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(54) **Apparatus and process for continuously plating fiber.**

(57) A process and apparatus for continuous high voltage plating of fibers are disclosed. Metal-coated fibers comprising a core of a semi-metallic or non-metallic filament may be plated with a thin, uniform, firmly adherent electrically conductive layer of an electrodepositable metal, such as nickel or the like, in a continuous high voltage process by electrodeposition from a solution onto the core. Uniformity and production speed are improved if the surface of the fibers is pretreated to provide a core fiber substantially free of adsorbed organic compounds. Non-metallic filaments comprising non-conductive polymers, such as aramid or the like, may be plated in the continuous process by roughening and sensitizing the core fiber of non-conductive polymer, and chemically depositing thereon a conductive metallic interlayer, followed by high voltage electrodeposition. Metallic filaments, especially the high strength metal coated fibers produced by the process, may be treated by oxidizing and/or sizing to improve processability and properties of the metal-coated fibers when mixed into plastic materials and when used in the form of filaments, yarns or tows in knitting and weaving machines.

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APPARATUS AND PROCESS FOR CONTINUOUSLY PLATING FIBER

BACKGROUND OF THE INVENTION

1. Field of the Invention.

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

2. Description of the Prior Art.

Filaments comprising non-metals and semi-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 chopped strands are known to be useful in reinforcing metals and organic polymeric materials. Articles comprising metals or plastics reinforced with such fibers find wide-spread 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.

Although a quantity of electricity is required to electrodeposit metal on the filament surface, an increase in voltage to increase the amperes 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 buring 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.

SUMMARY OF THE INVENTION

It is a basic object of the present invention to provide 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 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.

It has been found that these and other objects are obtained by the use of high voltages in the apparatus and process of the subject invention.

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 clean 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 elctrolytic 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 charaterized 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.

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 traverse 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.

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 fibers 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 resistancce 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 high 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 area of a short length can be covered and tolerated, without serious detriment.

In 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 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 acis are suitable in aqueous soltuion.

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 pre-treatment 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 station 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 that eight ounces of tri-sodium phosphate per gallon of water at 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. The discharge from the tee 36 is recycled to the fluid inlet of the tee 36 through stand pipe 308 in the tank 31 and recirculation 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, 2 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 roller 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 microns in diameter. However, the process of 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 microns 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 anisotrophic resistance is 1,000 times the long axis. Thus, the total contact area must be 1,000 times the tow diameter, which for 7 microns is 0.34 inches. Practice has taught that one-half inch of contact will properly serve the electrical requirement of the system when plating 7 micron tow, hence two and three 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 one-half to one inch from the electrolyte bath when voltages of 16 to 25 volts are applied. Further, it has been found that recirculation of about 2 gallons per minute per contact roller traveling at about 1½ 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 eight to ten ounces of metal, preferably in the form of $NiCl_2$ and $NiSO_4$ per gallon of solution. The pH of the solution is set at 4 to 4.5 and the temperature maintained between 145 and 150°F. Recirculation of the elecrolyte through the spray nozzles 130 at the desired rate requires that the nozzle openings be 3/32 inches in diameter on 1/8" centers 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 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 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 hold 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-electrolyte 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 microns
Metal Coating	Approximately 0.5 microns thick, about 50% of the total fiber weight
Density	2.50-3.00 grams/cm.^{3}
Tensile Strength	Up to 450,000 psi
Tensile Modulus	34 M psi
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 consist of a cascading tank with separate compartments 252, 254 and 256. The cascading tank is a conventional three station cascade counter-current 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.

In 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 pretreatment section 8 and rinse section 12 is shown in FIGURES 24-26. 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 overide 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 appartus 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 micron 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 thread 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, aluminum oxide, sand, etc. In conventional filaments, e.g., those 4 to 15 microns thick, 120 mesh abrasive will produce a suitably roughened surface. The roughened surfaces provides essential anchoring sites for interlayer 3, 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 soultion 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 334 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 a phenolic 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 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, filament 2 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 comprised 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: vinyltriethoxysilane, vinyl-tris(beta-methoxyethoxy) silane, gamma-methacryloxypropyltrimethoxy silane, beta-(3,4-epoxy-cyclohexyl) ethyltrimethoxysilane, gamma-glycidoxypropyltrimethoxysilane, gamma-aminopropyltriethoxysilane, n-beta-(aminoethyl) gamma-aminopropyltrimethoxysilane, gamma-ureidopropytriethoxysilane, 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 tetraoctyloxyltitanium di(dilaurylphosphite).

In practice, it has been found that aminosilane soltions of between 0.1 and 2.5 parts of gamma-aminopropyltriethoxysilane 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 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 disperants, 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 latex (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 of 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., at 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 sheer 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 15-50 angstroms thick, particularly compatible with aminosilane, and this is very useful to produce composites with polymers having desirable characteristics.

The following Examples illustrate the present invention, but are not intended to limit it.

EXAMPLE 1

Four tows (fiber bundles) of 12,000 strands each of 7 micron graphite fibers were continuously drawn through a solution of 8 oz./gal. of trisodium phosphate heated at 180-200°F., then through two rinse tanks. The effluent from the second rinse tank was returned to the first. The tows were then passed through a neutralizing tank containing 10% aqueous solution of C.P. hydrochloric acid (35%), then through two rinse tanks. The effluent from the second of these two rinse tanks was returned to the first, and the waste from all tanks was combined for self-neutralization.

In a continuous electroplating system, a plating solution was provided having the following composition:

INGREDIENTS	AMOUNT
nickel sulfate ($NiSO_4.6H_2O$)	40 oz./gallon
nickel chloride ($NiCl_2.6H_2O$)	12-20 oz./gallon
boric acid (H_3BO_3)	5-8 oz./gallon

The bath was heated to 140-160°F., and had a pH of 3.8-4.2.

The anode baskets were kept filled with electrolytic nickel pellets and four tows (fiber bundles) of 12,000 strands each of 7 micron carbon fibers stripped of organic contaminants as described above were continuously drawn through the bath at a tow speed of 5 feet/min. and with 120 amps. current, adjusted to give 5 ampere-minutes per 1,000 strands total. The voltage drop from anode to cathode was 30 volts. At the same time, electrolytic solution was recycled through a loop into contact with the entering and leaving paths of the tow. The tow was next passed continuously through an identical bath, at a tow speed of 5.0 ft./min. with 180 amps. current. The final product was a tow of high strength coated fibers according to this invention comprising a 7 micron fiber core and about 50% by weight of the coated fiber of crystalline electrodeposited nickel adhered firmly to the core. The metal coating was uniform and free from bare spots.

When a length of the fiber was sharply bent, then examined, there was no circumferential cracking on the metal coating in the tension side of the bend. The tow could be twisted and knotted without causing the coating to flake or come off as a powder.

EXAMPLE 2

When the procedure of Example 1 was repeated, substituting graphite tows which had been passed through hot liquid and condensing vapors of 1,1,1-trichlorethane in a degreaser to strip them free from organics, uniform metal coatings were ultimately produced.

To illustrate the adverse effects of organic compounds, when the concentration of organic impurities in the degreaser of Example 2 was allowed to build up, the organic recontaminated the graphite fibers and the nickel coating became non-uniform. When the trisodium phosphate cleaning bath in Example 1 was replaced with wetting agents containing organics (Wyandotte BN cleaner, Oakite 190 cleaner or Ivory Liquid detergent) ultimately the nickel plating was non-uniform.

EXAMPLE 3

A continuous tow comprised of smooth surfaced aramid filaments (4,000 fibers per bundle, average 12 microns in diameter, poly(paraphenylene terephthalamide), DuPont KEVLAR 49) was mechanically abraded with 120 mesh size silica slurried in water in a gas-fluidized bed until the surface of each fiber was roughened. The tow was dipped in an aqueous solution of 10 g/l stannous chloride and 10 ml/l of concentrated hydrochloric acid heated to 140°F. and permitted to reside therein for one minute, and rinsed. The tow was then dipped into an aqueous solution of 2.8 g. of palladium chloride and 10 ml. of concentrated aqueous hydrochloric acid per liter, heated to 140°F. and permitted to reside therein for one minute, and rinsed. This technique was repeated and a rough, sensitized surface was produced on the filaments. Next the tow was immersed in an aqueous solution of 31 g./l silver nitrate and then without rinsing, into a solution of 85% aqueous hydrazine hydrate (Hummel Chemical Corp., No. 85). A silver interlayer was adherently deposited thereby. A specimen was taken, washed and dried and resistance was measured with an ohmeter. If necessary, the silver deposition procedure was repeated until the resistance of the 4K, 12 micron tow was reduced to 20 ohms per foot, at which time it was suitable for electroplating.

In a continuous electroplating system, a plating solution was provided having the following composition:

INGREDIENTS	AMOUNT
nickel sulfate ($NiSO_4.6H_2O$)	40 oz./gallon
nickel chloride ($NiCl_2.6H_2O$)	12-20 oz./gallon
boric acid (H_3BO_3)	5-8 oz./gallon

The bath was heated to 140-160°F., and had a pH of 3.8-4.2.

The anode baskets were kept filled with electrolytic nickel pellets and four tows (fiber bundles) of 4,000 strands each of 12 micron carbon metallized aramid filaments are continuously drawn through the bath at a tow speed of 5 feet/ min. while an external voltage of 30 volts is applied at a current of 160 amps.. At the same time, electrolytic solution was recycled through a loop into contact with the entering and leaving paths of the tow. The tow was next passed continuously through an identical bath, at a tow speed of 5.0 ft./min. with 160 amps. current. The final product was a tow of high strength composite fibers according to this invention comprising a 12 micron fiber core, a thin silver interlayer and about 50% by weight of the composite of crystalline electrodeposited nickel adhered firmly to the core through the interlayer.

If a length of the filament is sharply bent, as in weaving or knitting, then examined, the metal coating may fracture, but it will not peel off.

WHAT IS CLAIMED IS:

1. A process for electroplating fiber comprising:

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

(b) passing D.C. current through the fibers to the anode; and

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

(d) whereby metal from the anode migrates to the fiber and is bonded thereto.

2. An apparatus for metal plating fibers, 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 through the fibers to the electrolyte;

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

3. A process for 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 fluid departs from the current carrying surface.

4. An electroplating apparatus for coating fibers with metal comprised of an electrolyte tank, electrolyte in the tank, rotating contact rollers secured to the top of the tank over which fiber is adapted to pass, 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, an electrically conductive bar extending from the bus bar to the contact roller, an array of conductive fingers extending from the electrically conductive bar into engagement with the contact roller.

5. An electrolyte tank comprised of:

(a) a pair of contact rollers mounted at the top of the tank;

(b) a pair of idler rollers mounted at the bottom of the tank in vertical alignment with the pair of contact rollers;

(c) an anode mount bar attached to the electrolyte tank between the pair of contact rollers;

(d) an anode basket depending from the anode bar;

(e) a well in the electrolyte tank;

(f) means for circulating electrolyte from the well to the remainder of the tank;

(g) means for sensing the level of electrolyte in the well; and

(h) means for delivering make up to the electrolyte when the level in the well is at a predetermined low level.

6. An apparatus for driving fiber through a continuous processing operation comprising a first drive motor; an array of rollers arranged as a capstan; a plurality of guide rollers; a plurality of processing rollers wherein the diameter of every roller on which the fiber passes is the same; means to drive the capstan rollers, the guide rollers and the processing rollers at the same speed; take up reels for the the processed fibers; a second drive motor to drive the take up reels.

7. An apparatus for imposing tension on a fiber being passed through a continuous processing operation comprising:

(a) means to pass the fiber through the continuous processing operation;

(b) an array of tension rollers around which the fibers pass in a mode reversing the direction of the path of the fiber; and

(c) means to drive the array of tension rollers in the same direction as the fiber at variable speeds equal to or less than the speed of the fiber.

8. A process for continuously processing fiber in an electrolyte wherein electrical current is delivered to the electrolyte through the fiber comprising the steps of:

(a) drawing the fiber through the process;

(b) passing the fiber through the electrolyte; and

(c) imposing a tension on the fiber at a location upstream of the location at which the fiber enters the electrolyte by passage of the fiber over an array of rollers driven selectively at some speed either equal to or less than the speed of the fiber.

9. A process for electroplating fiber comprising:

(a) continuously passing the fiber over a contact into an electrolyte solution in a tank in which a metal anode is immersed;

(b) passing D.C. current through the fibers to the anode; and

(c) imposing a tension on the fiber to insure a direct tight path from the fiber at the contact point to the electrolyte in the tank, whereby metal from the anode migrates to the fiber and is bonded thereto.

10. An apparatus for metal plating fibers, 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) an electrolyte sprayed contact member immediately above the electrolyte surface;

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

(g) means for delivering D.C. current from the rectifier through the fibers to the electrolyte; and

(h) means for maintaining tension on the fiber to insure a direct tight path from the fiber at the contact point to the electrolyte in the tank.

11. In the process for the production of coated fibers, said process comprising:

(a) providing a continuous length of a plurality of electrically conductive graphite core fibers;

(b) continuously immersing at least a portion of the length of said fibers in a solution capable of electrolytically depositing at least one metal; and

(c) providing a quantity of electricity while applying an external voltage between the fibers and an electrode immersed in the solution, which voltage is in excess of what is normally required to cause metal deposition, whereby (i) the metal is reduced on the surface of the fibers, (ii) the metal nucleates substantially uniformly onto the surface of the fibers; and (iii) there is produced a substantially uniform, firmly adherent layer of metal on said core,

the improvement which comprises providing graphite core fibers whose surfaces are substantially free of adsorbed organic compounds which interfere with the electrodeposition of the metal.

12. A continuous filament comprising an electrically non-conductive polymeric core having a rough surface sensitized to the chemical deposition of a metal and an electrically conductive metallic interlayer chemically deposited on the rough surface of said core and firmly bonded thereto, alone, or in further combination with at least one thin, uniform, firmly adherent, electrically conductive layer of at least one metal electrodeposited on said interlayer.

13. A continuous filament comprising an electrically non-conductive polymeric core having a rough surface sensitized to the chemical deposition of a metal and an electrically conductive metallic interlayer chemically deposited on the rough surface of said core and firmly bonded thereto, and at least one thin, uniform, firmly adherent, electrically conductive layer of at least one metal electrodeposited on said interlayer and wherein said filament can be knotted without substantial separation and loss of the metal coating.

14. A process for the production of continuous filaments comprising:

(a) providing a continuous length of at least one filament having a rough, electrically non-conductive polymeric core; and

(b) sensitizing said filament to the chemical deposition of a metal;

(c) chemically depositing a firmly adherent electrically conductive metal interlayer on the rough, sensitized surface of said filament; and, optionally,

(d) continuously immersing at least a portion of the length of said filament in a solution capable of electrolytically depositing at least one metal; and

(e) providing a quantity of electricity and applying an external voltage between the fibers and an electrode immersed in the solution, which voltage is in excess of what is normally required to cause metal deposition, whereby (i) the metal nucleates substantially uniformly on the surface of the filaments and (ii) there is produced a substantially uniform, firmly adherent layer of metal on said interlayer.

15. A continuous filament comprising an electrically non-conductive polymeric core having a rough surface sensitized to the chemical deposition of a metal and an electrically conductive metallic interlayer, chemically deposited on the rough surface of said core and firmly bonded thereto.

16. A metallic filament in which sizing material is on the surface.

17. A metallic filament comprising a bulk density characteristic in the form of additional surface material.

18. A metallic filament comprising an organic surface having considerable lubricity.

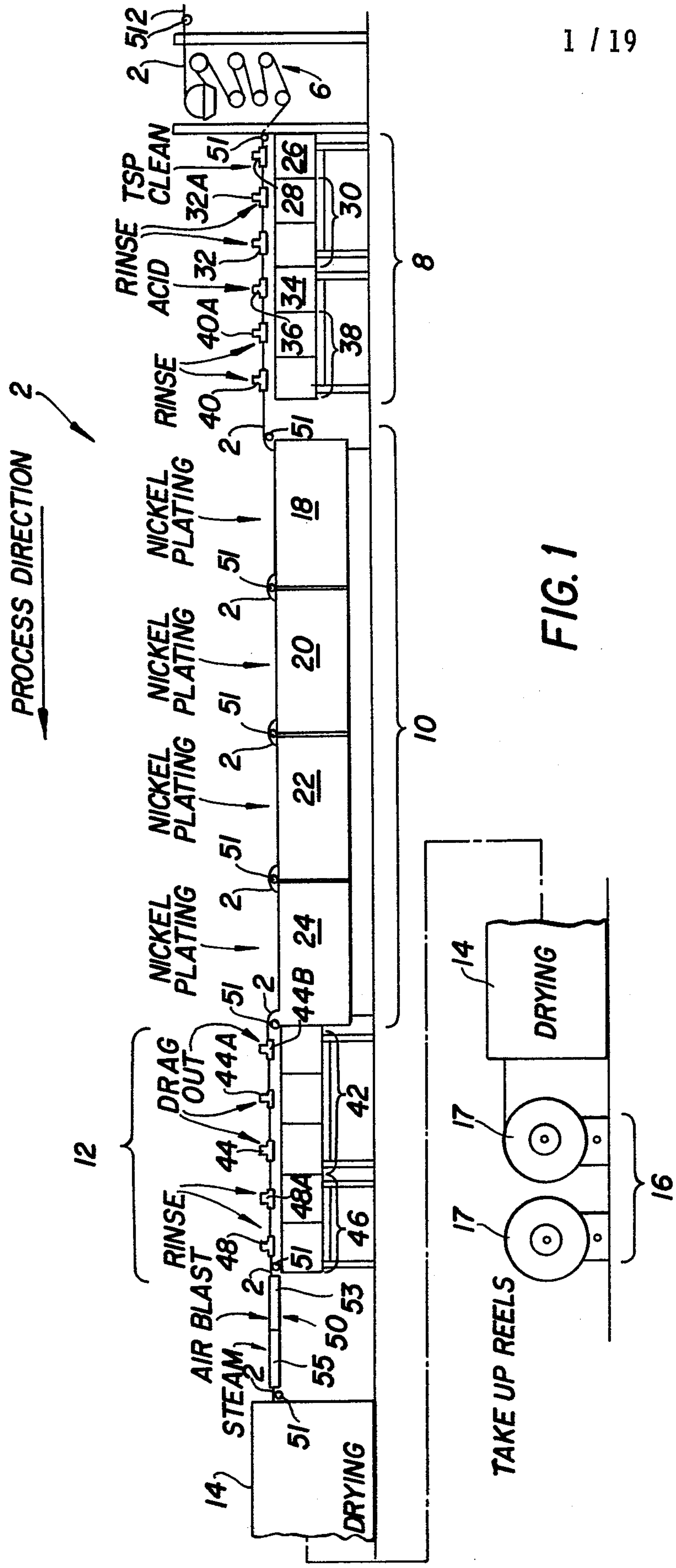
19. A metallic filament having a metal oxide surface in which sizing material is on the surface.

20. A process for sizing metallic filaments comprising:

(a) passing the metallic filaments through a sizing medium; and

(b) heating the metallic filaments to dry and set the sizing material on the filaments.

21. A process for oxidizing metallic filaments comprising passing the metallic filaments through an oxidizing medium at an elevated temperature until a substantially uniform surface oxide coating is produced on the filaments.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RINSE
40
8
2
51
NICKEL PLATING
18
NICKEL PLATING
20
NICKEL PLATING
22
NICKEL PLATING
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44B
DRAG OUT
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12
RINSE
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TAKE UP REELS

FIG. 1

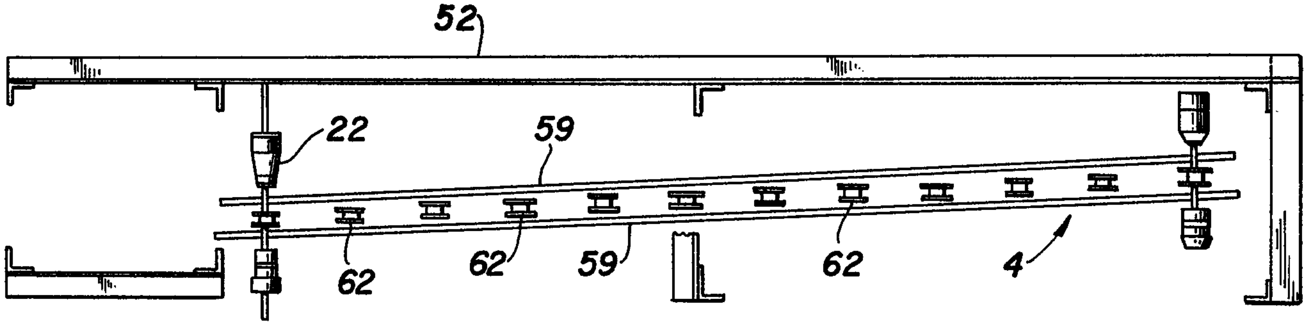

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FIG.3

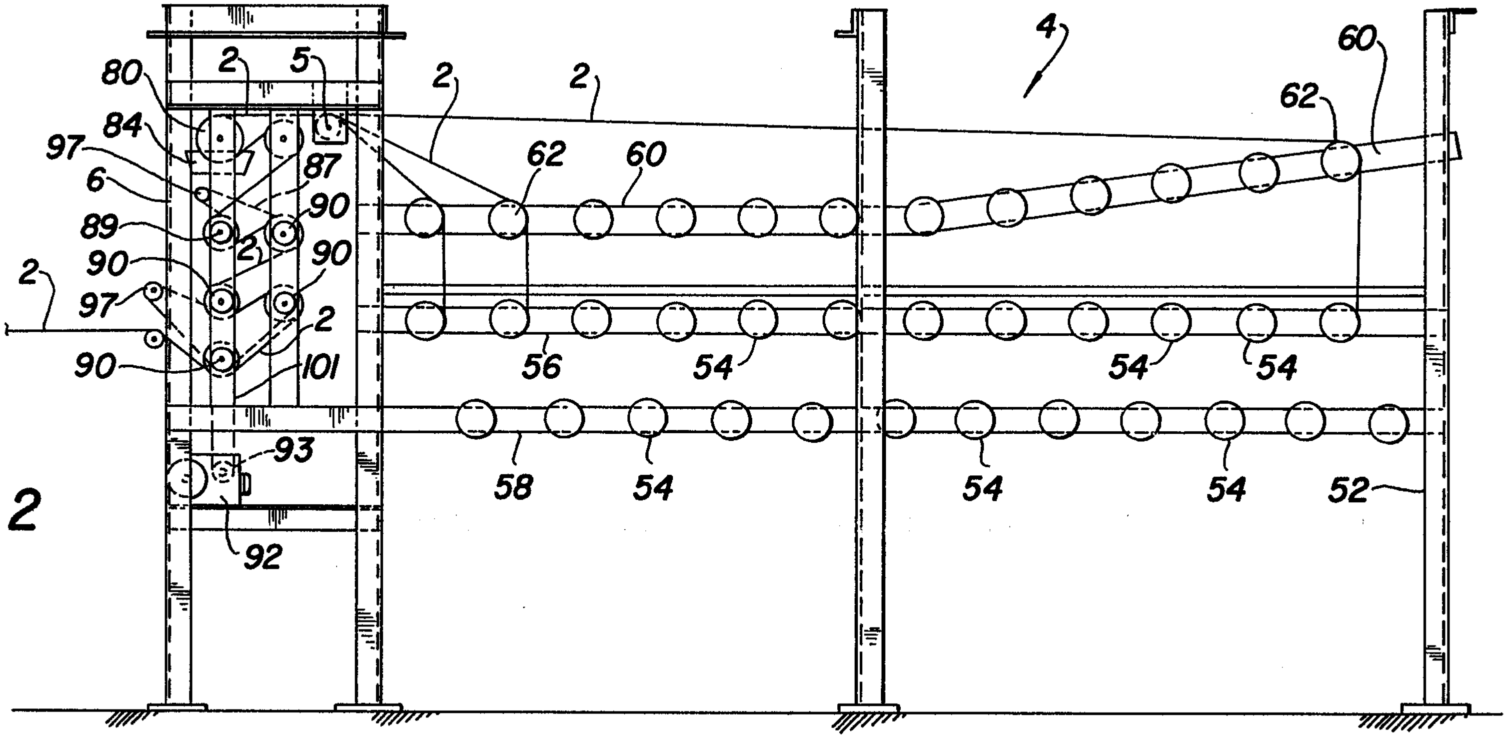

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FIG.2

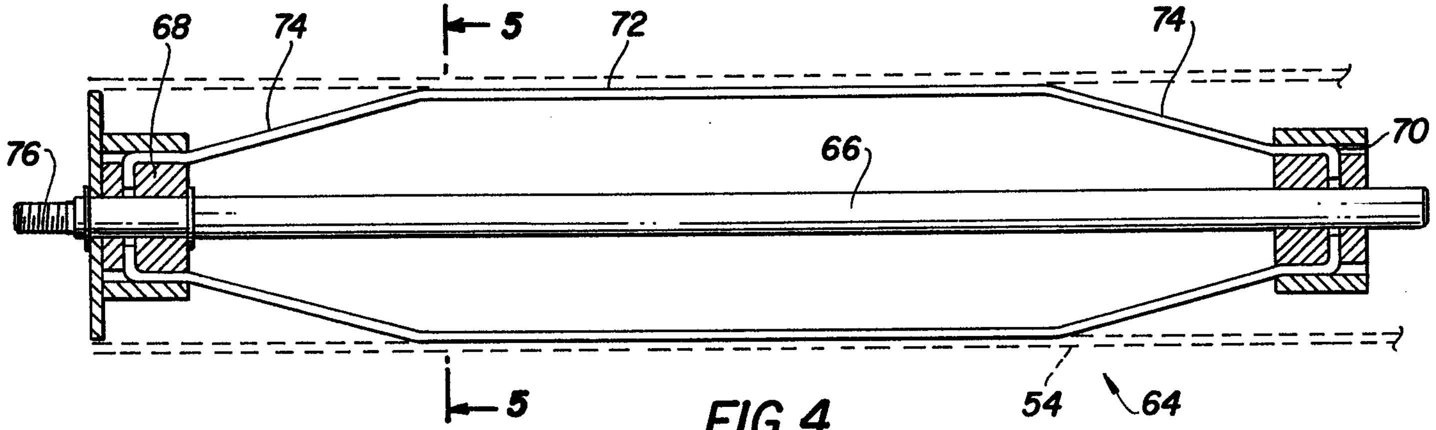


FIG. 4

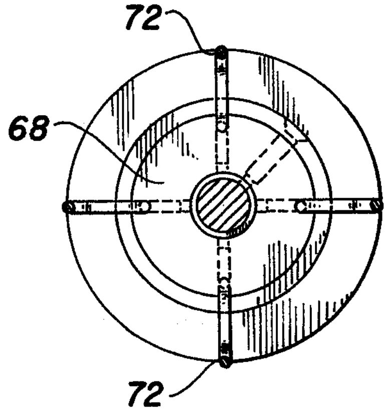


FIG. 5

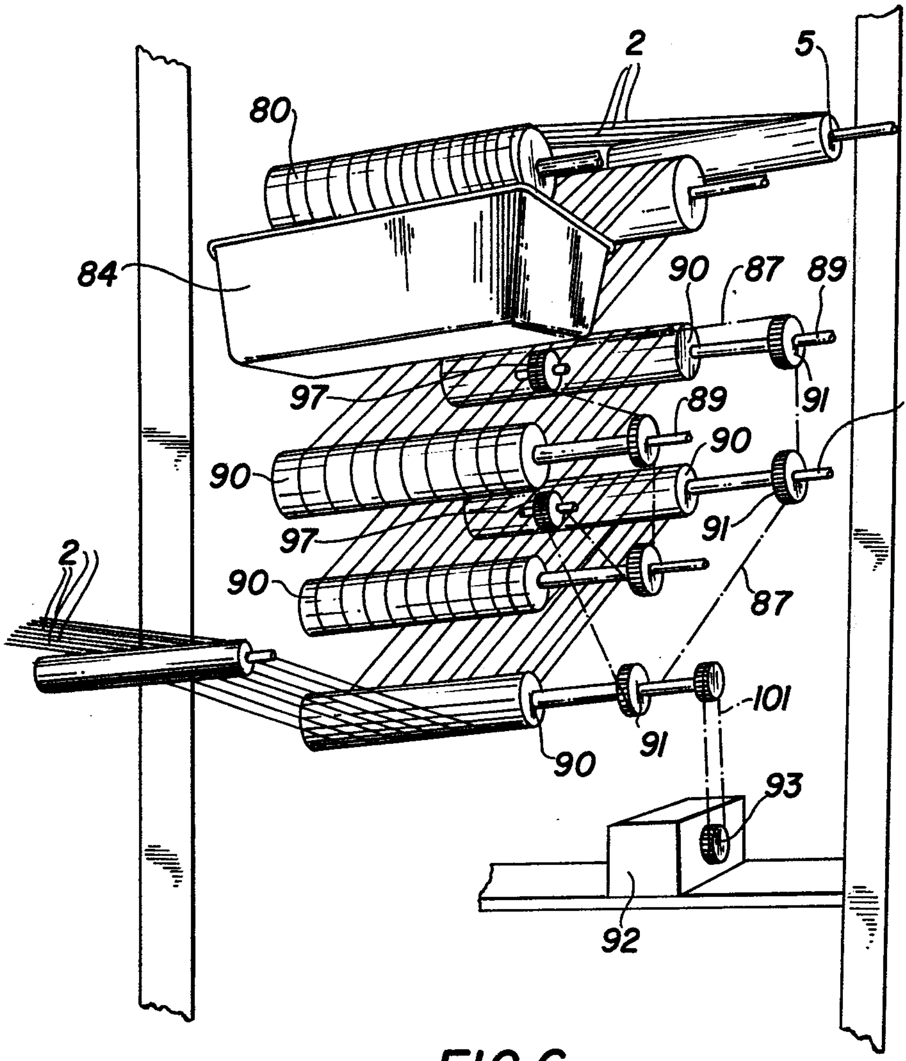
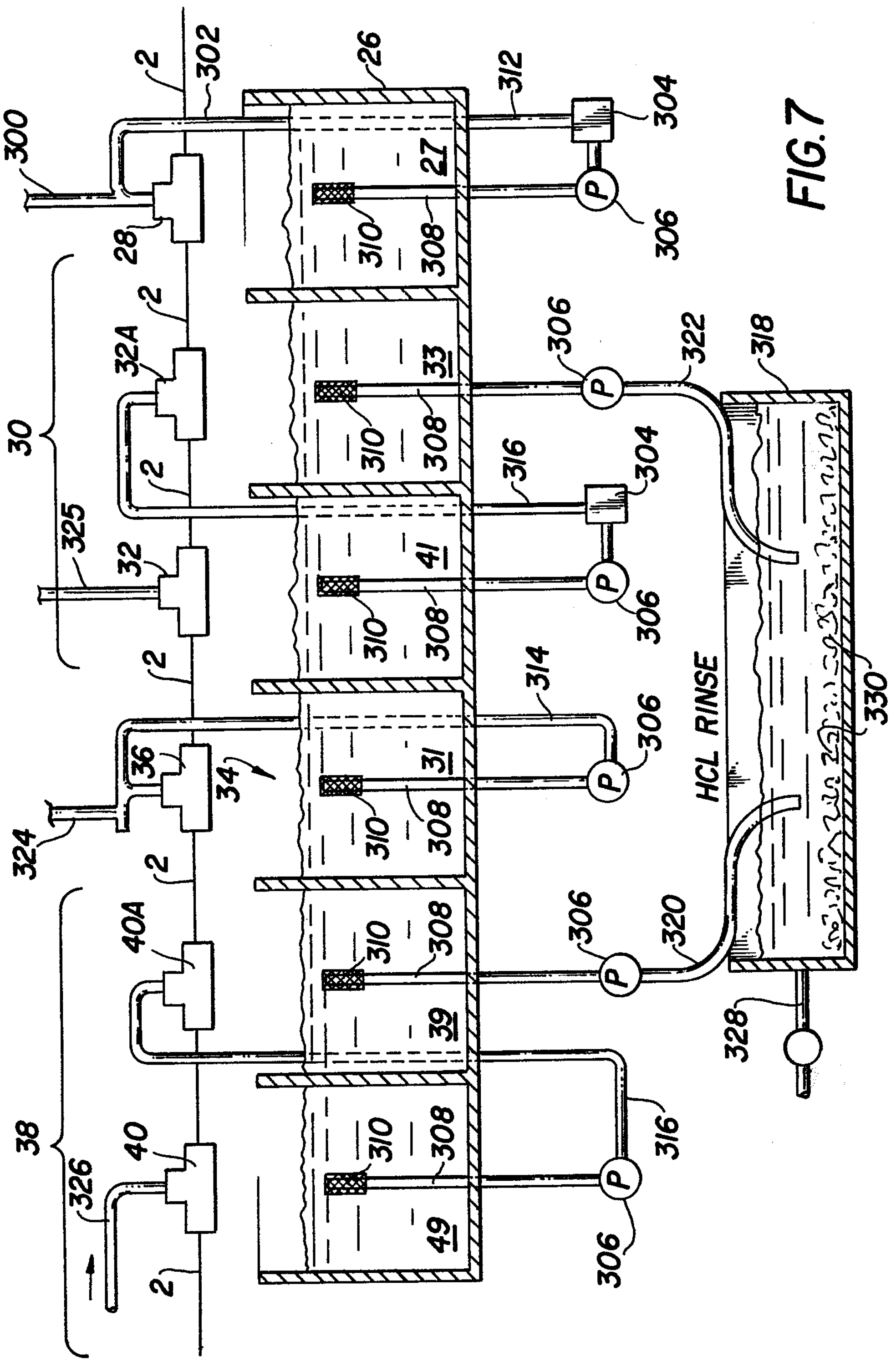


FIG.6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HCL RINSE
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49

FIG.7

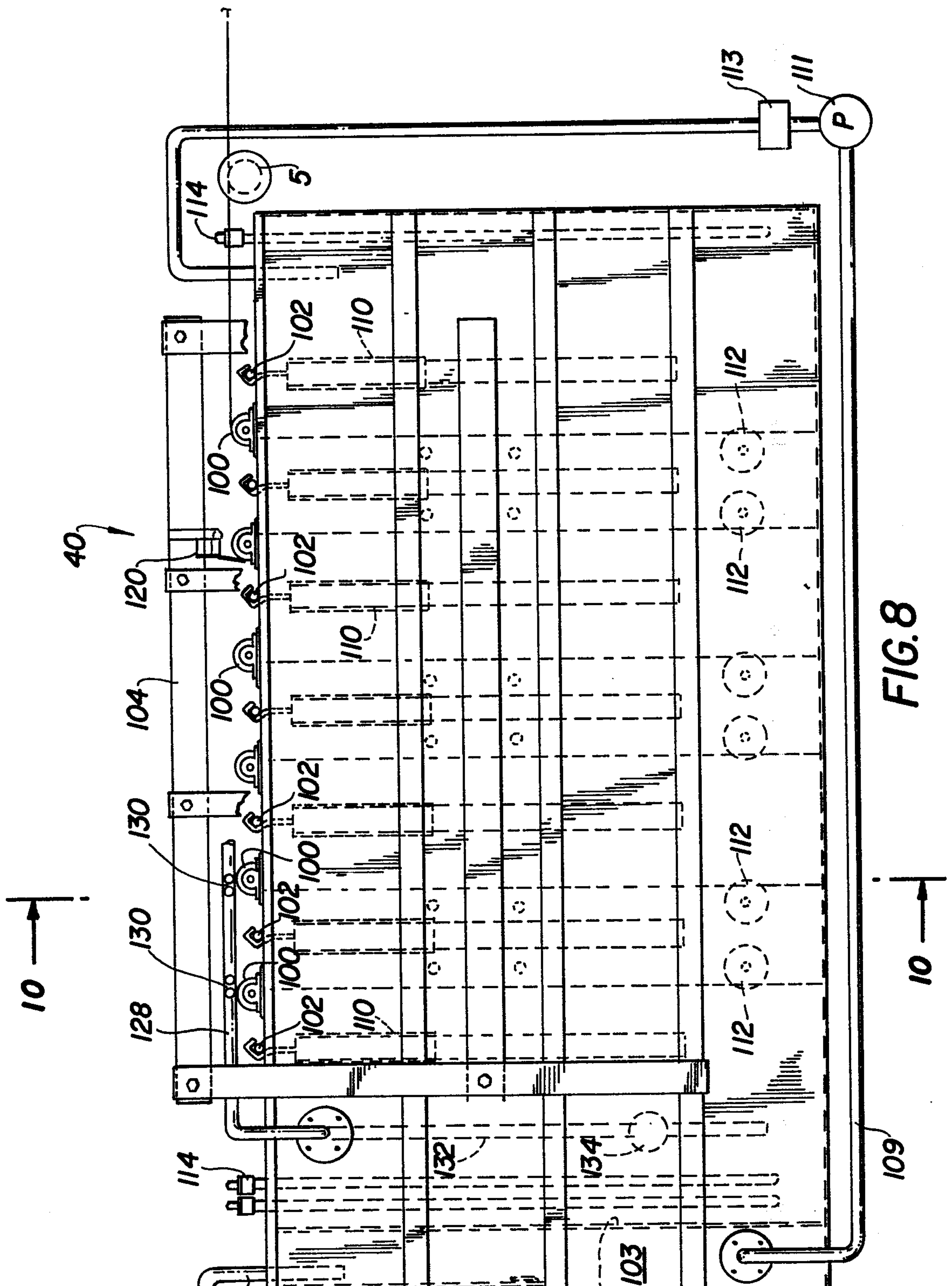
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FIG.8

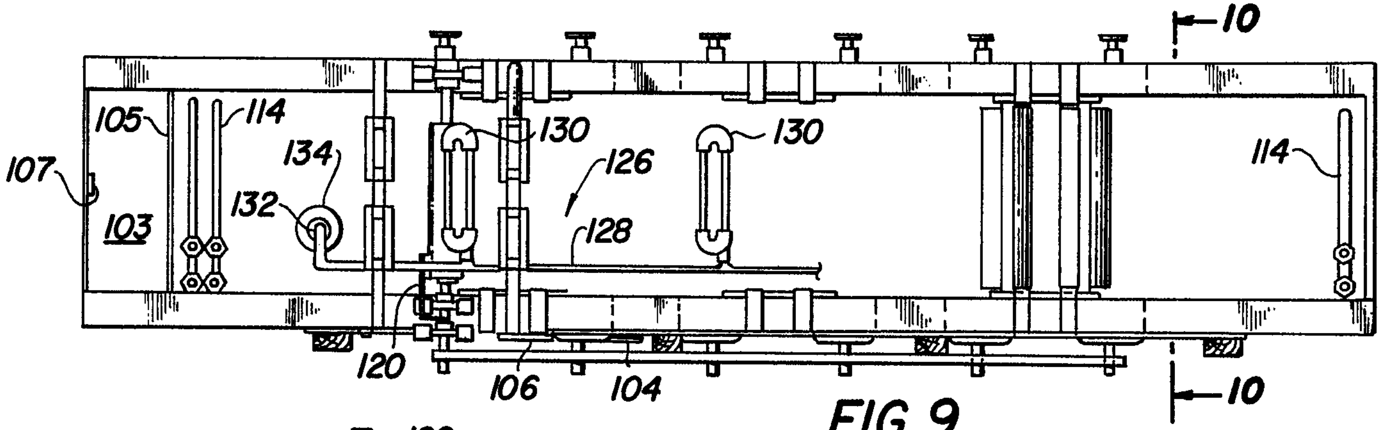

FIG. 9

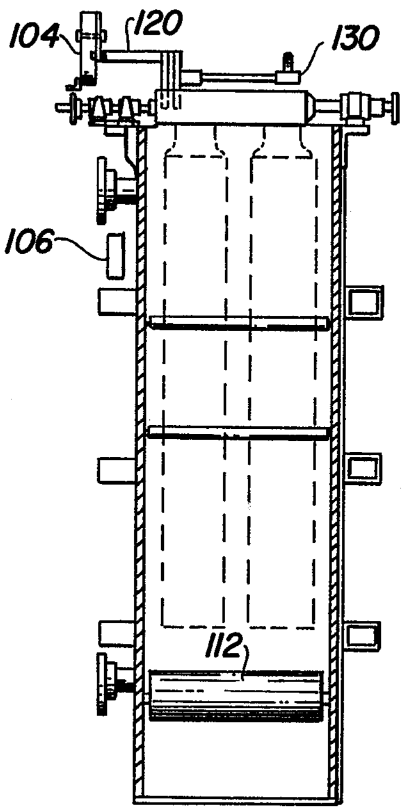

FIG. 10

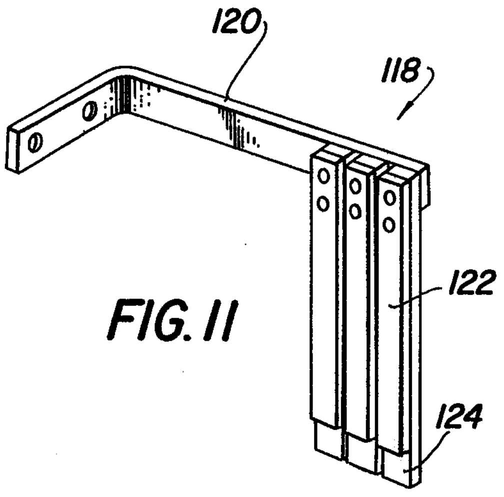

FIG. 11

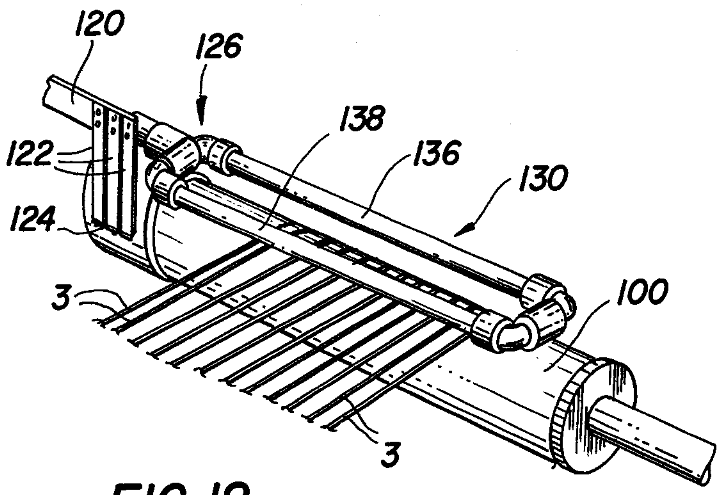
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FIG. 12

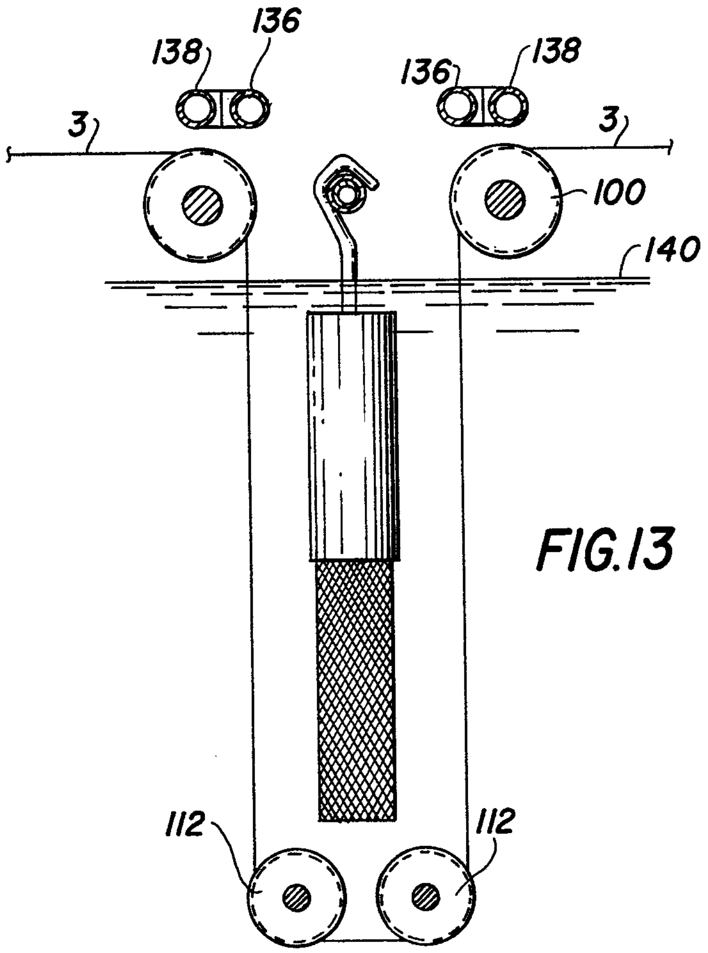
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FIG. 13

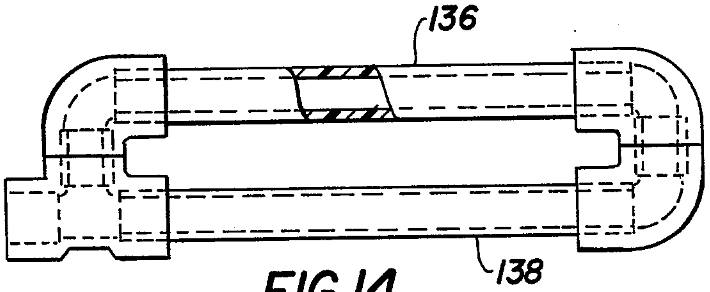

FIG. 14

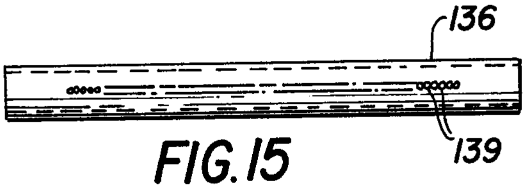

FIG. 15

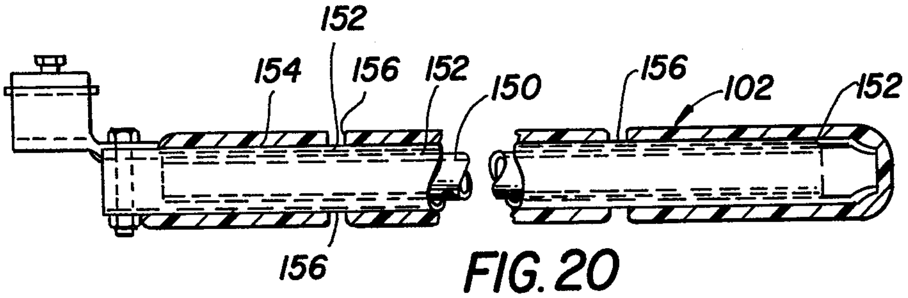

FIG. 20

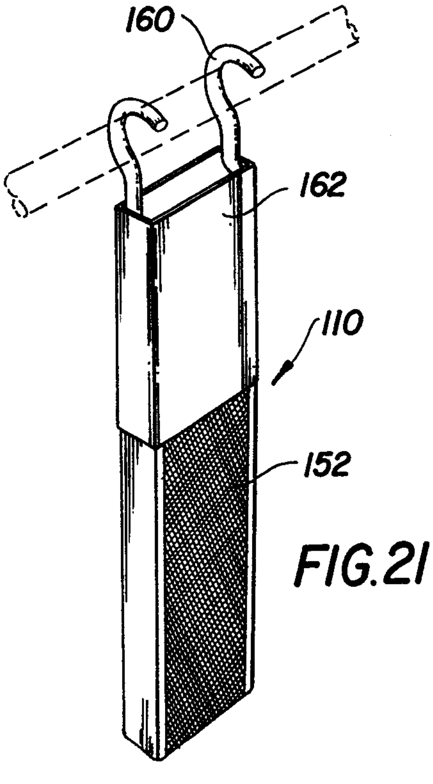

FIG. 21

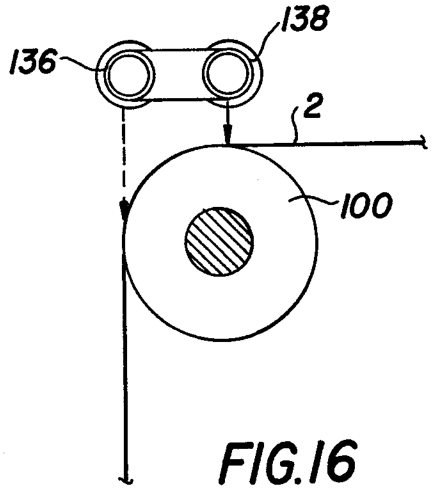

FIG. 16

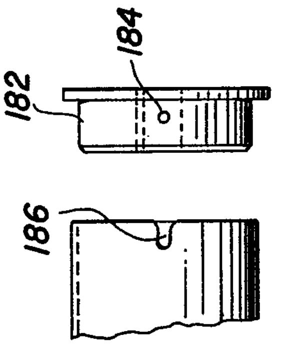

FIG.19

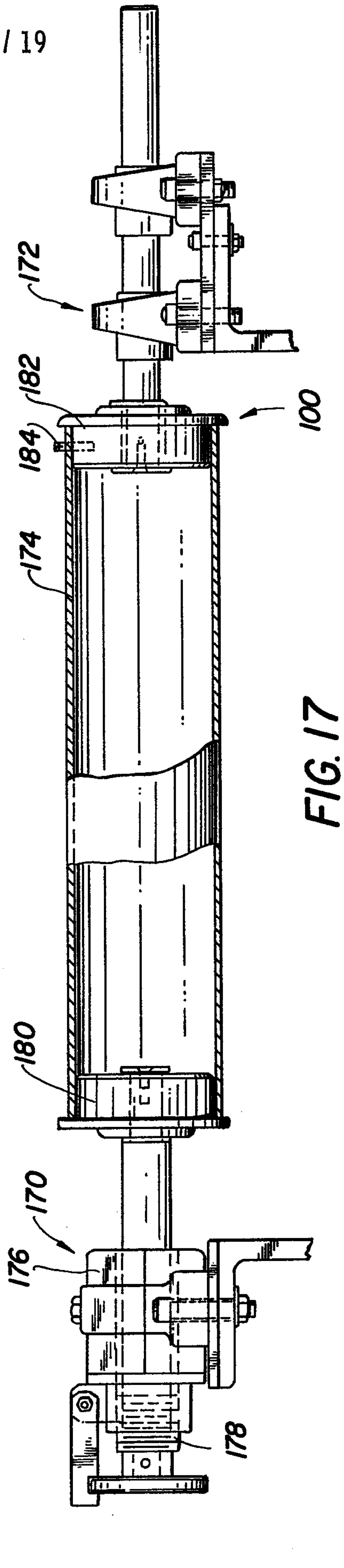

FIG. 17

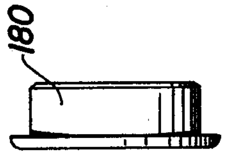

FIG.18

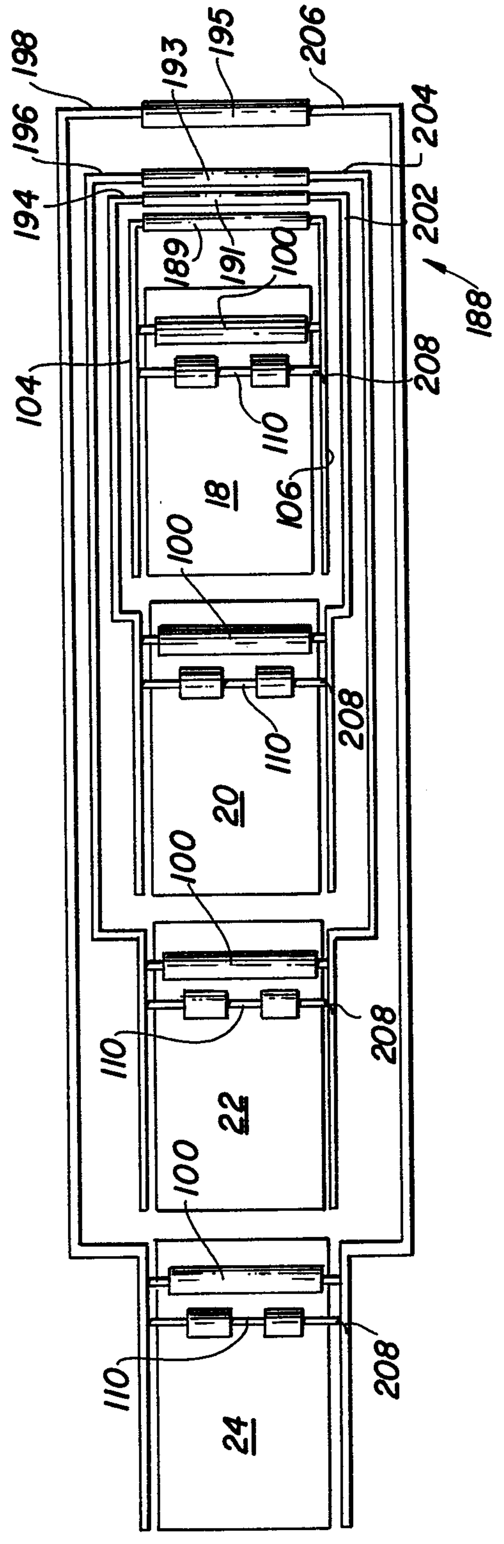
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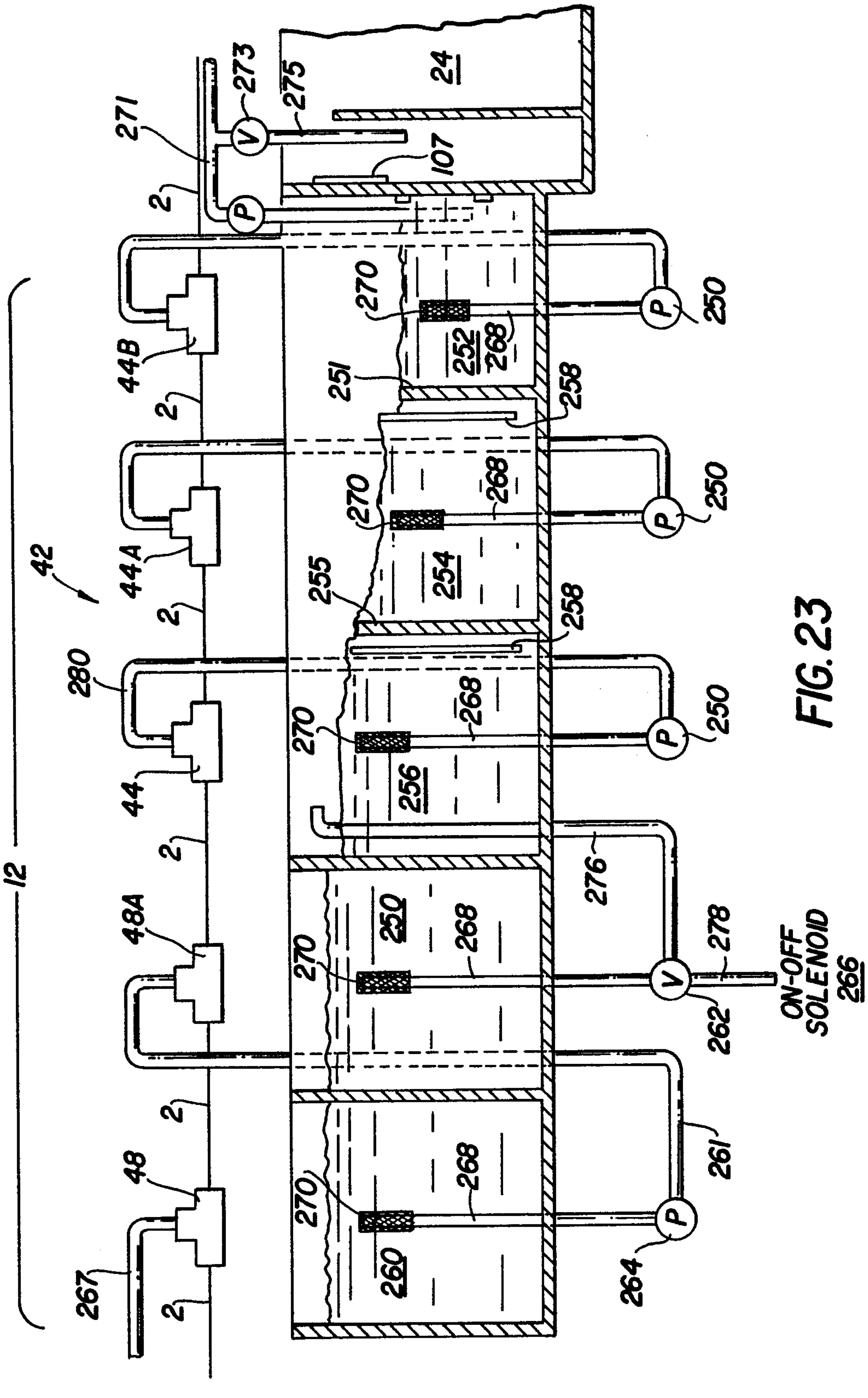
FIG. 22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ON-OFF
SOLENOID
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44
280
270
256
268
250
258
255
44A
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FIG. 23

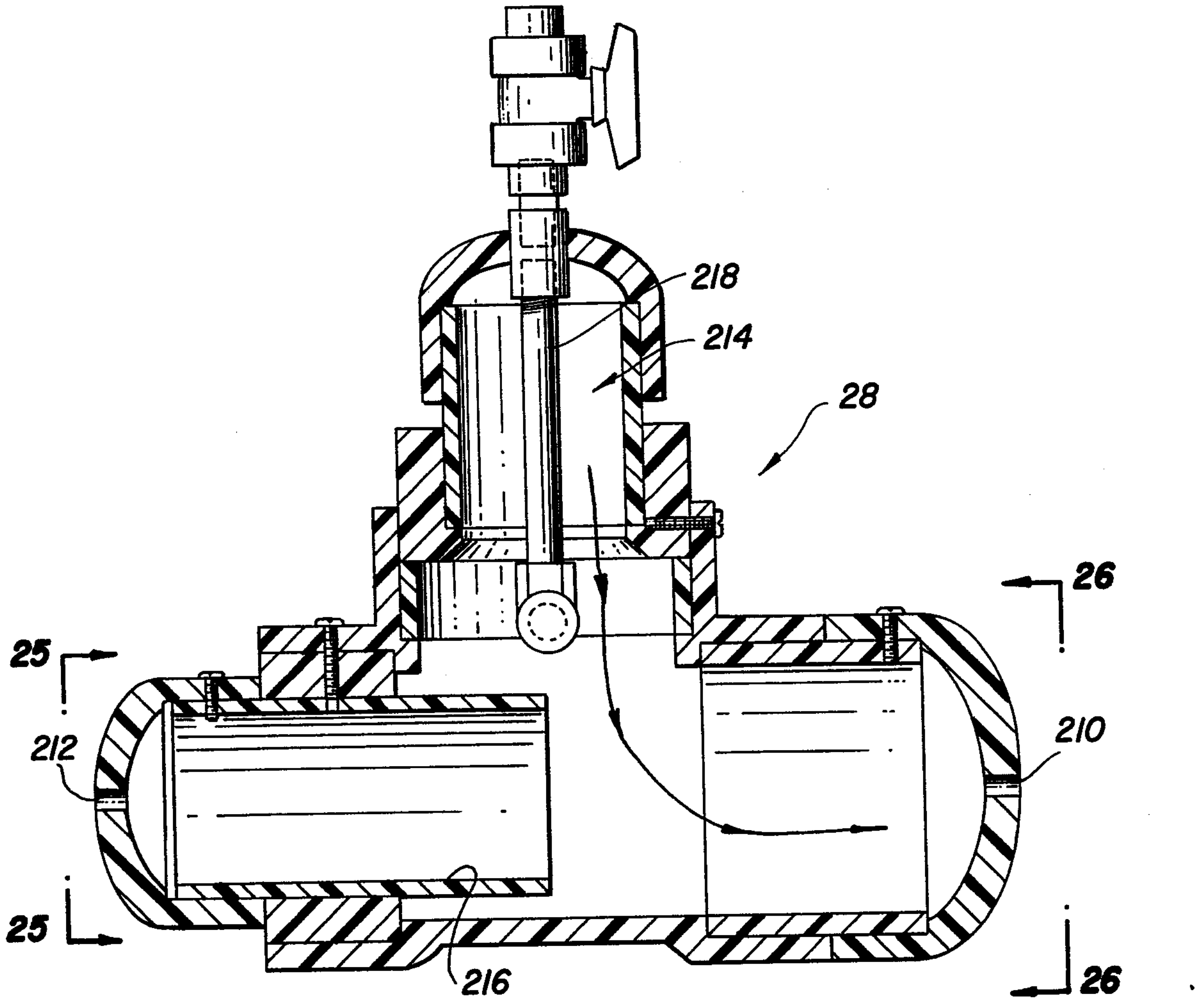

FIG.24

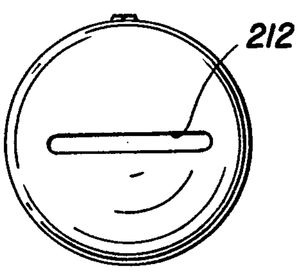

FIG.25

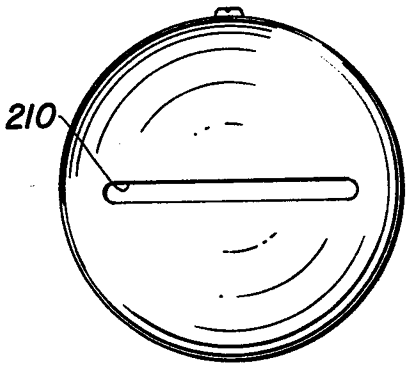

FIG.26

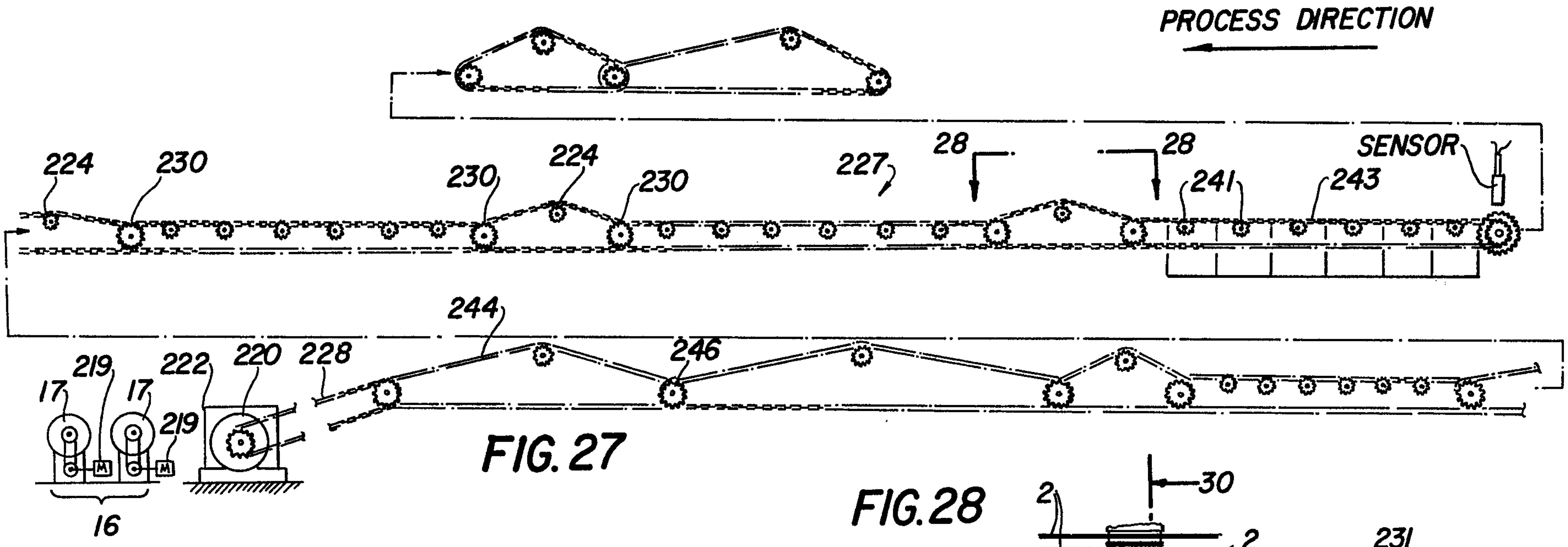

FIG. 27

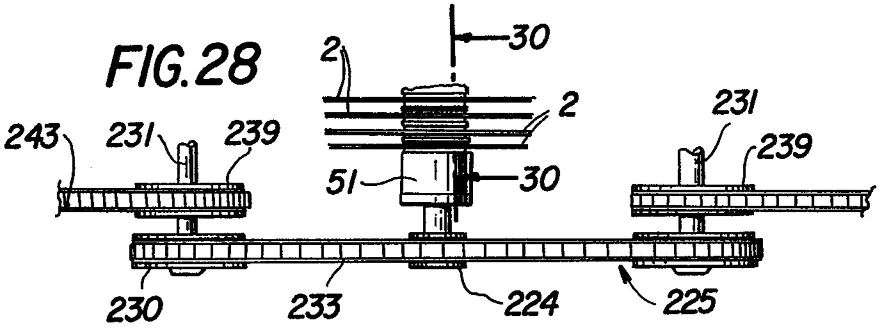

FIG.28

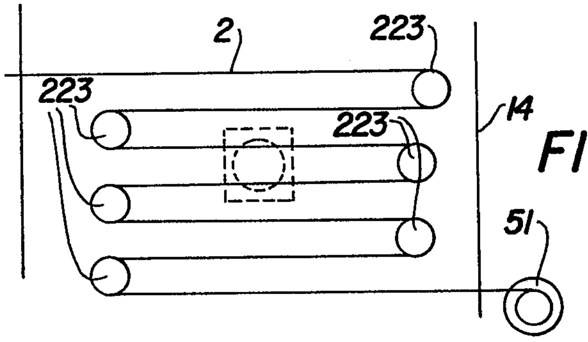

FIG.29

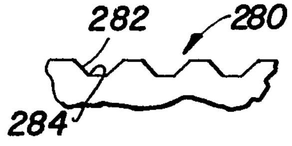

FIG.30

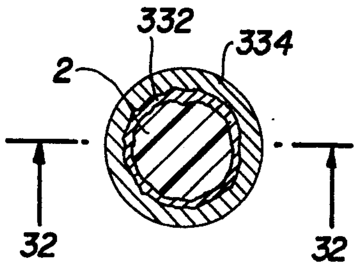

FIG. 31

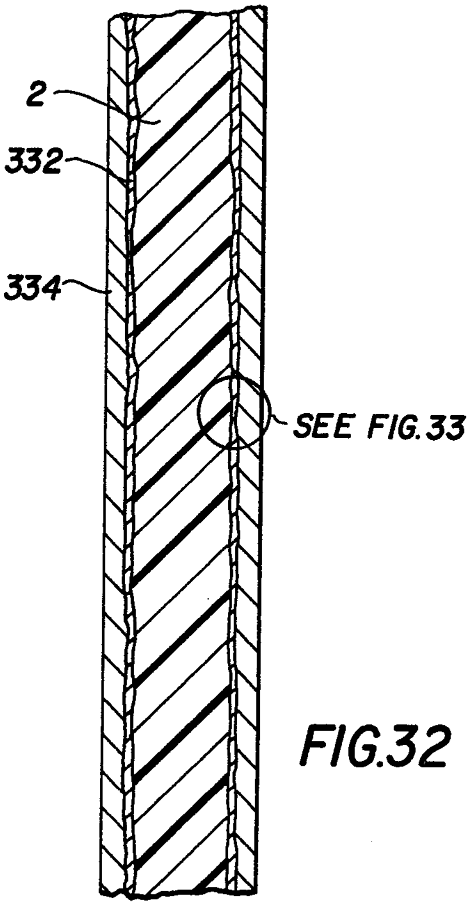

FIG.32

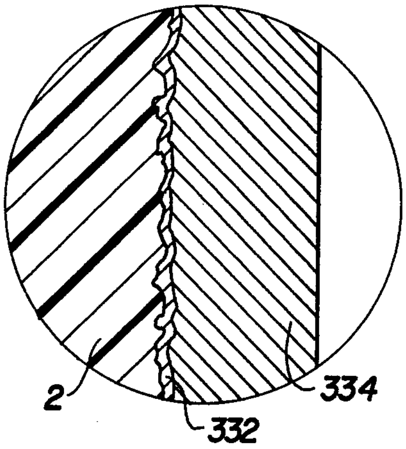

FIG. 33

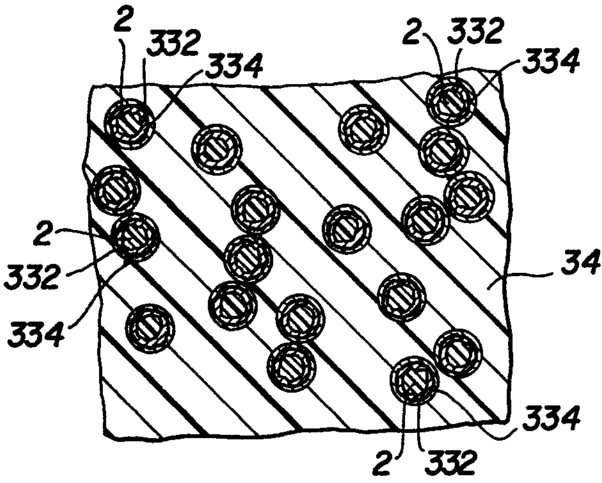
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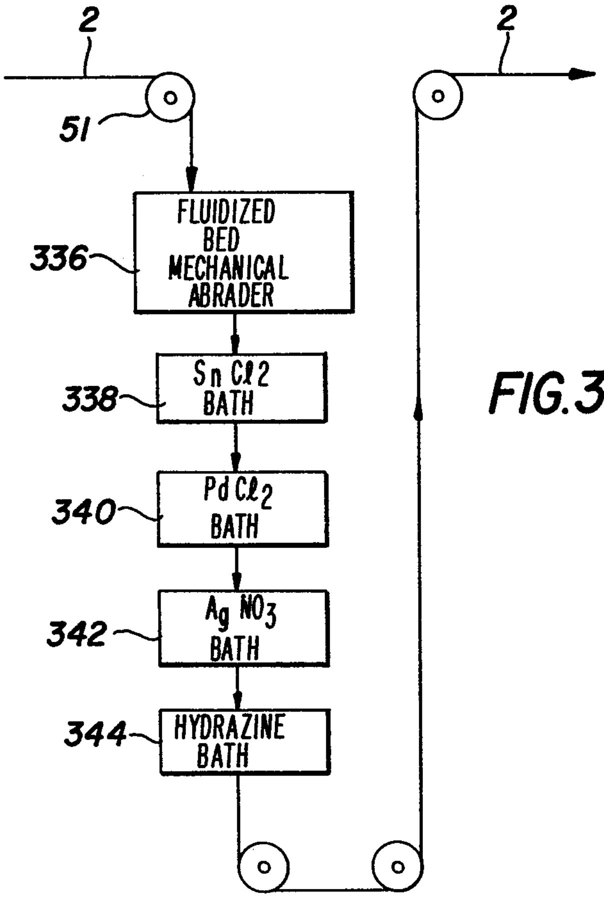
FIG.34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2
51
FLUIDIZED BED MECHANICAL ABRADER
336
$SnCl_2$ BATH
338
$PdCl_2$ BATH
340
$AgNO_3$ BATH
342
HYDRAZINE BATH
344

FIG.35

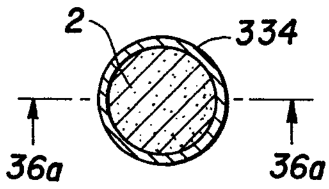

FIG.36

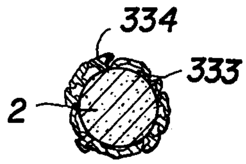

FIG.37

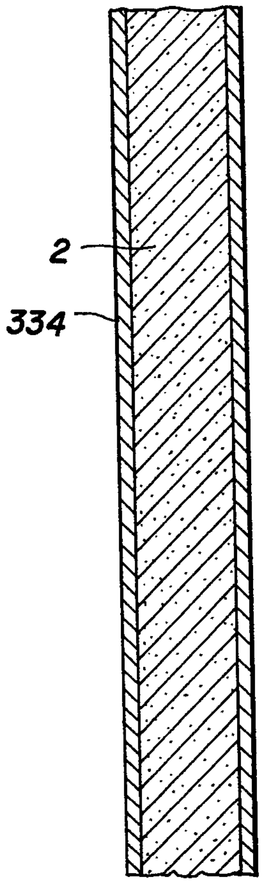

FIG.36a

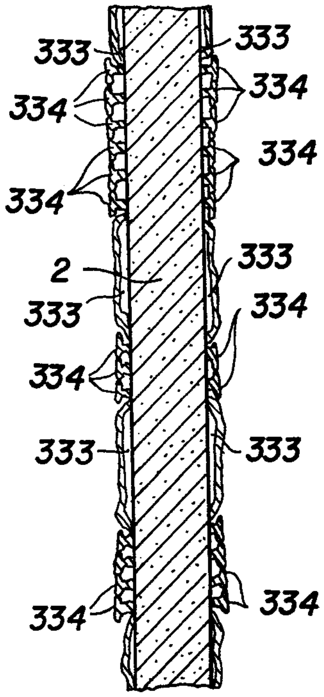

FIG.37a

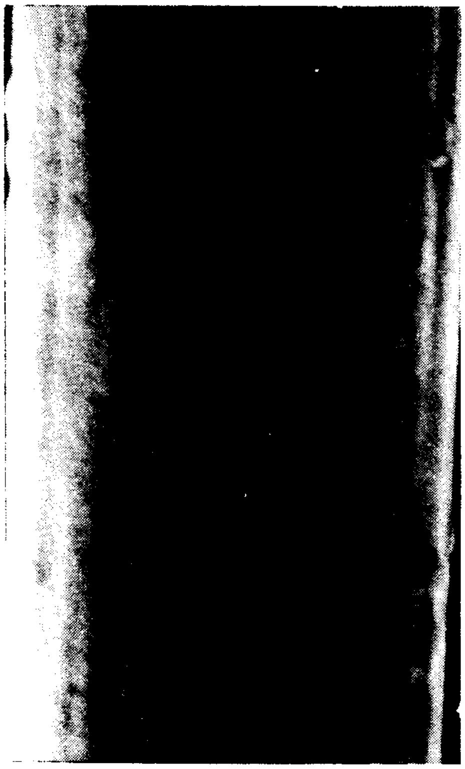

FIG.38

FIG. 39

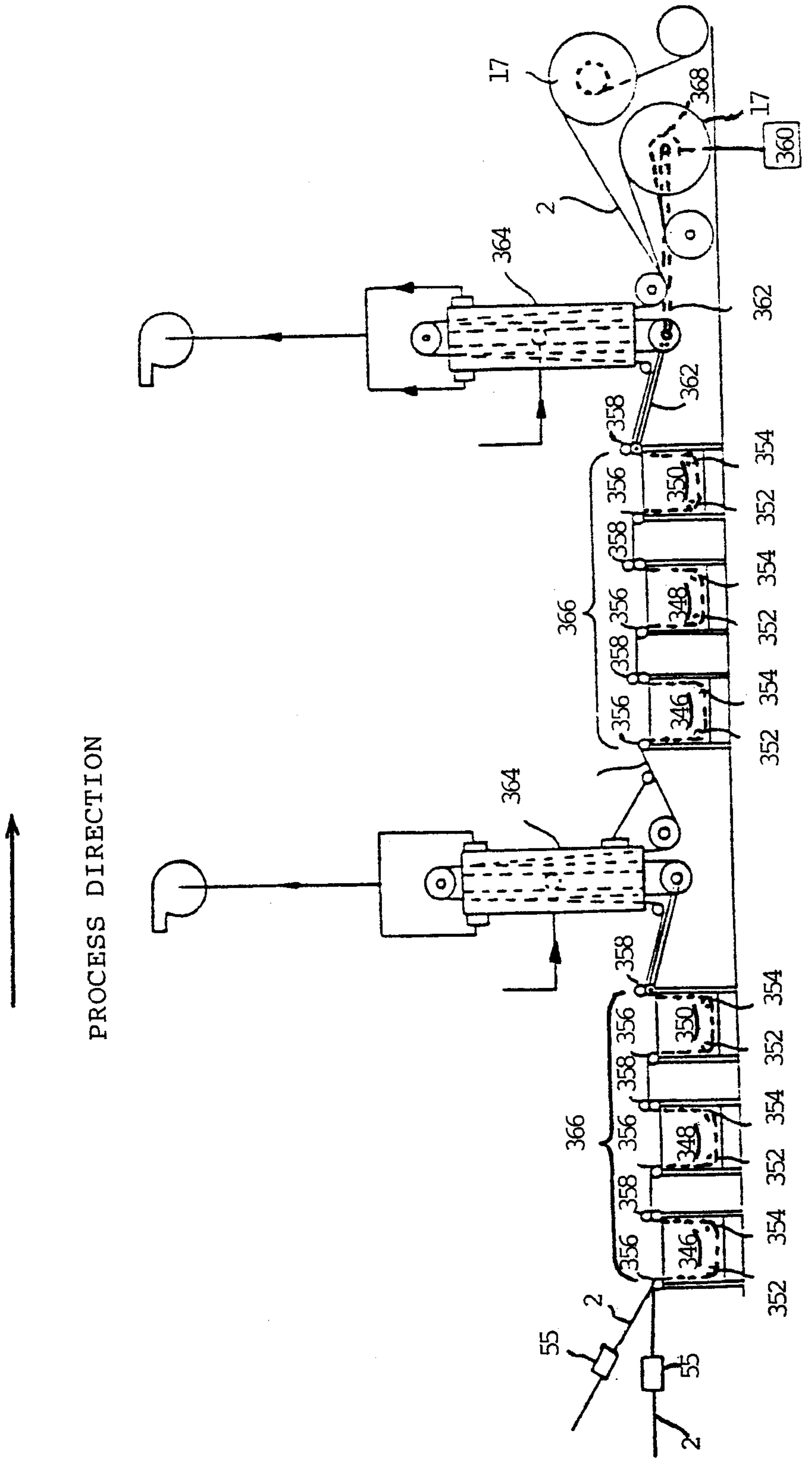
PROCESS DIRECTION
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FIG. 40

European Patent
Office

EUROPEAN SEARCH REPORT

Application number
EP 84107100.4

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Y	DE - A1 - 3 108 380 (TOHO BESLON CO., LTD.) * Claims, especially claim 8; page 10, lines 4-14 * --	1,3,8,9	C 25 D 7/06 C 25 D 5/56 C 25 D 17/02 C 25 D 19/00 D 01 F 11/10
Y	US - A - 3 896 010 (J. VETTER) * Abstract; fig. 1, examples; claims *	1,3,8,9,	
A	* Abstract; fig. 1; examples; claims * --	2,4-7,10	
A	US - A - 4 050 997 (H. HEISSLER et al.) * Abstract; fig.; table; claims * --	1,3,8,9	
A	GB - A - 1 309 252 (INTERNATIONAL RESEARCH & DEVELOPMENT COMPANY LTD.) * Fig. 1; claims * --	1-4,6-10	
A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 6, no. 165, August 28, 1982 THE PATENT OFFICE JAPANESE GOVERNMENT, page 12 C 121 * Kokai-No. 57-79 200 (TOYODA GASEI K.K.) * ----	2,4-6	

TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

C 25 D
D 01 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	31-08-1984	SLAMA

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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