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(54) **AN ARRANGEMENT FOR THE ELECTRODEPOSITION OF METAL ON CARBON NANOTUBE FIBRE**

(57) The invention relates to an arrangement for producing an electrically-conductive composite wire in which metal is deposited onto and within a fibre composed of a multiplicity of carbon nanotubes and in which the metal deposition is produced by electrolysis.

According the invention, the carbon nanotube fibre is the cathode and more than one anode (4) is employed.

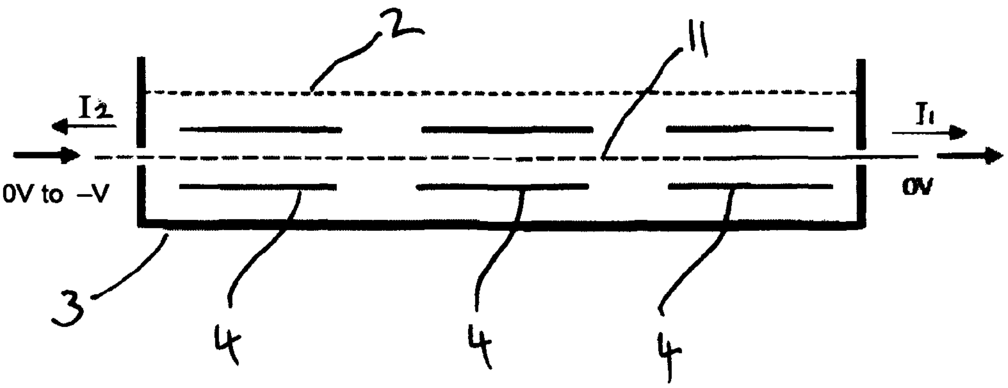


Figure 5

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## Description

**[0001]** Carbon nanotube wire or fibre consists of a multitude of carbon nanotubes (CNTs) combined to make a filament the length of which is many times the diameter of the individual CNTs. The diameter of the individual CNTs is typical of the order of 1 to 2 nanometers. Multi-walled CNTs have a larger diameter. The length of the CNTs is usually many times (e.g. hundreds of thousands or millions time longer than their diameter). CNTs can be formed into fibres of indefinite length since Van Der Waals forces will hold the CNTs together. A fibre with a diameter of the order of 10 micrometers is practical. In addition, fibres of greater diameter can be created either by spinning together multiple fibres or by creating a film of fibres and rolling it into a yarn or cord. There are various ways to create CNT fibre, yarns and ropes using single-wall or multi-wall carbon nanotubes. Hereinafter, all are referred to as CNT fibres.

**[0002]** CNT fibre is electrically conductive. Electrical contact is made between individual CNTs when they make physical contact. There are typically multiple contacts between the CNTs in a fibre. Twisting the fibre forces CNTs together and increases the number of contacts. Electrons can cross from one fibre to another. Typically this occurs by electron tunnelling across the small vacuum between the atoms of the sidewalls of the participating CNTs. A voltage is associated with maintaining a flow of electrons between CNTs by this process. Dividing this voltage by the current transferred give the so-called tunneling resistance. Current flow through the individual CNTs may be ballistic (involving only elastic collisions between the electrons and the CNT structure) and diffusive conduction, in which inelastic collisions occur. In addition there is a quantum of resistance associated with the transfer of an electron from the threedimensional world to doubly-confined one-dimensional conduction in the CNT. The result of these effects is that the CNT fibre, with is many interconnections between the CNTS which constitute it, has the characteristic of a conductor that is approximately Ohmic.

**[0003]** The following discussion and description describes the electroplating of CNT fibre and methods pertaining thereto. The description focusses on the deposition of copper but a person skilled in the art of electrochemistry will understand that this process is adaptable to the depositing of other metals. Hence the invention is not limited to the deposition of copper alone. The process may also be enhanced by preparation of the CNT fibre by an alternative deposition process of copper or another metal or by anodising.

**[0004]** A number of attempts have been made to produce a composite conductor material consisting of a mixture of CNTs and copper. The aim is to create a composite material which will have an acceptable conductivity and other useful properties. When the goal is to create a composite wire with a greater conductivity than copper, this composite is sometimes called Ultra-Conductive Copper or UCC. When a general term is needed (independent of the production method or final attributes) we refer to it hereinafter as "Cu-CNT composite". The copper employed in the Cu-CNT composite can provide more connection paths between the CNTs and hence may lower the resistance of the composite to below that of fibre employing CNTs alone.

**[0005]** The present invention relates to a method of producing the Cu-CNT composite in which CNT fibre and the CNTs of which it is composed are fully or partially plated with copper (or another metal) by electrolysis and the space between plated fibres is also fully or partially filled with copper (or another metal). This material is hereinafter referred to as "plated fibre" for convenience. Plating in the context of the Cu-CNT composite means plating means any form of deposition of metal in or on the CNT fibre including deposition of metal in or on the individual CNTs.

**[0006]** The invention addresses the problems which occur when CNT fibre is plated, rather than highly conductive metal wire. We first describe the process for plating highly conductive metal wire.

**[0007]** In a typical continuous wire plating process, such as is shown in side view in Figure 1, the wire 1, which is being plated, moves through a bath of electrolyte 2 contained in a tank 3. The wire 1 is surrounded by an anode 4. The anode 4 is made positive with respect to the wire 1 which forms the cathode in the electrolytic process which deposits copper (if that is the metal to be deposited) on the wire 1. The electrolyte 2 is typically a mixture of copper sulphate and sulphuric acid held at a suitable temperature by heaters in the electrolyte circuit (not shown). The anode 4 may be a tube or parallel plates or some other convenient arrangement of plates. In Figure 1 horizontal plates are implied though vertical plates may be more convenient. The wire to be plated is stored on the input side by, for example, being rolled onto a conductive drum 5 . The plated wire is collected on a second conductive drum 6. The conductive drums 5 and 6 are held at a potential of 0V (the cathode potential) and the anode 4 is made positive with respect to 0V via an external dc power supply (not shown). Current flowing from the anode 4 to the wire 1 (the cathode) causes copper to be deposited on the wire 1. Current entering the wire 1 flows along the wire and is collected by the conducting drums 5 and 6 and returned to the external power supply which holds the anode 4 positive and which supplies it with the necessary current. The wire passes through holes 7 in the tank. Electrolyte which leaks through these holes 7 is collected and pumped back into the tank 3.

**[0008]** Figure 2 shows an alternative method of passing the wire through the electrolyte bath which avoids electrolyte leaking from the tank. The delivery drum 5 and take-up drum 6 are above the level of the electrolyte 2. The wire 1 passes over conductive guides 8 and 9 which are held at 0V. The guides 8 and 9 may be rollers or non-rotating guides over which the wire slides. It is the function of the guides to collect current from the wire. The drums 5 and 6 may be conductive or non-conductive. If they are conductive they may be held at 0V and aid in the current collection process if necessary (for example in the case of a transient poor contact between the guides 8 or 9 and the wire 1). The guides 8 and 9 may need to be shrouded to some extent to reduce current entering them from the anodes 4 via the electrolyte 2. It may be convenient to collect current from the fibre 1 at an intermediate point between the guides 8 and 9 using one or more additional guides at 0V or some other potential though friction with the semi-plated fibre may not be desirable and to maintain physical contact the direction of the fibre may need to be changed each time it passes over a guide. Process activities may take place outside the tank before the fibre enters the tank (for example, some form of preparation process) and after the fibre exits the tank (for example a washing process). In these cases, it may not be convenient to use the conductive drum method of making electrical contact with the fibre and the use of conductive guides may be preferred with the conductive guides being either in the tank or outside of the tank.

**[0009]** The description that follows will use the arrangement of Figure 1 but a person skilled in the art will understand that a variety of physical arrangements for passing the wire (or fibre) through the anode tunnel or plating zones are possible.

**[0010]** Figure 3 shows an anode design which facilitates loading of the wire or fibre to be plated. The anode 3 is a metal channel open at the top, permitting the wire 1 or a fibre to be lowered into place.

**[0011]** During the electrolysis process described above, copper (if that is the metal to be deposited) is removed from the electrolyte and deposited on the wire 1 thus tending to reduce the concentration of copper sulphate. For a continuous process, the concentration of copper sulphate must be maintained constant. This is typically achieved by continually removing a stream of electrolyte 2 from the tank 3 and raising the concentration of copper sulphate in this electrolyte stream before returning it to the tank 3. The anodes 4 are made of an inert conductive metal (for example lead or titanium coated with material which enhances performance). The anodes 4 are not dissolved and oxygen is evolved at the anodes 4. The voltage applied to the anode 4 relative to the wire 1 in this process is of the order of 2.1 Volts.

**[0012]** Alternatively the anodes 4 may be made of copper (if that is the metal to be deposited). In this case the anodes 4 are dissolved by the electrolysis process thus refreshing the copper sulphate concentration so that it is not necessary to refresh the electrolyte via an external electrolyte circuit though such a circuit may still be used for the purpose of controlling the copper concentration. Oxygen is not evolved at the anodes 4. The voltage between the anodes 4 and the wire 1 (cathode) in this process is of the order of 0.2 Volts. The inconvenience of this process is that the anodes have to be replaced periodically. In the following description of the process and the invention, we assume that the first process described above (inert anodes, copper sulphate concentration restored externally, anode-cathode voltage about 2.1 Volts, oxygen evolution at the anodes) is the one in use.

**[0013]** The plating process uses a certain current density at the surface of the wire 1. This current density is chosen to obtain a good quality of plated copper. If too high a current density is employed, problems arise with the plating process. For a given current density, the amount of copper plated is related to the time during which any particular part of the wire surface is exposed to this current density. The plating time is proportional to the length of the anode tunnel and inversely proportional to the speed at which the fibre moves though the anode tunnel. If the anode tunnel length is short, the fibre has to move very slowly through the tunnel.

**[0014]** We now describe the plating of CNT fibre and identify the problems that the invention solves.

**[0015]** The plating of CNT fibre is complicated by the resistance per unit length of the fibre usually being greater than that of pure metal wire of the same diameter. The problems this creates are now explained by reference to Figure 4. A CNT fibre 11 enters the tank 3 at the left hand side and passes through the electrolyte 2 becoming plated as it progresses. The large arrows at each end of the tank 3 indicate the direction of fibre travel. The fibre exiting the tank 3 on the right hand side is at a voltage of 0V because it is being taken up on a conductive drum at 0V (not shown). The delivery drum to the left hand side of the tank 3 is for this present argument assumed to be nonconducting. It is assumed that an initialisation process has been completed and the production process has stabilised with the fibre 11 moving through the process at a constant speed. The fibre exiting the tank 3 at the right hand side has been plated and is more conductive than the unplated fibre entering the tank 3 on the left-hand side. The electrical conductivity of the fibre increases as it passes through the tank from left to right. The unplated fibre is fed into the tank 3 at the left from a conductive delivery drum (not shown) which we will initially assume to be not connected (electrically floating).

**[0016]** A varying voltage exists along the fibre 11, with the voltage being 0V at the right hand side of the tank 3 and becoming progressively more positive towards the left hand end of the tank 3. The current which the fibre 11 carries is greatest in that portion of the fibre 11 which is nearest the right hand side since it carries all the current accrued from the anode. Less current is carried by the fibre 11 at sites further to the left of the tank since less anode current has accrued. The voltage change over a short section of the fibre 11 at any location along the fibre 11 is given by the product of the current flowing in the fibre 11 at that location multiplied by the resistance of the section. The resistance per unit length of the fibre 11 is highest at the left side of the tank 3 and lowest at the right hand side of the tank 3. A graph of voltage at any point along the fibre 11 versus the distance from one end of the tank 3 is therefore difficult to predict or calculate. However, experience has shown that there arises a very short plating zone 12 where to the right there is highly-conductive, well-plated fibre and to the left there is CNT fibre with very little plating. This is because the anode voltage is held to approximately 2.1V (with respect to 0V) to ensure that the plating taking place on the already well plated fibre is at a current density which produces a copper deposition of good quality and without hydrogen evolution. The voltage of the fibre 11 to the left of the plating zone will be at voltage significantly greater than 0V because of the voltage drop along the unplated or lightly plated fibre due to cathode current flowing through this section of the fibre. The voltage difference between the anode and cathode it therefore significantly reduced in this section. Since little current can flow between anode and cathode when the voltage difference is below 1.5V, plating practically does not occur to the left of the plating zone. The plating zone 12 is indicated by a change from the fibre being represented by a dashed (broken) line, for unplated or lightly plated fibre, to a solid line for well plated fibre. (This convention is followed in later diagrams, even when multi-anode arrangements are used and the plating zone has been extended by the use of these multiple anodes). The plating zone has been found to be very short. Since the zone is short, and in order to achieve the required plating thickness (or deposition of copper on and within the CNT fibre), the fibre 11 has to move slowly. This means a very poor rate of production for a given equipment size and cost.

**[0017]** The following calculation demonstrates that there are significant gains in productivity to be made by lengthening the plating zone.

**[0018]** It is required to deposit a certain weight of copper per unit length of fibre.

**[0019]** Let this be W. Then:

$$W = L \times J \times T \times K$$

where L is the length of the plating zone, J is the average current density in the plating zone, T is the time any point in the fibre spends in the plating zone, and K is a constant.

$$T = L / S$$

where S is the speed of the fibre through the plating line.

**[0020]** Hence

$$W = L \times J \times K \times L / S$$

**[0021]** And

$$S = L^2 \times J \times K / W = L^2 \times J \times K_1$$

where $K_1$ is constant when J and W are constant.

**[0022]** Hence, for a given current density, the speed with which plated fibre is produced is proportional to the square of the plating zone length. This shows why the invention is particularly effective at increasing the speed of production in a CNT fibre plating line.

**[0023]** One way in which some lengthening of the plating can be achieved is by drawing current away from the plating zone in the opposite direction to that discussed to this point. That is achieved by connecting the delivery drum (now conductive) on the left hand side of the tank either to 0V or to a negative voltage source. The use of a negative source will lower the voltage of the fibre on the left hand side of the plating zone and promote plating in that region. However, if the voltage difference between the anode and the cathode becomes much greater than 2.1V the current density will be unacceptably high for good deposition of copper and hydrogen evolution may occur so that in practice this approach has limited effectiveness. Hence a more effective way of lengthening the plating zone is required although some current extraction via the conductive delivery drum may be used to good effect.

**[0024]** The invention overcomes the difficulty experienced in conventional plating practice (with a single anode) whereby the high resistance of the CNT fibre produces a short plating zone and precludes the use of long anode tunnel lengths and hence limits the production rate of plated fibre. In the invention multiple anode sections are employed, with each anode section driven electrically be independent current sources. The plating tunnel is therefore made up of a two or more anode sections. The voltage of each anode section with respect to a common 0V rail may vary independently. The anodes will typically be sourced from a power supply which is operated in the controlled-current mode. Each anode will assume a voltage with respect to 0V so that the voltage of the anode with respect to that of the fibre passing through it is of such that the required current density will be applied to the fibre passing through it. The length of each anode section will typically be set so that the current density at the fibre surface along the anode section does not vary too greatly due to voltage variation along the fibre that is being plated. The total plating tunnel length is unrestricted and consequently the speed of the fibre being plated may be of any convenient value and is not limited by the short plating zone problem that arises in single anode arrangements.

**[0025]** A further aspect of the invention is the management of electrical currents which may flow through the electrolyte between adjacent anodes due to adjacent anodes being at different voltages (with respect to the 0V reference). These currents can cause power loss and reduce the efficiency of the plating process. The inventor has realised that the leakage currents may be minimised by placing insulating separators across the tank containing the electrolyte between anode sections. The fibre to be plated passes through a small hole 22 in each insulating separator as shown in Figure 7. Some current can pass between anodes though the electrolyte in each section and thus through the hole 22 in the separator. However, if the hole 22 is suitably small, this current will be sufficiently small so as not to produce significant power loss or disturbance of the plating process. An alternative to using insulating separators is to leave a large space (distance) between anodes. However, this would increase the length of the plating tank and increase plant costs.

**[0026]** For easy loading of the fibre, a slot 23 may be used instead of a hole as shown in Figure 8. Some electrolyte flow through the tank may be required to permit refreshing of the electrolyte. Electrolyte may flow through the hole or slot of the separators illustrated in Figure 7 and Figure 8. Alternatively electrolyte may flow over the top of the separator as in a weir. A pump is needed to return electrolyte from the last section of the tank back to the first section of the tank (or, for example, from the ends of the tank to the centre).

**[0027]** The anode current employed in any section may be selected on the basis of the location of the anode in the series of anodes through which the fibre passes. For example, it may be necessary to apply high current density in the early stages of the plating process and a lower current density later in the process or vice versa.

**[0028]** A further aspect of the invention is that the average current densities employed in each anode section may be different and may be adjusted during operation in response to some measured variable. It is likely that the ideal current density employed in each anode section will be related to the amount of plating already deposited on the fibre in that zone. The state of plating of the fibre in any particular section may be determined, for example, by measuring the change in anode voltage produced in response to a step change in anode current.

**[0029]** While the above process is described with reference to copper deposition, the invention is not limited to the deposition of copper and other metals suitable for electrolytic deposition may be employed.

**[0030]** The present invention will further be described, by way of example, with reference to the accompanying drawings , in which:

Figure 1 shows a simple plating line with a single anode tunnel and with fibre feed through the tank wall.

Figure 2 shows a simple plating line with a single anode tunnel and with fibre feed from an external drum and take-up on an external drum.

Figure 3 shows a cross section of an anode tunnel in which an anode open one side is employed to facilitate loading of the fibre.

Figure 4 shows a simple plating line with a single anode and a restricted plating zone.

Figure 5 shows a plating line with multiple anodes.

Figure 6 shows a plating line with multiple anodes and separators between anode sections.

Figure 7 shows a separator with the fibre passing through a hole.

Figure 8 shows a separator with the fibre passing through a slot.

Figure 9 shows a plating line with multiple anodes, with each anode provided with electrical current from a separate current source.

Figure 10 shows a plating line with multiple anodes, with each anode provided with electrical current from separate regulators which derive current from a single voltage source.

Figure 11 shows the cross section of a plating line with multiple fibres passing between anode plates.

Figure 12 shows a multiple anode plating line with one electrode being used to anodise the fibre.

**[0031]** Figure 5 shows a plating line with multiple anodes 4 according the invention. The currents entering the fibre undergoing plating 11 are drawn off in the first case to the conductive take-up drum on the right hand side giving rise to cathode current I1 which is circulated back to the power supply or power supplies (converter or converters) which supply the anode currents. The take-up drum is assigned a voltage of 0V. The conductive delivery drum at the left-hand side of the tank may also draw cathode current I2 from the fibre by being connected to 0V. To enhance current flow in this direction, the delivery drum may be made negative with respect to 0V. Alternatively, the delivery drum may be left floating (not connected electrically or made of a nonconductive material) in which case I2 is forced to be zero. The above three conditions will give rise to varying conditions of voltage distribution along the fibre. A purpose of connecting the delivery drum to 0V or a more negative voltage will be to reduce the rise of voltage along the fibre. The advantage of reducing the voltage rise along the fibre is that the voltage difference between anodes will be less and hence there will be lower parasitic currents flowing through the electrolyte between anodes.

**[0032]** In Figure 5, the anodes are shown as being of equal length. However there is no necessity for them to be of equal length. If the fibre flowing through an anode section has a voltage that changes little with distance, then the anode section can conveniently be made long. If however the voltage along the fibre in any particular anode section changes greatly with distance, it would not be appropriate to use a long anode section since at one end there could be no plating and at the other end there could be an inappropriately high current density.

**[0033]** Figure 6 shows how separators may be located between anode sections to reduce the flow of parasitic currents between anodes due to voltage differences between anodes. The electrolyte 2 may be reach the top of the separators as shown in Figure 6 and flow over the separators or may be at a lower level and flow through holes or slots in separators. Electrolyte will typically enter the tank 3 at one end and exit at the other end. But electrolyte can be added or removed at any location in the tank as may prove convenient.

**[0034]** Figure 7 shows a separator 21 with a hole 22 through which the fibre 11 passes.

**[0035]** Figure 8 shows a separator 21 with a slot 23 through which the fibre 11 passes.

**[0036]** Figure 9 shows the electrical circuit for a plating system with multiple anodes, each powered by a separate current source. Each converter may supply a different value of current. The fibre undergoing plating 11 is connected to 0V at each end via the delivery drum at the left-hand end and the take-up drum on the right-hand end. There is an option for the voltage of the delivery end to vary, as described previously, in which case a voltage or current source will be inserted in the circuit between the conductive delivery drum and 0V. The current sources are connected between 0V and the anodes. The current sources are typically dc power supplies operating in the current-controlled, closed-loop manner with the current magnitude determined by an external demand signal from an overall process controller. The converters 25 will typically be of the switched-mode type to ensure high electrical efficiency. The power for the converters 25 will come from an external ac or dc source. The converters 25 can draw input current from a single dc source in which case they can be non-isolated buck regulators. Or they may contain transformer isolation if desired. The converters 25 may also be supplied from a common ac source which is rectified at the point of use. A person skilled in the art will understand the options available.

**[0037]** Figure 10 shows and alternative arrangement for feeding current to the anodes 4. Current for all the anodes is derived from a voltage-source dc power supply 27. The amount of current supplied to each anodes 4 is controlled by a regulator 28 (typically a series transistor) under closed-loop control in which the signal from a current transducer measures the current flowing in the associated anode 4. This current signal is compared with a reference signal and the conducting state of the regulator 28 is changed so as to force the current to the anode 4 to adopt the desired value. The reference signal can be of a predetermined value or can be varied by an external overall control system. The advantage of the arrangement over that shown in Figure 9 is that the components in the electrical circuit are likely to cost less. The disadvantage of the arrangement shown in Figure 10 is that such an arrangement dissipates energy in the regulators 28 and is likely to be less efficient than the arrangement shown in Figure 9.

**[0038]** Figure 11 shows a plating arrangement which permits many fibres to be plated simultaneously, thereby increasing productivity of the plating plant. As before, multiple anodes are used to ensure long effective plating tunnel lengths. Figure 11 is an end-on (cross section) view of the tank 3, anodes 4 and fibres being plated 30. The separators 21 between insulating sections now include a horizontal slot through which the multiple fibres pass in a horizontal row as shown in Figure 11. The current required by each anode will increase roughly in proportion the number of fibres being plated so that the converters supplying the anode currents will need to have a proportionately higher current rating.

**[0039]** Figure 12 shows an option in which an anodising section is included in the process. One or more anodes 31 have reverse polarity (i.e. they become cathodes) and are driven by reverse polarity current sources 32 or reverse polarity voltage sources. The fibre passing beneath them is thereby anodised as a preparation for plating.

## Claims

**1.** An arrangement for producing an electrically-conductive composite wire in which metal is deposited onto and within a fibre composed of a multiplicity of carbon nanotubes and in which the metal deposition is produced by electrolysis, **characterized in that** the carbon nanotube fibre is the cathode and more than one anode (4) is employed.

**2.** An arrangement as claimed in claim 1 **characterized in that** the carbon nanotube wire (11) moves at a constant speed relative to the anodes (4).

**3.** An arrangement as claimed in claim 2 **characterized in that** the anodes (4) are linearly deployed along the path of the cathode.

**4.** An arrangement as claimed in claim 3 **characterized in that** the electrical current flowing from each anode to the cathode is independently maintained at a required value.

**5.** An arrangement as claimed in claim 4 **characterized in that** the required value of each anode current is varied by a control system which measures one or more electrolysis process variable.

**6.** An arrangement as claimed in any preceding claim **characterized in that** an insulating separator (20) is disposed between anodes (4).

**7.** An arrangement as claimed in claim 6, **characterized in that** said insulating separator (20) comprises hole (22) or slot (13) which the fiber passes through.

**8.** An arrangement as claimed in any preceding claim **characterized in that** said metal is copper.

**9.** An arrangement as claimed in claim 8 **characterized in that** the electrolyte is a mixture of sulphuric acid and copper sulphate solution.

**10.** An arrangement as claimed in claim 8 or 9 **characterized in that** the anodes are made of copper.

**11.** An arrangement as claimed in claim 8 or 9 **characterized in that** the anodes consist of a coated titanium mesh.

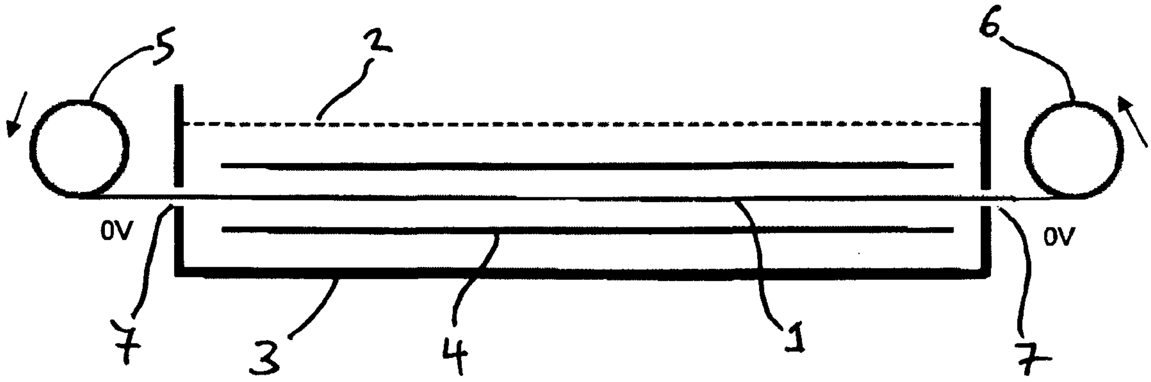


Figure 1

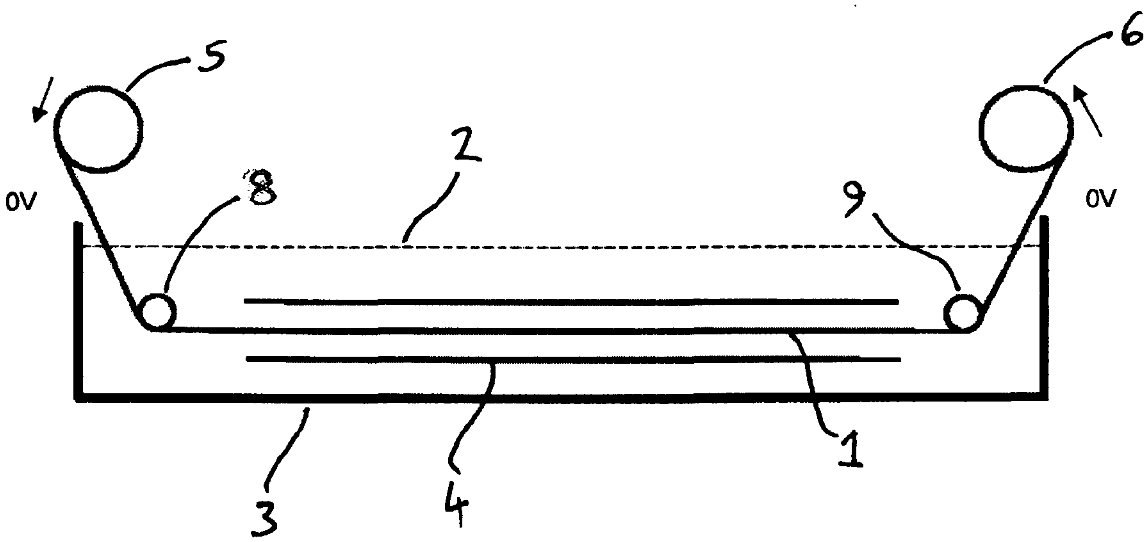


Figure 2

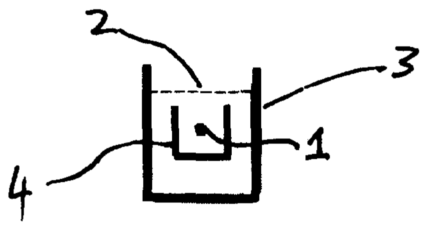


Figure 3

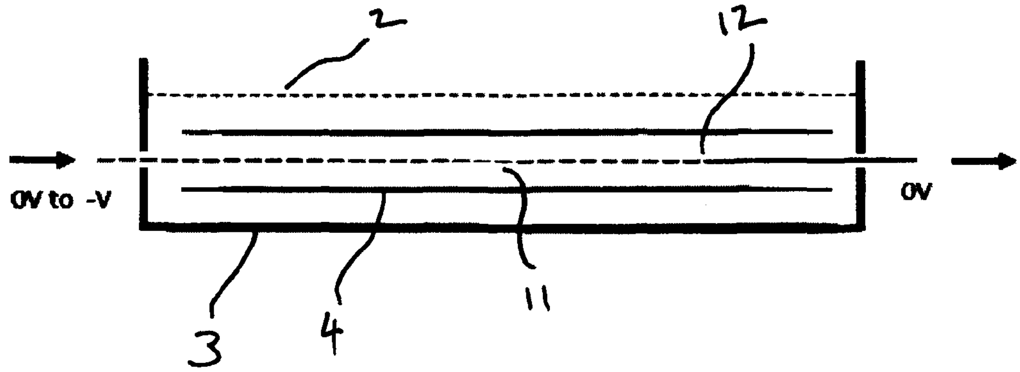


Figure 4

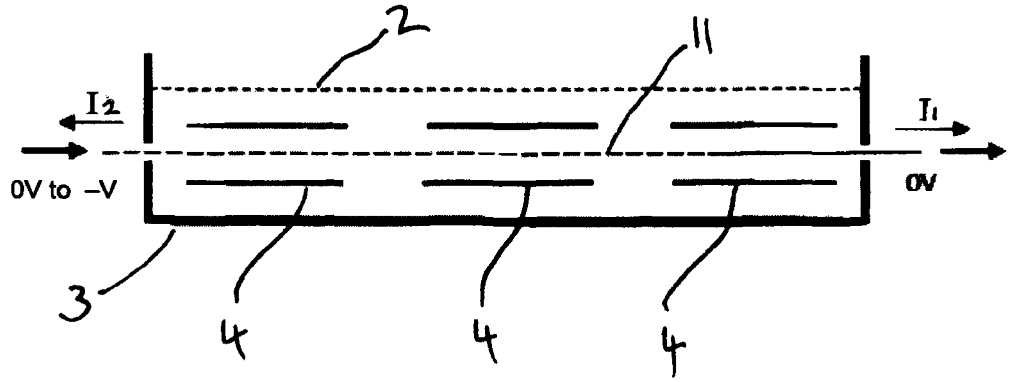


Figure 5

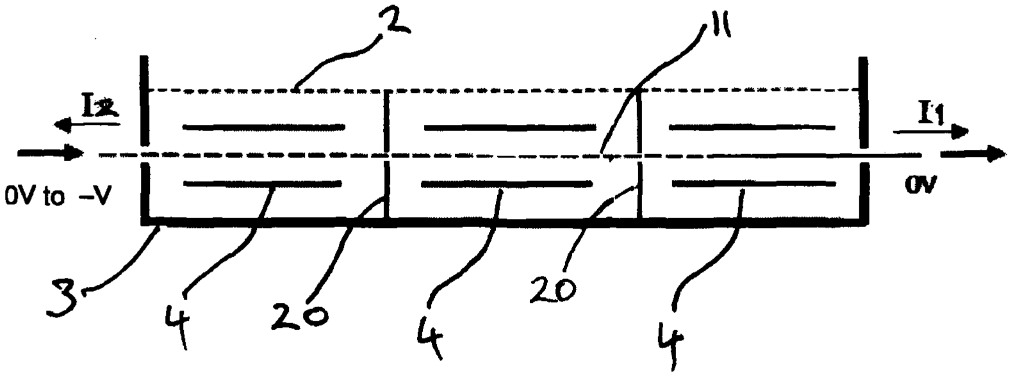


Figure 6

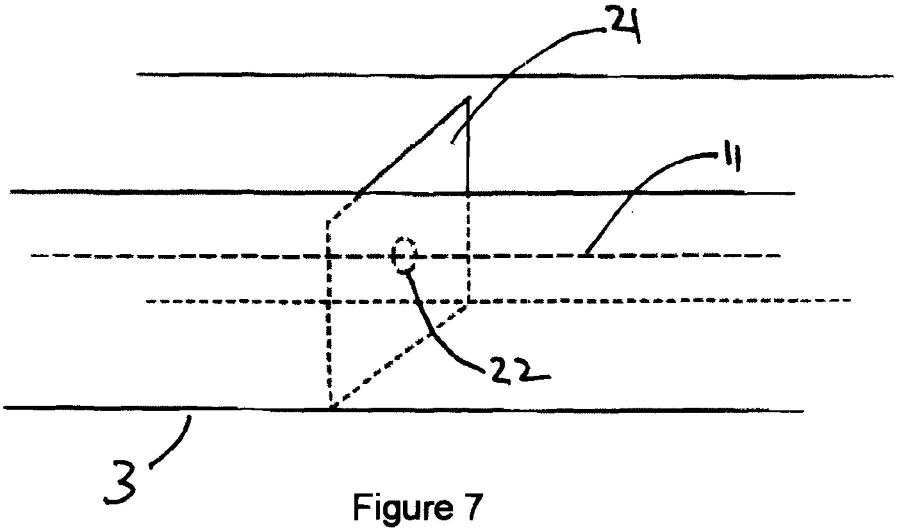


Figure 7

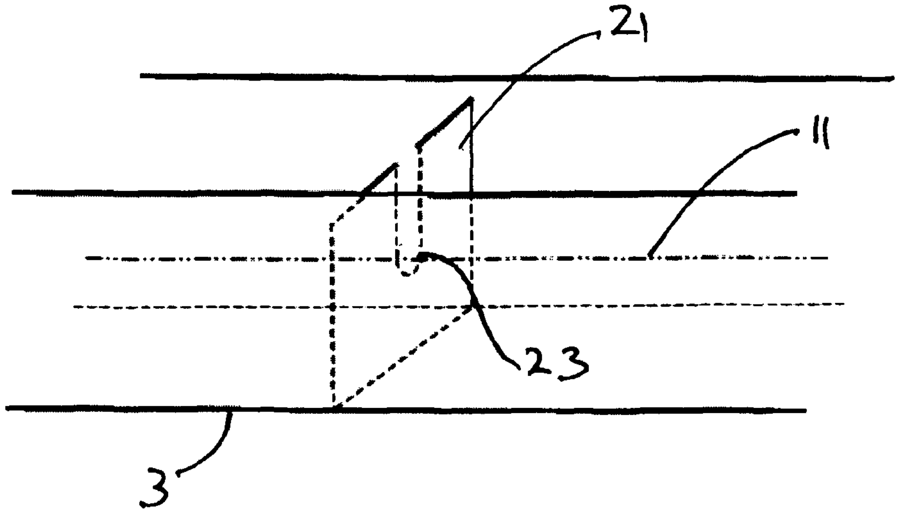


Figure 8

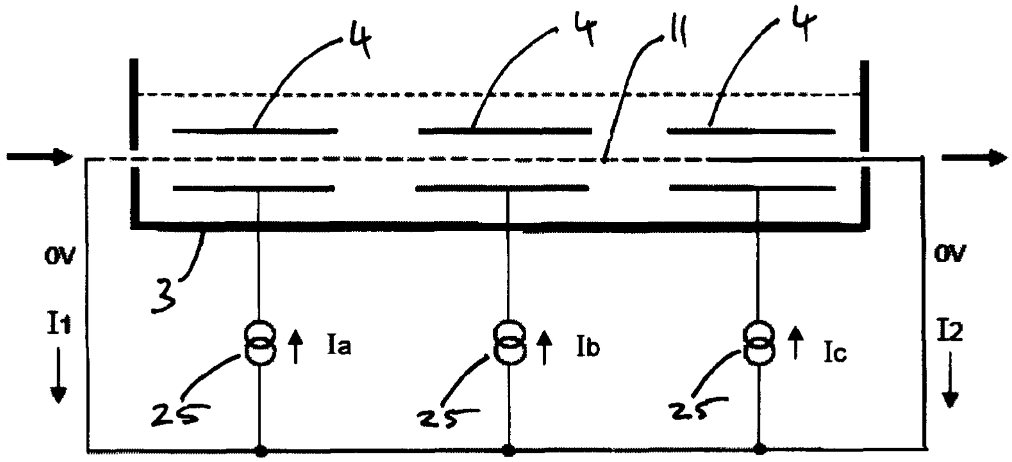


Figure 9

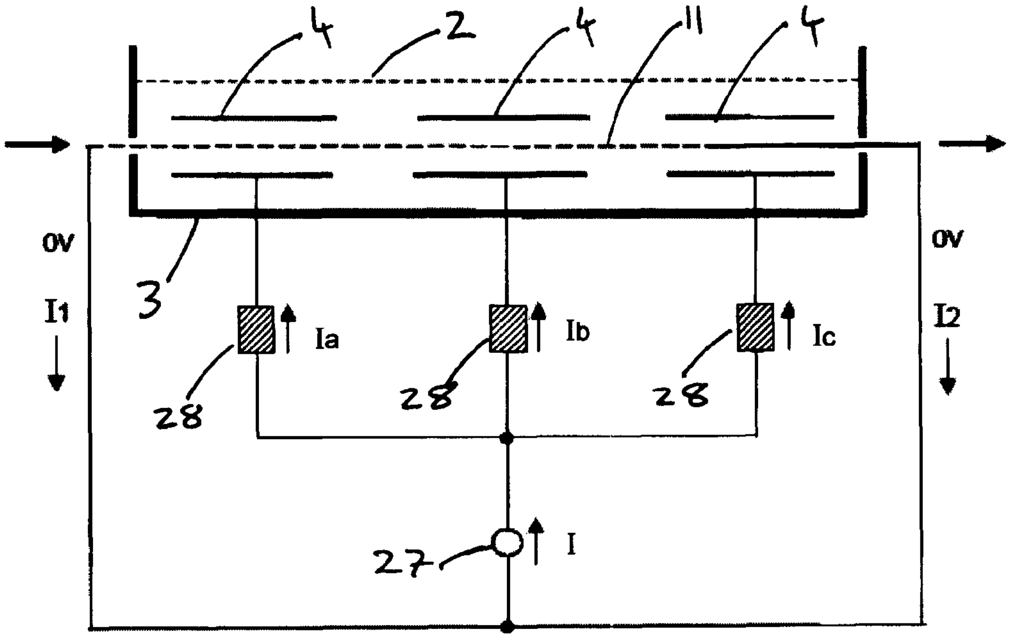


Figure 10

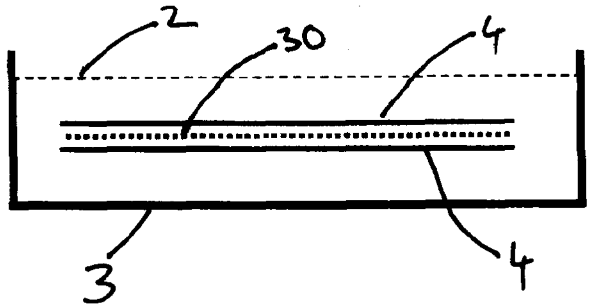


Figure 11

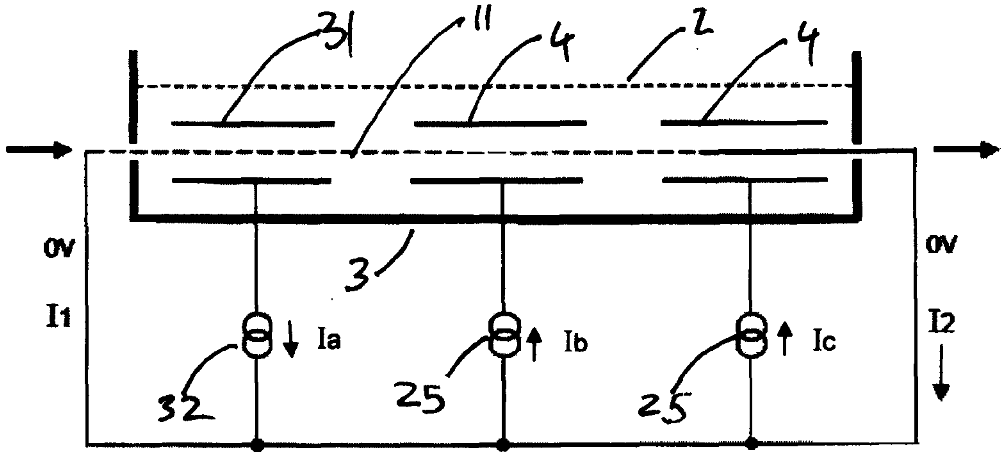


Figure 12

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# EUROPEAN SEARCH REPORT

Application Number
EP 17 30 5165

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (IPC) |
|---|---|---|---|
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