⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 431 237 A1**

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **90104679.7**

㉒ Date of filing: **12.03.90**

(51) Int. Cl.5: **C25D 5/54**, D01F 9/16

㉚ Priority: **04.12.89 US 337199**

(43) Date of publication of application:
12.06.91 Bulletin 91/24

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB IT LI NL SE

(71) Applicant: **AMERICAN CYANAMID COMPANY**
1937 West Main Street P.O. Box 60
Stamford Connecticut 06904-0060(US)

(72) Inventor: **D'Andrea, Gregory**
76 Cedarhurst Lane
Milford,Connecticut 06460(US)
Inventor: **Yahalom, Joseph**
19 Antwerpen Street
Haifa(IT)

(74) Representative: **Wächtershäuser, Günter, Dr.**
Tal 29
W-8000 München 2(DE)

(54) Direct deposition of gold on carbon fiber.

(57) A process is disclosed for the production of metal-coated fibers involving an anodic pretreatment of said fibers in an electrolytic bath wherein a D.C. voltage having a polarity opposite to that normally used to electrolytically deposit metal on said fibers. Subsequent to its pretreatment, the fibers are electroplated in a conventional manner to produce fibers having a thin, uniform metal layer electrodeposited thereon.

EP 0 431 237 A1

BACKGROUND OF THE INVENTION

Bundles of high strength fibers of non-metals and semi-metals, such as carbon, silicon carbide, and the like, in the form of filaments, 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 of lower strength conventional materials such as aluminum, steel, titanium, vinyl polymers, nylons, polyesters, etc., in aircraft, automobiles, office equipment, sporting goods, and in many other fields.

A common problem in the use of such fibers, and also glass, asbestos, and others, is a seeming lack of ability to translate the properties of the high strength fibers to the material to which ultimate and intimate contact is to be made.

The problem is manifested in a variety of ways: for example, if a length of high strength carbon fiber yarn is enclosed lengthwise in the center of a rod formed from solidified molten lead, and the rod is pulled until broken, its breaking strength will be less than expected from the rule of mixtures, and greater than that of a rod formed from lead alone, due to the mechanical entrapment of the fibers. The lack of reinforcement is entirely due to poor translation of strength between the carbon fibers and the lead. The same result occurs if an incompatible high strength fiber is mixed with a plastic material. If some types of carbon fibers, boron fibers, silicon carbide fibers, and the like in the forms of strands, chopped strands, non-woven mats, felts, papers, etc. or woven fabrics are mixed with organic polymeric substances, such as phenolics, styrenics, epoxy resins, polycarbonates, and the like, or mixed into molten metals, such as lead, aluminum, titanium, etc., they merely fill them without providing any reinforcement, and in many cases even cause their physical properties to deteriorate.

All of these problems are generally recognized now, after years of research, to result from the need to insure adequate bonding between the high strength fiber and the so-called matrix material, the metal or plastic sought to be reinforced. It is also known that such bonding can be improved with careful attention to the surface layer on each macro-micro filament or fibril in the material selected for use. Glass filaments, for example, are flame cleaned and then sized with a plastic-compatible organosilane to produce reinforcements uniquely suitable for plastics.

Such techniques do not work well with other fibrous materials and, for obvious reasons, are not suitable for use with carbon fibers, which would not surface texture, and which have different boundary layers.

High strength carbon fibers are made by heating polymeric fiber, e.g. acrylonitrile polymers of co-polymers, in two stages, one to remove volatiles and carbonize and another to convert amorphous carbon into crystalline carbon. During such procedure, it is known that the carbon changes from amorphous to single crystal then orients into fibrils. If the fibers are stretched during graphitization, then high strength fibers are formed. This is critical to the formation of the boundary layer, because as the crystals grow, there are formed high surface energies, as exemplified by incomplete bonds, edge-to-edge stresses, differences in morphology, and the like. It is also known that the new carbon fibrils in this form can scavenge nascent oxygen from the air, and even organic materials, to produce non-carbon surface layers which are firmly and chemically bonded thereto, although some can be removed by solvent treating, and there are some gaps or open spaces in the boundary layers. Not unlike the contaminants or uncleaned, unsized glass filaments, these boundary layers on carbon fibers are mainly responsible for failure to achieve reinforcement with plastics and metals.

Numerous unsuccessful attempts have been reported to provide such filaments, especially carbon filaments, in a form uniquely suitable for reinforcing metals and plastics. Most have involved depositing layers of metals, especially nickel and copper as thin surface layers on the filaments. Such composite fibers were then used in a plastic or metal matrix. The metals in the prior art procedures have been vacuum deposited, electrolessly deposited, and electrolytically deposited, but the resulting composites were not suitable.

Vacuum deposition, e.g., of nickel, as described in U.S. Pat. No. 4,132,828, results in what appears to be a continuous coating, but really isn't upon closer inspection because the vacuum deposited metal first touches the fibrils through spaces in the boundary layers, then grows outwardly like a mushroom, then joins away from the surface, as observed under a scanning electron microscope as nodular nucleation. If the fiber is twisted, such a coating will separate from the core and fall off. The low density non-crystalline deposit limits use.

Electroless nickel baths have been employed to plate such fibers but again there is the same problem, the initial nickel or other electroless metal seeds only small spots through holes in the boundary layer, then new metal grows up like a mushroom and joins into what looks like a continuous coating. It too will fall off when the fiber is twisted. The intermetallic compound is very locally nucleated and this, too, limits its use. In the case of both vacuum deposition and electroless deposition, the strength of the metal-to-core bond is always substantially less than one-tenth that of the tensile strength of the metal deposit itself.

Electroplating with nickel and other metals is also featured in reported attempts to provide carbon fibers with a metal layer to make compatible with metals and plastics, e.g., R. V. Sara, U.S. Pat. No. 3,622,283. Short lengths of carbon fibers were clamped in a battery clip, immersed in an electrolyte, and electroplated with nickel. When the plated fibers were put into a tin metal matrix, the fibers did not translate their strength to the matrix to the extent expected from the rule of mixtures. when fibers produced by such a process are sharply bent, on the compression side of the bend there appear a number of transverse cracks and on the tension side of the bend the metal breaks and flakes off. If the-metal coating is mechanically stripped, and the reverse side is examined under a high-power microscope, there is either no replica or at best only an incomplete replica of the fibril, the replica defined to the 40 angstrom resolution of the scanning electron microscope. The latter two observations are strongly suggestive that failure to reinforce the tin matrix was due to poor bonding between the carbon and the nickel plating. In these cases, the metal-to-core bond strength is no greater than one-half of the tensile strength on at most 10% of the fibers, and substantially less than one-tenth on the remaining 90%.

U.S. Pat. No. 4,661,403, the contents of which are hereby incorporate by reference, is directed to the production of continuous yarns or tows of high strength composite fibers, the majority of which have an electrically conductive semi-metallic core and at least one thin, uniform and firmly adherent, electrically conductive layer of at least one metal on said core. The process with which said yarns and tows are produced involves the application of high voltages sufficient to provide uniform nucleation of the yarns or tow fibrils directly. The yarns and tows produced thereby are said to be superior to those of the prior art because they possess a superior core-to-metal bond which prevents transverse cracking of the metal on the compression side of a bent fibril and breaking or flaking of the metal on the tension side of the bent fibril.

U.S. Pat. No. 4,624,751, the contents of which are also hereby incorporated by reference, is directed to a process and apparatus for metal plating of fibers utilizing an array of tensioning rollers and contact rollers to insure a direct tight path for the fiber during its plating.

It has been discovered that continuous yarns or tows of high strength metal-coated fibers having superior qualities may be produced by subjecting the fibers to an anodic pretreatment prior to their introduction into the traditional plating process.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention may be more readily understood by reference to the accompanying drawings in which:

FIG 1: is a transverse cross sectional view of a metal coated fiber produced in accordance with this invention.

FIG 1a: is a transverse cross sectional view of a metal coated fiber produced in accordance with this invention.

FIG 2: is a view showing an apparatus for carrying out the process of the present invention.

All the drawings represent models of the articles, apparatus and processes described.

SUMMARY OF THE INVENTION

According to the present invention, a process is provided for the production of continuous tows or yarns of high strength metal-coated fibers each of which has a core and at least one thin, uniform, firmly adherent, electrically conductive layer of at least one electrodepositable metal.

The process of the present invention comprises

(a) providing a continuous length of a plurality of electrically conductive semi-metallic fibers;

(b) subjecting said fibers to an anodic pretreatment comprising

(i) immersing at least a portion of the length of said fibers in a first bath containing an electrolyte solution which optionally contains a metal capable of being electrolytically deposited on said length of fiber, and

(ii) applying an external positive D.C. voltage between the fibers and said solution in said first bath,

(c) electrolytically depositing metal upon said fiber by

(i) immersing said length of fiber in a second bath capable of electrolytically depositing at least one metal on said fiber, and

(ii) applying an external negative D.C. voltage between the fibers and said second bath, said D.C. voltage being applied for duration and in an intensity sufficient to affect the electrodeposition of said at least one metal on said fibers.

Other preferred features include carrying out the process with a portion of the solution(s) of said first and/or second bath(s) being recycled into contact with the fibers immediately prior to and subsequent to their immersion in the negative bath(s) so as to cool the fibers, provide increased current carrying capacity to the fibers and replenish the electrolyte on the surface of the fibers.

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIGS. 1 and 1a continuous yarns and tows for use according to the present invention are available from a number of sources commercially. For example, suitable carbon fiber yarns are available from Amoco Performance Products, Hercule Company, Hitco, Great Lakes Carbon Company, AVCO Company and similar sources in the United States, and overseas. All are made, in general, by procedures described in U.S. Pat. No. 3,677,705. The fibers can be long and continuous or they can be short, e.g., 1 to 15 cm. in length. As mentioned above, all such carbon fibers will contain a thin, imperfect boundary layer (not shown) of chemically bonded oxygen and chemically or mechanically bonded other materials, such as organics. Also suitable for use in the present invention are fibers composed of boron and silicon carbide. The use of carbon fibers is preferred.

Metal layer 4 will be of any electrodepositable metal, and it will be electrically continuous. Two layers, or even more, of metal can be applied and metal can be the same of different, as will be shown in the working examples. In any case, the innermost layer will be so firmly bonded to core 2 that sharp bending will neck the metal down snapping the fiber core and breaking the metal on the tension side of the bend when its elastic limit is exceeded. This is accomplished without causing the metal to flake off when broken which is a problem in fibers metal coated according to the prior art. As a further distinction from the prior art, the metal layer of the present invention fills interstices and "cracks" in fibers, uniformly and completely.

Examples of coating metals useful in the practice of the present invention are nickel, silver, zinc, copper, lead, arsenic, cadmium, tin, cobalt, gold, indium, iridium, iron, palladium, platinum, tellurim, tungsten or mixtures thereof. Preferably, the metals are in crystalline form.

The high strength metal coated fibers of this invention can be assembled by conventional means into composites in which matrix 6 is a plastic, e.g., epoxy resin, or a metal, e.g., lead, the matrix being reinforced by virtue of the presence of high strength fibrous cores 2.

Formation of the metal coating layer by the electrodeposition process of this invention can be carried out in a number of ways. For example, a plurality of core fibers can be immersed in an electrolytic bath and through suitable electrical connections the required external voltage can be applied. In one manner of proceeding, a voltage is applied for a short period of time. A pulse generator, for example, will send a surge of voltage through the electrolyte, sufficient to bind the metal ion with the carbon or other fiber comprising the cathode. The short time elapsing in the pulse will prevent heat from building up in the fiber and burning it up or out. Because the fibers are typically so small, e.g., 5 to 10 microns in diameter, and because the innermost fibers are usually surrounded by hundreds or even thousands of other, even though only 0.5 or 2.6 volts are needed to dissociate the electrolytic metal ion, e.g., nickel, gold, silver, copper, depending on the salt used, significantly higher external voltages may be used, on the order of 5 times the dissociation values, to uniformly nucleate the ions through the bundle of fibers into the innermost fibril and then through the boundary layer. External voltages of e.g., 10 to 50, or even more, volts may therefore be supplied. However, voltages on the order of 1-5 volts (sce) may be used. Current densities of 1-100 milliamps/cm^2 should also be employed.

Although pulsing as described above is suitable for small scale operations, for example, to metallize pieces of woven fabrics, and small lengths of carbon fiber yarns or tows, it is preferred to carry out the procedure in a continuous fashion on a moving tow of fibers. If high voltages are used, to overcome the problem of fiber burnout because of the high voltages, (i.e. to keep them cool enough outside the bath), one can separate the fibers and pour water on them, for example, but it is preferred to operate in an apparatus shown schematically in FIG. 2. Electrolytic bath solution 8 is maintained in tank 10. Also included are anode baskets 12 and idler rolls 14 near the bottom of tank 10. Two electrical contact roller 16 are located above the tank. Tow 24 is pulled by means not shown off feed roll 26, over first contact roller 16 down into the bath under idler rolls 14, up through the bath, over second contact roller 16 and into take up roller 28. By way of illustration, the immersed tow length may be about 6 feet. Optional, but very much preferred, is a simple recycle loop comprising pump 18, conduit 20, and feed head 22. This permits recirculating the electroplating solution at a large flow rate, e.g., 2-3 gallons/min. and pumping it onto contact rolls 16. Discharged just above the rolls, the sections of tow 24 and leaving the plating solution are totally bathed, thus cooling them. At the high current carried by the tow, the I^2R heat generated in some cases might destroy them before it reachs or after it leaves the bath surface without such cooling. The flow of the electrolyte overcomes anisotropy. Of course, more than one plating bath can be used in series, and the fibers can be rinsed free of electrolyte solution, treated with other conventional materials and dried, chopped, woven into fabric, all in accordance with conventional procedures.

In accordance with the present invention, the fibers of tow 24 are subjected to an anodic pretreatment process prior to their introduction into the plating bath. Such anodic pretreatment process comprises the application to the tow of a positive D.C. current during which time it is introduced into at least one electrolytic bath to which has been applied a negative D.C. current. Basically, the anodic pretreatment process and the apparatus associated therewith is identical to the process and apparatus used in the electrolytic plating of the tow, except that the polarity of the applied D.C. current is reversed.

The voltage applied to the tow in the anodic pretreatment process generally ranges from about 1 to about 10 volts although higher voltage can be applied. Preferably, the voltages employed ranges from about 1 to about 5 volts. Current densities of about 1 to about 100 millamps/cm^2 are preferably used.

While the electrolytic bath used in the anodic pretreatment process of the present invention may contain a solution different from that contained in the bath electroplating process it is preferred that similar solutions, perhaps differing only in the concentration of their respective components, are used in both baths 10 and 10A. Most preferably, baths 10 and 10A contain identical solutions.

As an example of the anodic pretreatment process used in the present invention, a schematic representation of apparatus used to carry out the process is set forth in Figure 2.

Electrolytic bath solution 8A is maintained in tank 10A. Also included are cathode/baskets 12A and idler roller 14A near the bottom of tank 10A. Two electrical contact roller 16A are located above the tank. Tow 24 is pulled by means not shown off feed roller 26 over contact roller 16A down into the bath under idler rolls 14A, up through the bath, over second contact roller 16A and into bath 10 by way of contact roller 16. Optional, but very much preferred, is a simple recycle loop comprising pump 18A, conduit 20 A, and feed head 22A. This also permits recirculating the plating solution at a large flow rate, e.g. 2-3 gallons/min. and pumping it onto contact rolls 16A. Discharged just above the rolls, the sections of tow 24 and leaving the plating solution are totally bathed, thus cooling them. If high currents are carried by the tow, the I^2R heat generated in some cases might destroy them before they reach or after they leave the bath surface without such cooling. The flow of the electrolyte overcomes anisotropy. A serial array of more than one anodic pretreatment bath can also be used.

It has been noted that superior results are achieved in the practice od the present invention by limiting the time of fiber immersion in the anodic pretreatment bath to under 60 seconds. Preferably, this time is limited to between about 1 and about 20 seconds. To achieve this reduced immersion time, the path of fiber travel in the pretreatment bath may need to be modified relative to the schematic representation shown in Figure 2. Specifically, the vertical fiber travel between rollers 16A and 14A may require reduction. Alternatively, at least one roller 14A can optionally be eliminated so long as provisions are made to ensure that fiber 24 achieves complete immersion in the bath during its travel between contact rollers 16A.

It has further been noted that fibers having superior properties are produced if the elapsed time between anodic treatment and electroplating is reduced. In the practice of the present invention as a continuous process, this requires that the distance between the preteatment bath and the electroplating bath be minimized.

EXAMPLES

The following Example illustrates the present invention, but is not intended to limit it.

EXAMPLE 1

In a continuous electroplating system, bath 10 and 10A are provided with solutions having the following composition:

Ingredient	Amount
nickel sulfate ($NiSO_4$-$6H_2O$)	40 ounces/gallon
nickel chloride ($NiCl_2$-$6H_2O$)	12-20 ounces/gallon
boric acid (H_3BO_3)	5-8 ounces/gallon
wetting agent (WA-129, State Chemical)	2% by volume
brightener (Starlite 915, State Chemical)	2% by volume

The solutions of baths 10 and 10A are heated to 140°-160° F. and each has a pH of 3.8-4.2.

The cathode baskets 12A in bath 10A are filled with nickel pellets and 4 tows of 12,000 strand each of 7 micron carbon fibers are continuously drawn through bath 10A while an external voltage of 30 volts is applied at a current adjusted to give 10 ampere-minute per 1000 strands total. At the same time, electrolytic solution is recycled through conduit 20A and head 22A so as to contact the tow as it passes over rollers 16A. A tow speed of 5.0 ft./min is used. After the tow exits the anodic pretreatment process, it proceeds on to the electroplating apparatus.

The anode baskets in bath 10 are kept filled with electrolytic nickel pellets and 4 tows (fiber bundles) of 12,000 strands each of 7 micron carbon fibers are continuously drawn through the bath while an external voltage of 30 volts is applied at a current adjusted to give 10 ampere-minutes per 1000 strands total. At the same time, electrolytic solution is recycled through conduit 20 and head 22 so as to contact the tows as it passes over rollers 16. The tow is next passed continuously through an identical bath, at a tow speed of 5.0 ft./min. with 180 amps. current in each bath. The final product is a tow of high strength composite fibers according to this invention comprising of 7 micron fiber core and about 50% by weight of the composite of crystalline electrodeposited nickel adhered firmly to the core.

If a length of the fiber so produced is sharply bent, then examined, there is no circumferential cracking on the metal coating in the tension side of the bend. The tow can be twisted and knotted without causing the coating to flake or come off. If a section of the coating is mechanically stripped from the fibrils, there will be a perfect reverse image (replica) on the reverse side.

Claims

1. A process for the production of continuous yarns or tows of metal-coated fibers, said process comprising:
   (a) providing a continuous length of a plurality of electrically conductive semi-metallic fibers;
   (b) subjecting said fibers to an anodic pretreatment comprising
   (i) immersing at least a portion of the length of said fibers in a first bath containing an electrolyte solution which optionally contains a metal capable of being electrolytically deposited on said length of fiber, and
   (ii) applying an external positive D.C. voltage between the fibers and said said solution in said first bath;
   (c) electrolytically depositing metal upon said fiber by
   (i) immersing said length of fiber in a second bath capable of electrolytically depositing at least one metal on said fiber, and
   (ii) applying an external positive D.C. voltage between the fibers and said solution in said second bath, said D.C. voltage being applied for a duration and in an intensity sufficient to affect the electrodeposition of said at least one metal on said fibers is promoted and opposite to the that applied to said fibers during the anodic pretreatment step (b).

2. The process of Claim 1 wherein the semi-metallic fibers are selected from the group of carbon fibers, boron fibers and silicon carbide fibers.

3. The process of Claim 1 wherein the semi-metallic fibers comprise carbon fibers.

4. The process of Claim 1 wherein the metal is selected from the group consisting of nickel, silver, zinc, copper, lead, arsenic, cadmium, tin, cobalt, gold, indium, iridium, iron, palladium, platinum, tellurium, tungsten or mixtures thereof.

5. The process of Claim 1 wherein the metal is selected from the group consisting of gold and copper, and the semi-metallic comprise carbon fibers.

6. The process of Claim 1 wherein said first and second baths contain substantially identical plating solutions.

7. The process of Claim 1 wherein the external D.C. voltage used in step (b) has a value of from about 1 to about 5 volts.

8. The process of Claim 1 wherein the current density used in step (b) has a value of from about 1 to about 100 milliamps/cm^2.

9. The process of Claim 1 wherein the external D.C. voltage used in step (c) has a value of from about 1 to about 50 volts.

10. The process of Claim 1 wherein the external D.C. voltage used in step (c) has a value of from about 1 to about 5 volts.

11. The process of Claim 1 wherein the solution of said first bath is recycled during step (b) such that it contacts the fibers while said fibers are not immersed in said first bath during the application of said external voltage.

12. The process of Claim 1 wherein the solution of said second bath is recycled during step (c) such that it contacts the fibers while said fibers are not immersed in said second bath during the application of said external voltage.

13. The product produced by the process of Claim 1.

14. In a process for the production of continuous metal-coated fibers through the electrolytic deposition of metal on continuous semi-metallic fibers, the improvement comprising:

subjecting said semi-metallic fibers to an anodic pretreatment prior to the electrolytic deposition of metal thereon, said anodic pretreatment comprising

(i) immersing at least a portion of the length of said fibers in a first bath containing an electrolyte solution which optionally contains a metal capable of being electrolytically deposited said length of fiber, and

(ii) applying an external positive D.C. voltage between the fibers and said solution in said first bath.

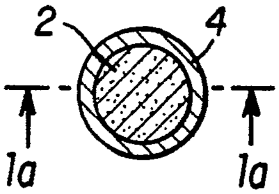

FIG. 1

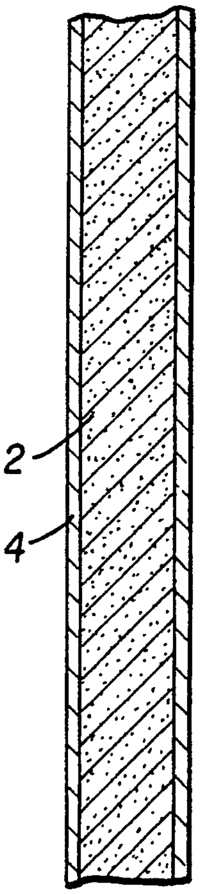

FIG. 1a

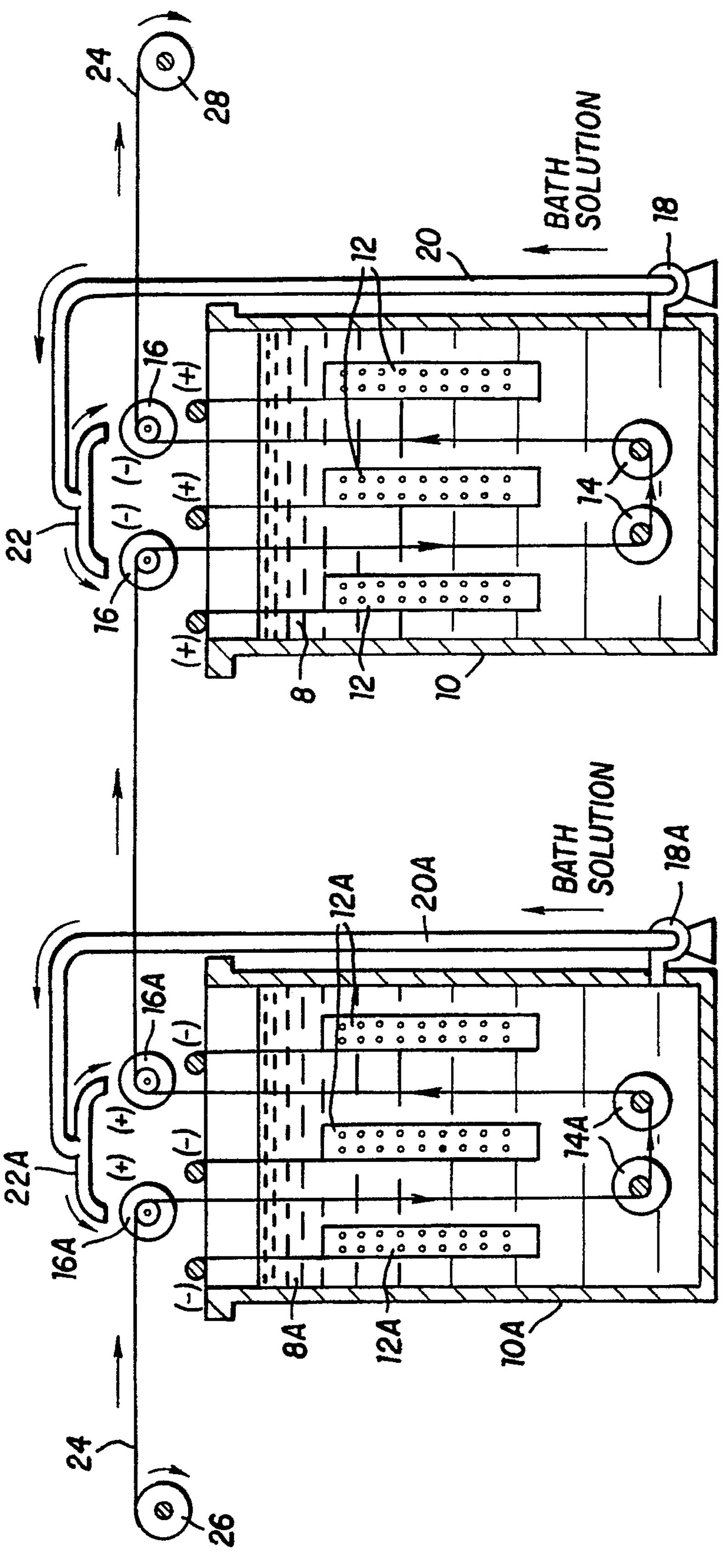
24
28
BATH SOLUTION
18
20
12
16
(+)
(-)
(-)
(+)
(-)
22
16
14
(+)
8
12
10
BATH SOLUTION
18A
20A
12A
16A
(-)
(+)
(-)
(+)
22A
16A
14A
(-)
8A
12A
10A
24
26

FIG. 2

European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 10 4679

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.5)
X	DERWENT WPI, accession no. 77-15976Y [09], Derwent Publications Ltd, London, GB; & SU-A-496 331 (AMLA) – – – – –	1-3,6,13, 14	C 25 D 5/54 D 01 F 9/16

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C 25 D 5/54 C 25 D 5/56 D 01 F 9/16

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	26 February 91	VAN LEEUWEN R.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same catagory
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention

E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document