrolyte tank.

29. An apparatus as in Claim 28, wherein the means for pre-treating the fiber prior to delivery to the first rectifier is comprised of a washing tee, means for passing the fiber continuously through the washing tee and means for passing tri-sodium phosphate through the washing tee in the direction counter to the direction of the passage of the fiber therethrough.

30. An apparatus as in Claim 29, wherein the washing tee is comprised of:

(a) an inner chamber for the passage of fiber therethrough;

(b) an entry opening for the fiber to enter the tee;

(c) an exit opening for fiber to leave the tee, which exit opening is at an elevation above the elevation of the entry opening; and

(d) interference means to direct the flow of tri-sodium phosphate introduced into the tee outwardly through the entry opening for the fiber.

31. An apparatus as in Claim 30, wherein the interference means in the washing tee is a sleeve extending inwardly from the entry opening to an intermediate point in the chamber.

32. An apparatus as in Claim 25, further comprising means to mount a plurality of fibers for delivery to the electrolyte in parallel.

33. An apparatus as in Claim 32, wherein the means for mounting the fibers is comprised of:

(a) a horizontally disposed rail;

(b) means on the rail to mount a plurality of spools of fiber;

(c) a second rail horizontally above and aligned with the first rail; and

(d) guide means on the second rail member, which guide means are offset from each other in adjacent spaced relationship whereby the fibers pass from a spool on the first rail over a guide roller essentially in vertical alignment with the spool to the electrolyte plating system in parallel spaced relationship.

34. An apparatus as in Claim 33, further comprising means for reeling the plated fibers and providing the motive force to pass the fibers through the process apparatus.

35. An apparatus as in Claim 34, wherein the means for reeling the fibers and providing the motive force is comprised of a motor driving a plurality of reels, each of which is arranged to reel an individual fiber, and an array of driven rollers upstream of the reels arranged to reverse the path of the fiber and thereby prevent a slack in the fibers.

36. An apparatus as in Claim 35, comprising means to rinse the metal-coated fibers leaving the final metal plating tank.

37. An apparatus as in Claim 36, wherein the means for rinsing the metal-coated fibers is comprised of a series of washing tees arranged for the passage of fiber therethrough in one direction and water therethrough in a direction counter-current to the passage of fiber.

38. An apparatus as defined in Claim 25, means for spraying fluid on fiber through which electric current is passed, comprising:

(a) a first tubular member having an aligned array of nozzle openings on the lower surface, which nozzle openings are directed at a first location on the fiber;

(b) a second tubular member having an aligned array of nozzle openings on the lower surface, which nozzle openings are directed at a second location on the fiber; and

(c) means for delivering fluid to the first and second tubular members, said apparatus further comprising means for continuously passing the fiber from a contact roller to an electrolyte solution; means for directing electrolyte to the first tubular member and over the fiber at the point at which the fiber



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engages the contact roller and means for directing electrolyte to the second tubular member and over the fiber at the point which the fiber departs from the contact roller.

39. An apparatus as in Claim 38, further comprising means to recirculate electrolyte from the electrolyte into which the fiber passes to the first and second tubular members.

5 40. An apparatus as in Claim 39, wherein the contact roller is cylindrical and is adapted for rotation; the fiber is in engagement with the contact roller over one-quarter of the surface; the first tubular member is arranged above and in alignment with the contact roller at a location directly above the center of the contact roller at which the fiber engages the contact roller to direct electrolyte directly at the contact roller and the second tubular member is located above the contact roller 90 degrees from the point at which the
10 first tubular member directs fluid and is oriented to direct electrolyte on the fiber tangential to the contact roller.

41. An apparatus as in Claim 40 further comprising an electrolyte tank; a plurality of contact rollers mounted on the top of an electrolyte tank in series over which fiber passes and through which D.C. current is delivered to the fiber; electrolyte in the electrolyte tank to a level in close proximity to the bottom of the contact rollers; means for passing fiber first over a first contact roller into the electrolyte; then from the
15 electrolyte to a second contact roller immediately downstream of the first contact roller and thereafter continuously over subsequently disposed contact rollers in a pattern of over a contact roller into the electrolyte and from the electrolyte over the next roller.

42. An electroplating apparatus as defined in Claim 25 for coating fiber with metal comprised of an
20 electrolyte tank; electrolyte in the tank, rotating contact rollers secured to the top of the tank over the fiber is adapted to pass immediately prior to the surface of the electrolyte in the tank; idler rollers located at the bottom of the electrolyte tank disposed in alignment with the contact rollers for the passage of fiber therearound; a rectifier; a bus bar extending from the rectifier to the electrolytic tank; and electrically conductive bar extending from the bus bar to the contact roller; an array of conductive fingers extending
25 from the electrically conductive bar into engagement with the contact roller and a means for cooling the fiber from the point of contact to the electrolyte.

43. An apparatus as in Claim 42, wherein the array of conductive fingers is comprised of two rows of resilient fingers, the row nearest the contact roller being of a shorter length than the other row wherein the ends of both rows bear against the contact roller.

30 44. An apparatus as in Claim 42, wherein the means of cooling the fiber comprises means for directing electrolyte to the contact rollers at the point at which the fiber engages the contact rollers.

Patentansprüche

1. Verfahren zur Metall-Elektroplattierung von Fasern, umfassend

(a) das kontinuierliche Hindurchführen der Faser durch eine Elektrolytlösung, die frei von organischen Verbindungen ist, in einem Tank, in den eine Metallanode eingetaucht ist;

(b) das Hindurchleiten von Gleichstrom durch die Faser zu der Anode durch Beaufschlagung der Faser mit dem Strom an einem Kontaktpunkt unmittelbar vor der Oberfläche des Elektrolyttanks;

40 (c) die Aufrechterhaltung der Spannung über den Elektrolyten von der Faser zu der Anode bei oberhalb 16 Volt; und

(d) das Abkühlen der Faser von dem Kontaktpunkt bis zum Elektrolyten, wobei Metall von der Anode zur Faser wandert und daran gebunden wird, wobei das Verfahren außerdem folgende Schritte umfaßt:

45 (a') das kontinuierliche Hindurchführen der metallbeschichteten Faser durch eine zweite Elektrolytlösung, die frei von organischen Verbindungen ist, in einem zweiten Tank, in den eine Metallanode eingetaucht ist;

(b') das Hindurchleiten von Gleichstrom durch die metallbeschichtete Faser zu der Anode in dem zweiten Tank durch Beaufschlagung der Faser mit dem Strom an einem Kontaktpunkt unmittelbar vor der Oberfläche des Elektrolyten in dem Tank;

50 (c') die Einstellung der Spannung über den Elektrolyten von der Faser zu der Anode auf einen Wert über 14 Volt als Funktion des von der metallbeschichteten Faser in dem zweiten Tank entwickelten Widerstands; und

(d') das Abkühlen der Faser von dem Kontaktpunkt bis zu dem Elektrolyten, wobei Metall von der Anode zu der metallbeschichteten Faser wandert, um die metallbeschichtete Faser weiter zu beschichten, wobei das Verfahren ferner folgende Stufen umfaßt:

55 (a'') das kontinuierliche Hindurchführen der metallbeschichteten Faser aus dem zweiten Tank des Elektrolyten durch eine dritte Elektrolytlösung, die frei von organischen Verbindungen ist, in einem dritten Tank, in den eine Metallanode eingetaucht ist;

60 (b'') das Hindurchleiten von Gleichstrom durch die metallbeschichtete Faser zu der Anode im dritten Tank durch Beaufschlagung der Faser mit dem Strom an einem Kontaktpunkt unmittelbar vor der Oberfläche des Elektrolyten in dem Tank;

(c'') die Einstellung der Spannung in dem dritten Elektrolyten von der Faser zu der Anode auf einen Wert über 12 Volt als Funktion des Widerstands, der von der metallbeschichteten Faser in dem dritten Tank entwickelt wird; und

65 (d'') das Kühlen der Faser von dem Kontaktpunkt bis zu dem Elektrolyten, wobei Metall von der Anode



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in dem dritten Tank zu der metallbeschichteten Faser wandert, um die metallbeschichtete Faser weiter zu beschichten.

2. Verfahren gemäß Anspruch 1, wobei die Spannung in (c) über 24 Volt beträgt.

3. Verfahren gemäß Anspruch 1, wobei die Spannung in dem ersten Tank etwa 45 Volt und der Strom etwa 1400 Ampere beträgt; die Spannung in dem zweiten Tank etwa 26 Volt und der Strom etwa Ampere beträgt;

und die Spannung in dem dritten Tank etwa 17 Volt und der Strom etwa 1400 Ampere beträgt.

4. Verfahren gemäß Anspruch 1, ferner umfassend das kontinuierliche Hindurchführen der metallbeschichteten Faser, die in der Stufe (d'') erhalten wurde, durch Elektrolytlösungen in mindestens einem zusätzlichen, nachfolgenden, in Serie angeordneten Tank, in den Metallanoden eingetaucht sind, wobei Gleichstrom durch die metallbeschichtete Faser zu der Anode geleitet wird, und die Durchführung einer weiteren Metall-Elektroplattierung in jedem Tank, um die metallbeschichtete Faser weiter zu beschichten.

5. Verfahren gemäß Anspruch 1, ferner umfassend die Stufe der Vorbehandlung der Faser, um die Faser vor der Einführung in den Elektrolyten zu reinigen.

6. Verfahren gemäß Anspruch 5, wobei die Vorbehandlung zur Reinigung der Faser folgende Schritte umfaßt:

(a) das Hindurchführen der Fasern im Gegenstrom mit einer Lösung von Trinatriumphosphat; und

(b) das Hindurchführen der die Trinatriumphosphatwäsche verlassenden Fasern durch ein Spülbad.

7. Verfahren gemäß Anspruch 6, wobei die Vorbehandlung ferner die Stufe des Hindurchführens der Fasern im Gegenstrom durch eine Chlorwasserstoffsäure-Wäsche und das Spülen der Fasern mit Wasser nach der Chlorwasserstoffsäure-Wäsche umfaßt.

8. Verfahren gemäß Anspruch 6, wobei die Trinatriumphosphatlösung eine Mischung von 226,8 g (8 Unzen) Trinatriumphosphat pro 3,785 l (1 Gallone) Wasser von 82°C (180°F) ist.

9. Verfahren gemäß Anspruch 7, wobei die Chlorwasserstoffsäurelösung eine 10%ige Chlorwasserstoffsäurelösung ist.

10. Verfahren gemäß Anspruch 1, wobei eine Vielzahl von Fasern durch das System in paralleler Anordnung hindurchgeführt und simultan mit Metall beschichtet wird.

11. Verfahren gemäß Anspruch 10, wobei der Kontakt an dem Kontaktpunkt eine Kontaktwalze ist und ferner umfassend die Stufe des Rotierens der Kontaktwalze in der Richtung der Faser.

12. Verfahren gemäß Anspruch 1, wobei das Kühlen der Faser bewirkt wird, indem man Elektrolyten über die Faser am Kontaktpunkt recycliert.

13. Verfahren gemäß Anspruch 12, ferner umfassend die Stufe des Sprühens von recycliertem Elektrolyten auf die Faser sowohl an dem Punkt des ersten Zusammenwirkens mit dem Kontakt als auch an dem Punkt, wo der Kontakt verlassen wird.

14. Verfahren gemäß Anspruch 1 oder 4, ferner umfassend die Verfahrensstufe des Spülens der metallbeschichteten Faser, nachdem die Metallbeschichtung vollständig ist.

15. Verfahren gemäß Anspruch 14, wobei die metallbeschichtete Faser mit Wasser gespült wird in einer Strömung, die in Gegenstrom bezüglich der Bewegung der Faser verläuft.

16. Verfahren gemäß Anspruch 15, ferner umfassend die Stufe der Dampfbehandlung der gespülten, metallbeschichteten Faser.

17. Verfahren gemäß Anspruch 16, ferner umfassend die Stufe des Trocknens der dampfbehandelten, metallbeschichteten Faser.

18. Verfahren gemäß Anspruch 17, ferner umfassend die Stufe des Aufwickelns der metallbeschichteten Faser auf Haspeln.

19. Verfahren gemäß Anspruch 18, wobei die Haspel die Antriebskraft liefert, um die Faser durch das System hindurchzuführen.

20. Verfahren gemäß Anspruch 1, umfassend das Kühlen der Faser, durch die elektrischer Strom hindurchgeleitet wird, umfassend die folgenden Verfahrensstufen:

(a) das kontinuierliche Führen der Faser über eine mit elektrischem Strom beaufschlagte Oberfläche, die oberhalb eines Reservoirs des Elektrolyten angeordnet ist, zu dem Elektrolytreservoir; und

(b) das Richten von Kühlflüssigkeit auf die Faser an dem Punkt, an dem die Faser mit der strombeaufschlagten Oberfläche in Wirkbeziehung kommt, und dem Punkt, an dem die Faser die strombeaufschlagte Oberfläche verläßt.

21. Verfahren gemäß Anspruch 20, wobei die strombeaufschlagte Oberfläche eine erste Kontaktrolle ist.

22. Verfahren gemäß Anspruch 21, wobei die Kühlflüssigkeit im Kreislauf geführter Elektrolyt aus dem Elektrolytreservoir ist.

23. Verfahren gemäß Anspruch 22, ferner umfassend die Stufe, bei der ein Spühstrom des im Kreislauf geführten Elektrolyten am Zentrumspunkt auf die Oberseite der Kontaktrolle gerichtet wird und der andere Spühstrom tangential nach unten auf die Faser gerichtet wird an dem Punkt auf der Kontaktrolle, die dem Elektrolytreservoir am nächsten ist.

24. Verfahren gemäß Anspruch 21, ferner umfassend die Verfahrensstufen der kontinuierlichen Passage der Faser aus dem Elektrolytreservoir über eine zweite Kontaktrolle zur weiteren Bearbeitung; das Richten von Kühlmittel über die erste Kontaktrolle an dem Punkt, an dem die Faser mit der ersten Kontaktrolle in Wirkbeziehung kommt, und tangential nach unten an dem Punkt, an dem die Faser die ersten Kontaktrolle



verläßt, tangential nach unten an dem Punkt, an dem die Faser mit der zweiten Kontaktrolle in Wirkbenziehung kommt, und direkt auf die Oberseite des zweiten Kontakts an dem Punkt, an dem die Faser die zweite Kontaktrolle verläßt.

25. Vorrichtung zur Metall-Elektroplattierung von Faser nach dem Verfahren gemäß Anspruch 1, ferner umfassend

- (a) einen Gleichrichter;
- (b) einen Elektrolyttank, an den der Gleichrichter Strom abgibt;
- (c) einen Elektrolyten in dem Elektrolyttank;
- (d) eine Metallanode in dem Elektrolyten;
- (e) Einrichtungen zur kontinuierlichen Hindurchführung der Faser durch den Elektrolyten;
- (f) Einrichtungen zur Abgabe von Gleichstrom von dem Gleichrichter an die Faser an einem Kontakt unmittelbar vor der Oberfläche des Elektrolyten in dem Tank;
- (g) Einrichtungen zur Aufrechterhaltung der Spannung zwischen der Faser und der anode bei über 16 Volt; und
- (h) Einrichtungen zum Kühlen der Faser von dem Kontaktpunkt bis zu dem Elektrolyten, wobei die Vorrichtung ferner umfaßt:
 - (a') einen zweiten Gleichrichter;
 - (b') einen zweiten Elektrolyttank, an den der zweite Gleichrichter Strom abgibt;
 - (c') einen Elektrolyten in dem zweiten Elektrolyttank;
 - (d') eine Metallanode in dem Elektrolyten in dem zweiten Elektrolyttank;
 - (e') Einrichtungen zur kontinuierlichen Hindurchführung von metallbeschichtete Faser aus dem ersten Elektrolyttank durch den zweiten Elektrolyttank;
 - (f') Einrichtungen zur Abgabe von Gleichstrom aus einem zweiten Gleichrichter zu der Faser an einem Kontakt unmittelbar vor der Oberfläche des Elektrolyten in dem zweiten Elektrolyttank;
 - (g') Einrichtungen zur Aufrechterhaltung der Spannung in dem zweiten Elektrolyttank zwischen der metallbeschichteten Faser und der Anode bei über 14 Volt als Funktion des Widerstands, der durch die metallbeschichtete Faser entwickelt wird; und
 - (h') Einrichtungen zum Kühlen der Faser von dem Kontaktpunkt bis zu dem Elektrolyten, wobei die Vorrichtung ferner umfaßt:
 - (a'') einen dritten Gleichrichter;
 - (b'') einen dritten Elektrolyttank, an den der dritte Gleichrichter Strom abgibt;
 - (c'') einen Elektrolyten in dem dritten Elektrolyttank;
 - (d'') eine Metallanode in dem Elektrolyten in dem dritten Elektrolyttank;
 - (e'') Einrichtungen zur kontinuierlichen Hindurchführung der metallbeschichteten Faser aus dem zweiten Tank durch den Elektrolyten in dem dritten Tank;
 - (f'') Einrichtungen zur Abgabe von Gleichstrom von dem dritten Gleichrichter an den dritten Elektrolyttank durch die metallbeschichtete Faser an einem Kontakt unmittelbar vor der Oberfläche des Elektrolyten in dem dritten Elektrolyttank;
 - (g'') Einrichtungen zur Aufrechterhaltung der Spannung in dem dritten Elektrolyttank zwischen der metallbeschichteten Faser und der Anode bei über 12 Volt; und
 - (h'') Einrichtungen zum Kühlen der Faser von dem Kontaktpunkt bis zum Elektrolyten.

26. Vorrichtung gemäß Anspruch 25, wobei die Spannung in (g) zwischen der Faser und der Anode über 24 Volt beträgt.

27. Vorrichtung gemäß Anspruch 25, ferner umfassend:

- (a) vier oder mehr Gleichrichter;
- (b) vier oder mehr Elektrolyttanks, an die die vier oder mehr Gleichrichter Gleichstrom abgeben;
- (c) Elektrolyten in jedem der vier oder mehr Elektrolyttanks;
- (d) eine Metallanode in dem Elektrolyten jedes der vier oder mehr Elektrolyttanks;
- (e) Einrichtungen zur kontinuierlichen Hindurchführung von metallbeschichteter Faser durch die vier oder mehr Elektrolyttanks;
- (f) Einrichtungen zur Abgabe von Gleichstrom von dem jeweiligen Gleichrichter an die metallbeschichtete Faser an einem Kontakt unmittelbar vor der Oberfläche des Elektrolyten in jedem der vier oder mehr Elektrolyttanks;
- (g) Einrichtungen zur Aufrechterhaltung der Spannung in dem vier oder mehr Elektrolyttanks zwischen der metallbeschichteten Faser und der Anode bei einer Spannung, die bestimmt wird als Funktion des Widerstands, der aus der metallbeschichteten Faser resultiert; und
- (h) Einrichtungen zum Kühlen der Faser von dem Kontaktpunkt bis zum Elektrolyten in jedem der vier oder mehr Tanks.

28. Vorrichtung gemäß Anspruch 25, ferner umfassend Einrichtungen zur Vorbehandlung der Faser vor der Einführung in den ersten Elektrolyttank.

29. Vorrichtung gemäß Anspruch 28, wobei die Einrichtungen zur Vorbehandlung der Faser vor der Einführung in den ersten Tank eine Wascheinrichtung umfassen, Einrichtungen zum kontinuierlichen Durchleiten der Faser durch die Wascheinrichtung und Einrichtungen zum Hindurchleiten von Trinatriumphosphat durch die Wascheinrichtung in der Gegenrichtung bezüglich der Bewegungsrichtung der Faser.

30. Vorrichtung gemäß Anspruch 29, wobei die Wascheinrichtung folgende Komponenten umfaßt:



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(a) eine innere Kammer zum Hindurchführen der Faser;
(b) eine Eintrittsöffnung für die Faser zum Eintritt in die Wascheinrichtung;
(c) eine Austrittsöffnung für die Faser, um die Wascheinrichtung zu verlassen, wobei die Austrittsöffnung höher angeordnet ist als die Eintrittsöffnung; und

(d) Einwirkungsmittel, um den Fluß des in die Wascheinrichtung eingespeisten Trinatriumphosphats durch die Eintrittsöffnung für die Faser nach außen zu leiten.

31. Vorrichtung gemäß Anspruch 30, wobei die Einwirkungseinrichtungen in der Wascheinrichtung ein Führungskörper ist, der sich von der Eintrittsöffnung bis zu einem mittleren Punkt in der Kammer nach innen erstreckt.

32. Vorrichtung gemäß Anspruch 25, ferner umfassend Einrichtungen, um eine Vielzahl von Fasern für die Abgabe an den Elektrolyten in paralleler Anordnung anzubringen.

33. Vorrichtung gemäß Anspruch 32, wobei die Einrichtung zum Anbringen der Fasern folgende Komponenten umfassen:

(a) eine horizontal angeordnete Schiene;

(b) Einrichtungen auf der Schiene, um eine Vielzahl von Faserspulen anzubringen;

(c) eine zweite Schiene, die horizontal oberhalb und mit der ersten Schiene fluchtend angeordnet ist; und

(d) Führungseinrichtungen auf dem zweiten Schienenbauteil, welche Führungseinrichtungen in Nachbarschaftsbeziehung mit Abstand voneinander angeordnet sind, wobei die Fasern von einer Spule auf der ersten Schiene über eine Führungsrolle in im wesentlichen vertikaler Ausrichtung mit der Spule zu dem Elektrolyt-Plattierungssystem geführt werden, und zwar in einer parallelen Abstandsbeziehung.

34. Vorrichtung gemäß Anspruch 33, ferner umfassend Einrichtungen zum Aufwickeln der plattierten Fasern und zur Schaffung der Antriebskraft, um die Fasern durch die Bearbeitungsvorrichtung hindurchzuführen.

35. Vorrichtung gemäß Anspruch 34, wobei die Einrichtungen zum Aufwickeln der Fasern und zur Schaffung der Antriebskraft einen Motor umfassen, der eine Vielzahl von Aufwickelspulen antreibt, wobei jede so angeordnet ist, daß sie eine einzelne Faser aufwickelt, und eine Anordnung von angetriebenen Rollen stromauf der Aufwickelspulen angeordnet ist, um den Pfad der Faser umzukehren und auf diese Weise einen Durchhang in den Fasern zu verhindern.

36. Vorrichtung gemäß Anspruch 35, umfassend Einrichtungen zum Spülen der metallbeschichteten Fasern, die den letzten Metall-Plattierungstank verlassen.

37. Vorrichtung gemäß Anspruch 36, wobei die Einrichtungen zum Spülen der metallbeschichteten Fasern eine Serie von Waschvorrichtungen umfassen, die so angeordnet sind, daß die Fasern in einer Richtung hindurchgehen und Wasser in einer Gegenstromrichtung bezüglich der Passage der Fasern hindurchgeht.

38. Vorrichtung gemäß Anspruch 25, mit Einrichtungen, um Fluid auf Faser zu versprühen, durch die elektrischer Strom hindurchgeleitet wird, umfassend

(a) ein erstes Tubusorgan mit einer fluchtenden Anordnung von Düsenöffnungen auf der unteren Oberfläche, welche Düsenöffnungen an einem ersten Ort auf die Faser gerichtet sind;

(b) ein zweites Tubusorgan mit einer fluchtenden Anordnung von Düsenöffnungen auf der unteren Oberfläche, welche Düsenöffnungen an einem zweiten Ort auf die Faser gerichtet sind; und

(c) Einrichtungen zur Abgabe von Fluid an die ersten und zweiten Tubusorgane, wobei die Vorrichtung ferner Einrichtungen umfaßt, um die Faser kontinuierlich von einer Kontaktrolle zu einer Elektrolytlösung zu führen; Einrichtungen, um Elektrolyt zu dem ersten Tubusorgan und über die Faser an dem Punkt, an dem die Faser mit der Kontaktrolle in Wirkbeziehung kommt, zu richten, und Einrichtungen, um Elektrolyt zu dem zweiten Tubusorgan und über die Faser an dem Punkt, an dem die Faser die Kontaktrolle verläßt, zu richten.

39. Vorrichtung gemäß Anspruch 38, ferner umfassend Einrichtungen zur Kreislaufführung des Elektrolyten von dem Elektrolyten, durch den die Faser hindurchgeht, zu den ersten und zweiten Tubusorganen.

40. Vorrichtung gemäß Anspruch 39, wobei die Kontaktrolle zylindrisch ist und zur Rotation eingerichtet ist, die Faser mit der Kontaktrolle über ein Viertel der Oberfläche in Wirkbeziehung steht, das erste Tubusorgan oberhalb und mit der Kontaktrolle fluchtend angeordnet ist an einem Ort direkt über dem Zentrum der Kontaktrolle, an dem die Faser mit der Kontaktrolle in Wirkbeziehung gelangt, um elektrolyten direkt auf die Kontaktrolle zu richten, und das zweite Tubusorgan oberhalb der Kontaktrolle mit 90° bezüglich des Punktes angeordnet ist, auf den das erste Tubusorgan fluid richtet, und so orientiert ist, daß der Elektrolyt tangential zu der Kontaktrolle auf die Faser gerichtet wird.

41. Vorrichtung gemäß Anspruch 40, ferner umfassend einen Elektrolyttank; eine Vielzahl von Kontaktrollen, die über dem Elektrolyttank in Reihe angebracht sind und über die Faser geleitet wird und durch die Gleichstrom an die Faser abgegeben wird; Elektrolyten in dem Elektrolyttank bis zu einem Niveau in der Nähe der Unterseite der Kontaktrollen; Einrichtungen, um die Faser zunächst über eine erste Kontaktrolle in den Elektrolyten zu führen; anschließend von dem Elektrolyten zu einer zweiten Kontaktrolle unmittelbar stromabwärts von der ersten Kontaktrolle und anschließend kontinuierlich über nachfolgend angeordnete Kontaktrollen in einem Muster von über eine Kontaktrolle in den Elektrolyten und von dem Elektrolyten über die nächste Rolle.



42. Elektro-Plattier Vorrichtung gemäß Anspruch 25 zur Beschichtung von Faser mit Metall, umfassend einen Elektrolyttank; Elektrolyten in dem Tank, rotierende Kontaktrollen, die über dem Tank befestigt sind und über die Faser unmittelbar vor der Oberfläche des Elektrolyten in dem Tank geführt werden kann; am Boden des Elektrolyttanks angeordnet Umlenkrollen, die fluchtend mit den Kontaktrollen angeordnet sind für die Passage der Fasern um sie herum; einen Gleichrichter; eine Zuleitungsstange, die sich von dem Gleichrichter zu dem Elektrolysetank erstreckt; und eine elektrisch leitende Stange, die sich von der Zuleitungsstange zu den Kontaktrollen erstreckt; eine Anordnung von leitenden Fingern, die sich von den elektrisch leitenden Stangen in Wirkbeziehung mit dem Kontaktrollen erstrecken, und Einrichtungen zum Kühlen der Faser vom Kontaktpunkt bis zu dem Elektrolyten.

43. Vorrichtung gemäß Anspruch 42, wobei die Anordnung der leitfähigen Finger zwei Reihen von federnden Fingern umfaßt, wobei die Reihe, die der Kontaktrolle am nächsten liegt, eine kürzere Länge aufweist als die andere Reihe, wobei die Enden beider Reihen gegen die Kontaktrollen drücken.

44. Vorrichtung gemäß Anspruch 42, wobei die Einrichtungen zum Kühlen der Faser Einrichtungen umfassen, um Elektrolyten an dem Punkt auf die Kontaktrollen zu richten, an dem die Faser mit den Kontaktrollen in Wirkbeziehung kommt.

Revendications

1. Procédé de galvanoplastie de fibres consistant à:

(a) faire passer la fibre en continu à travers une solution d'électrolyte exempte de composés organiques dans un réservoir dans lequel est immergée une anode métallique;

(b) faire passer un courant continu à travers la fibre vers l'anode en appliquant ledit courant à la fibre en un point de contact situé juste avant la surface de l'électrolyte dans le réservoir;

(c) maintenir le voltage à travers l'électrolyte depuis la fibre jusqu'à l'anode à une valeur supérieure à 16 volts; et

(d) refroidir la fibre depuis le point de contact jusqu'à l'électrolyte, le métal migrant ainsi de l'anode vers la fibre et se fixant à celle-ci, ledit procédé comprenant en outre les étapes suivantes:

(a') faire passer en continu la fibre méallisée à travers un second bain électrolytique exempt de composés organiques dans un second réservoir dans lequel est immergée une anode métallique;

(b') faire passer un courant continu à travers la fibre métallisée vers l'anode dans le second réservoir en appliquant ledit courant à la fibre en un point de contact situé juste avant la surface du réservoir d'électrolyte;

(c') ajuster le voltage à travers l'électrolyte depuis la fibre jusqu'à l'anode à une valeur supérieure à 14 volts en fonction de la résistance développée par la fibre métallisée dans le second réservoir; et

(d') refroidir la fibre depuis le point de contact jusqu'à l'électrolyte, le métal migrant ainsi de l'anode vers la fibre métallisée pour continuer à recouvrir la fibre métallisée, ledit procédé comprenant en outre les étapes suivantes:

(a'') faire passer en continu la fibre méallisée du second réservoir d'électrolyte à travers un troisième bain électrolytique exempt de composés organiques dans troisième réservoir dans lequel est immergée une anode métallique;

(b'') faire passer un courant continu à travers la fibre métallisée vers l'anode dans le troisième réservoir en appliquant ledit courant à la fibre en un point de contact situé juste avant la surface de l'électrolyte dans le réservoir;

(c'') ajuster le voltage à travers le troisième électrolyte depuis la fibre jusqu'à l'anode à une valeur supérieure à 12 volts en fonction de la résistance développée par la fibre métallisée dans le troisième réservoir; et

(d'') refroidir la fibre depuis le point de contact jusqu'à l'électrolyte, le métal migrant ainsi de l'anode dans le troisième réservoir vers la fibre métallisée pour continuer à recouvrir ladite fibre métallisée.

2. Procédé selon la revendication 1, dans lequel le voltage dans (c) est supérieur à 24 volts.

3. Procédé selon la revendication 1, dans lequel le voltage dans le premier réservoir est d'environ 45 volts et l'intensité d'environ 1400 amps; le voltage dans le second réservoir est d'environ 26 volts et l'intensité d'environ 1400 amps; le voltage dans le troisième réservoir est d'environ 17 volts et l'intensité d'environ 1400 amps.

4. Procédé selon la revendication 1, consistant en outre à faire passer en continu la fibre métallisée obtenue en (d'') à travers des bains d'électrolyte dans au moins un autre réservoir supplémentaire disposé en série, dans lequel des anodes métalliques sont immergées, procédé dans lequel on fait passer du courant continu à travers la fibre métallisée jusqu'à l'anode, et consistant à poursuivre la galvanoplastie dans chaque réservoir pour continuer à revêtir la fibre métallisée.

5. Procédé selon la revendication 1, consistant en outre à prétraiter la fibre pour la nettoyer avant passage dans l'électrolyte.

6. Procédé selon la revendication 5, dans lequel le prétraitement nettoyant des fibres consiste à:

(a) faire passer les fibres à contre-courant d'une solution de phosphate trisodique; et

(b) faire passer dans un rinçage les fibres quittant le lavage au phosphate trisodique.

7. Procédé selon la revendication 6, dans lequel le prétraitement consiste en outre à faire passer à



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contre-courant les fibres dans de l'acide chlorhydrique de lavage; et rincer lesdites fibres avec de l'eau après le lavage à l'acide chlorhydrique.

8. Procédé selon la revendication 6, dans lequel la solution de phosphate trisodique est un mélange de 226,8 g (8 onces) de phosphate trisodique pour 3,785 l (1 gallon) d'eau à 82°C (180°F).

5 9. Procédé selon la revendication 7, dans lequel la solution d'acide chlorhydrique est une solution à 10% d'acide chlorhydrique.

10. Procédé selon la revendication 1, dans lequel on fait passer plusieurs fibres parallèlement à travers le système et on les recouvre simultanément de métal.

11. Procédé selon la revendication 10, dans lequel le contact au point de contact est un cylindre de contact, et qui consiste en outre à faire tourner le cylindre de contact dans le sens de la fibre.

12. Procédé selon la revendication 1, dans lequel le refroidissement de la fibre est effectué en recyclant l'électrolyte sur la fibre au point de contact.

13. Procédé selon la revendication 12, consistant en outre à pulvériser l'électrolyte recyclé sur la fibre à la fois au point d'engagement initial avec le contact et au point de rupture du contact.

15 14. Procédé selon la revendication 1 ou 4, consistant en outre à rincer la fibre métallisée après fin de dépôt du métal.

15. Procédé selon la revendication 14, dans lequel on rince la fibre métallisée avec de l'eau à contre-courant du déplacement de la fibre.

20 16. Procédé selon la revendication 15, consistant en outre à traiter à la vapeur d'eau la fibre métallisée rincée.

17. Procédé selon la revendication 16, consistant en outre à sécher la fibre métallisée traitée à la vapeur d'eau.

18. Procédé selon la revendication 17, consistant à enrouler la fibre métallisée sur des cabestans.

25 19. Procédé selon la revendication 18, dans lequel le cabestan fournit la force motrice pour faire passer la fibre à travers le système.

20. Procédé selon la revendication 1, comprenant le refroidissement de la fibre à travers laquelle on fait passer le courant électrique et comprenant les étapes suivantes:

(a) faire passer en continu la fibre dans un réservoir d'électrolyte, par-dessus une surface conduisant le courant électrique située au-dessus du réservoir d'électrolyte; et

30 (b) diriger du fluide de refroidissement vers la fibre au point où la fibre vient au contact de la surface conductrice du courant et au point où la fibre quitte la surface conductrice du courant.

21. Procédé selon la revendication 20, dans lequel la surface conductrice du courant est un premier cylindre de contact.

22. Procédé selon la revendication 21, dans lequel le fluide de refroidissement est de l'électrolyte recyclé du réservoir d'électrolyte.

23. Procédé selon la revendication 22, consistant en outre à pulvériser de l'électrolyte recyclé d'une part au point central du sommet du cylindre de contact et d'autre part, tangentielllement vers le bas, sur la fibre au point du cylindre de contact le plus proche du réservoir d'électrolyte.

40 24. Procédé selon la revendication 21, consistant en outre à faire passer en continu la fibre du réservoir d'électrolyte par-dessus un second cylindre de contact pour continuer le traitement; à diriger l'agent de refroidissement par-dessus le premier cylindre de contact au point où la fibre s'engage sur le premier cylindre de contact et, tangentielllement vers le bas, au point où la fibre quitte le premier cylindre de contact, tangentielllement vers le bas, au point où la fibre s'engage sur le second cylindre de contact et directement au sommet du second contact au point où la fibre quitte le second cylindre de contact.

45 25. Appareillage pour galvanoplastie d'une fibre selon le procédé de la revendication 1, consistant en:

(a) un redresseur pour courant continu;

(b) un réservoir d'électrolyte auquel le redresseur fournit du courant;

(c) de l'électrolyte dans le réservoir d'électrolyte;

(d) une anode métallique dans l'électrolyte;

50 (e) un moyen pour faire passer en continu une fibre à travers l'électrolyte;

(f) un moyen pour fournir du courant continu du redresseur à la fibre, à un contact situé juste avant la surface de l'électrolyte dans le réservoir;

(g) un moyen pour maintenir au-dessus de 16 volts le voltage entre la fibre et l'anode; et

55 (h) un moyen pour refroidir la fibre du point de contact à l'électrolyte, ledit appareillage comprenant en outre:

(a') un second redresseur pour courant continu;

(b') un second réservoir d'électrolyte auquel le second redresseur fournit du courant;

(c') de l'électrolyte dans le second réservoir d'électrolyte;

(d') une anode métallique dans l'électrolyte contenu dans le second réservoir d'électrolyte;

60 (e') un moyen pour faire passer en continu une fibre métallisée du premier réservoir d'électrolyte à travers le second réservoir d'électrolyte;

(f') un moyen pour fournir du courant continu d'un second redresseur à la fibre, à un contact situé juste avant la surface de l'électrolyte dans le second réservoir d'électrolyte;

65 (g') un moyen pour maintenir, dans le second réservoir d'électrolyte, au-dessus de 14 volts le voltage entre la fibre et métallisée et l'anode, en fonction de la résistance développée par la fibre métallisée; et



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(h') un moyen refroidir la fibre depuis le point de contact jusqu'à l'électrolyte, ledit appareillage comprenant en outre:

(a'') un troisième redresseur pour courant continu;

(b'') un troisième réservoir d'électrolyte auquel le troisième redresseur fournit du courant;

(c'') de l'électrolyte dans le troisième réservoir d'électrolyte;

(d'') une anode métallique dans l'électrolyte du troisième réservoir d'électrolyte;

(e'') un moyen pour faire passer en continu la fibre métallisée du second réservoir d'électrolyte à travers l'électrolyte contenu dans le troisième réservoir d'électrolyte;

(f'') un moyen pour fournir du courant continu du second redresseur au troisième réservoir d'électrolyte, à travers la fibre métallisée, à un contact situé juste avant la surface de l'électrolyte dans le troisième réservoir d'électrolyte;

(g'') un moyen pour maintenir, dans le troisième réservoir d'électrolyte, au-dessus de 12 volts le voltage entre la fibre métallisée et l'anode; et

(h'') un moyen pour refroidir la fibre depuis le point de contact jusqu'à l'électrolyte.

26. Appareillage de la revendication 25, dans lequel le voltage en (g) à travers la fibre et l'anode est supérieur à 24 volts.

27. Appareillage de la revendication 25, consistant en outre en:

(a) au moins quatre redresseurs pour courant continu;

(b) au moins quatre réservoirs d'électrolyte auxquels lesdits redresseurs fournissent du courant continu;

(c) de l'électrolyte dans chacun des quatre ou plus réservoirs d'électrolyte;

(d) une anode métallique dans l'électrolyte de chacun des quatre ou plus réservoirs d'électrolyte;

(e) un moyen pour faire passer en continu une fibre métallisée à travers les quatre ou plus réservoirs d'électrolyte;

(f) un moyen pour fournir du courant continu du redresseur respectif à la fibre métallisée, à un contact situé juste avant la surface de l'électrolyte dans chacun des quatre ou plus réservoirs d'électrolyte;

(g) un moyen pour maintenir le voltage dans les quatre ou plus réservoirs d'électrolyte entre la fibre métallisée et l'anode à une valeur déterminée en fonction de la résistance manifestée par ladite fibre métallisée; et

(h) un moyen pour refroidir la fibre depuis le point de contact jusqu'à l'électrolyte dans chacun des quatre ou plus réservoirs.

28. Appareillage de la revendication 25, comprenant en outre un moyen pour prétraiter la fibre avant son passage dans le premier réservoir d'électrolyte.

29. Appareillage de la revendication 25, dans lequel les moyens pour prétraiter la fibre avant son passage dans le premier réservoir sont constitués d'un té de lavage, d'un moyen pour faire passer en continu la fibre à travers le té de lavage et un moyen pour faire passer du phosphate trisodique à travers le té de lavage à contre-courant du passage de la fibre à travers ledit té.

30. Appareillage de la revendication 29, dans lequel le té est constitué de:

(a) une chambre interne pour le passage de la fibre;

(b) un orifice d'entrée de la fibre dans le té;

(c) un orifice de sortie de la fibre du té, orifice de sortie situé à un niveau supérieur à l'orifice d'entrée; et

(d) un moyen d'intervention pour diriger le courant de phosphate trisodique introduit dans le té vers l'extérieur, par l'orifice d'entrée de la fibre.

31. Appareillage de la revendication 30, dans lequel le moyen d'intervention à l'intérieur du té de lavage est un manchon interne allant de l'orifice d'entrée à un point intermédiaire de la chambre.

32. Appareillage de la revendication 25, comprenant en outre un moyen pour agencer plusieurs fibres en vue de les diriger en parallèle vers l'électrolyte.

33. Appareillage de la revendication 32, dans lequel le moyen pour agencer lesdites fibres consiste en:

(a) un rail disposé horizontalement;

(b) un moyen sur le rail pour porter plusieurs bobines de fibres;

(c) un second rail horizontal situé au-dessus et aligné avec le premier rail; et

(d) des moyens de guidage sur le second rail, qui sont proches l'un de l'autre, les fibres passant ainsi d'une bobine sur le premier rail, par l'intermédiaire d'un cylindre guide essentiellement aligné verticalement avec la bobine, au système de dépôt électrolytique en position parallèle.

34. Appareillage de la revendication 33, comprenant en outre un moyen d'enroulement des fibres métallisées et fournissant la force motrice pour faire passer les fibres à travers l'installation selon le présent procédé.

35. Appareillage de la revendication 34, dans lequel le moyen pour enrouler les fibres métallisées et fournir la force motrice est constitué d'un moteur actionnant plusieurs bobines, chacune étant prévue pour enrouler une seule fibre, et une série de cylindres entraînés en amont des bobines disposés de manière à inverser le parcours de la fibre et éviter ainsi un relâchement desdites fibres.

36. Appareillage de la revendication 35, comprenant un moyen de rinçage des fibres métallisées quittant le dernier réservoir de galvanoplastie.

37. Appareillage de la revendication 36, dans lequel le moyen de rinçage des fibres métallisées est



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consistué d'une série de tés de lavage disposés pour le passage de la fibre dans un sens et pour la passage d'eau à contre-courant du passage de la fibre.

38. Appareillage défini dans la revendication 25, comprenant un moyen de pulvérisation d'un fluide sur la fibre à travers laquelle passe le courant électrique, et comprenant:

(a) un premier élément tubulaire pourvu d'une série alignée d'orifices de buses à la surface inférieure dirigés vers un premier point de la fibre;

(b) un second élément tubulaire pourvu d'une série alignée d'orifices de buses à la surface inférieure dirigés vers un second point de la fibre;

(c) un moyen pour répartir le fluide dans les premier et second éléments, ledit appareillage consistant en outre en un moyen pour faire passer en continu la fibre d'un cylindre de contact à une solution d'électrolyte; un moyen pour diriger l'électrolyte vers le premier élément tubulaire et, par dessus la fibre, au point où la fibre s'engage sur le cylindre de contact, et un moyen pour diriger l'électrolyte vers le second élément tubulaire et, par dessus la fibre, au point où la fibre quitte le cylindre de contact.

39. Appareillage de la revendication 38, comprenant en outre un moyen pour recycler l'électrolyte à partir du réservoir d'électrolyte dans lequel passe la fibre vers les premier et second éléments tubulaires.

40. Appareillage de la revendication 39, dans lequel le cylindre de contact est cylindrique et adapté pour tourner; la fibre est engagée avec le cylindre de contact sur un quart de sa surface; le premier élément tubulaire est disposé directement au-dessus et aligné avec le cylindre de contact en un point directement au-dessus du centre du cylindre de contact, point où la fibre s'engage sur le cylindre de contact, pour diriger l'électrolyte directement au cylindre de contact, et le second élément tubulaire est situé au-dessus du cylindre de contact à 90 degrés du point où le premier élément tubulaire dirige le fluide et est orienté de manière à diriger l'électrolyte sur la fibre tangentiellement au cylindre de contact.

41. Appareillage de la revendication 40, consistant en outre en un réservoir d'électrolyte; plusieurs cylindres de contact montés en série au sommet d'un réservoir d'électrolyte, sur lesquels passe la fibre et qui fournissent à ladite fibre du courant continu; de l'électrolyte dans le réservoir d'électrolyte à un niveau très proche de la base des cylindres de contact; un moyen pour faire passer la fibre d'abord sur un premier cylindre de contact jusqu'à l'électrolyte; puis de l'électrolyte à un second cylindre de contact immédiatement en aval du premier cylindre de contact et ensuite en continu sur des cylindres de contact successifs selon un schéma de parcours: cylindre de contact — électrolyte — cylindre de contact suivant.

42. Appareillage de galvanoplastie défini dans la revendication 25, pour revêtir une fibre avec un métal, consistant en un réservoir d'électrolyte; de l'électrolyte dans le réservoir; des cylindres de contact rotatifs fixés au sommet du réservoir au-dessus duquel on fait passer la fibre juste avant la surface de l'électrolyte dans le réservoir; des cylindres fous placés au fond du réservoir d'électrolyte disposés en alignement avec les cylindres de contact pour le passage de la fibre autour; un redresseur; une barre collectrice allant du redresseur au réservoir d'électrolyte; et une barre conductrice de l'électricité allant de la barre collectrice au cylindre de contact; une série de doigts conducteurs allant de ladite barre conductrice jusqu'à l'engagement avec le cylindre de contact, et un moyen pour le refroidissement de la fibre entre le point de contact et l'électrolyte.

43. Appareillage de la revendication 42, dans lequel la série de doigts conducteurs est constituée de deux rangées de doigts élastiques, la rangée la plus proche du cylindre de contact étant d'une longueur plus courte que l'autre rangée, les extrémités des deux rangées s'appuyant contre le cylindre de contact.

44. Appareillage de la revendication 42, dans lequel le moyen de refroidissement de la fibre consiste en un moyen pour diriger l'électrolyte vers les cylindres de contact au point où la fibre s'engage sur lesdites cylindres de contact.