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(71) Applicant: **Brandao, Ulisses**
04018-030 Sao Paulo - SP (BR)

(72) Inventor: **Brandao, Ulisses**
04018-030 Sao Paulo - SP (BR)

(74) Representative: **Büchel, Kurt F., Dr. et al**
Büchel, Kaminski & Partner,
Letzanaweg 25
9495 Triesen (LI)

(54) A replenishment process for metal electrodeposition baths

(57) In a process of replenishing the concentration of a metal cation in an electrolyte solution in an electroplating process, the electrolyte is circulated from a working bath (2) to an enrichment bath in an enrichment cell (11) in which metal anodes (1a; 1b) are dissolved to increase the concentration of metal cations; metal deposition at the cathode of the enrichment cell is reduced or substantially avoided by carrying out cathodic reduction reactions that produce or consume a gas, and without using ion chemical separation means located between anode and cathode (1a,3a; 1b,3b) of the enrichment cell.

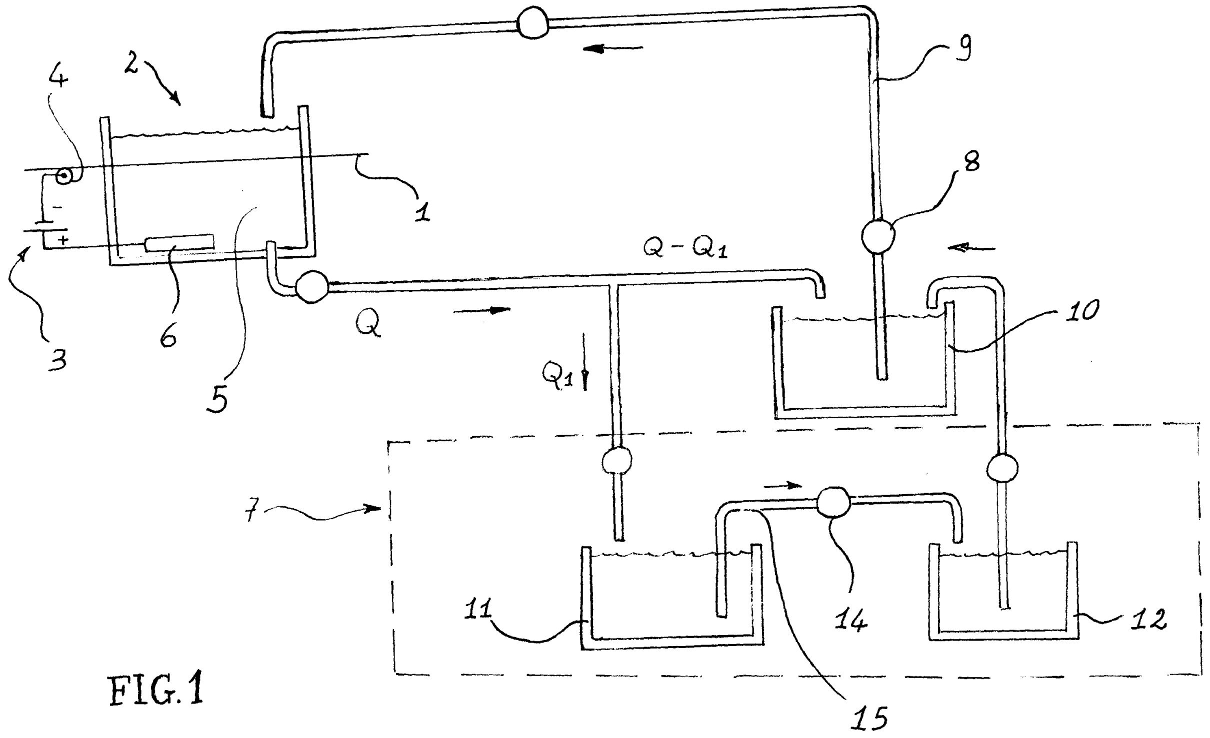

FIG.1

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Description

OBJECT OF THE INVENTION

[0001] The present invention deals with a replenishment process for metal electrodeposition baths, i.e. with a step of metal plating processes in which the electrolyte is enriched in metal cations to maintain substantially constant the metal cations concentration of the electrodeposition baths. More particularly, the invention relates to the replenishment step in plating processes from Copper-containing alkaline pyrophosphate or acid sulphate baths and from Zinc-containing acid sulphate baths, using insoluble anodes.

[0002] In these processes the concentration of Cu^{2+} and Zn^{2+} is kept constant by recirculating the working solution in an enrichment cell, or replenishment cell.

STATE OF THE ART

[0003] In almost all industrial processes involving metal electroplating, and particularly in Cu and Zn electroplating, it is required that the concentration of the metal cations, namely Cu^{2+} and Zn^{2+}, is kept constant.

[0004] This is presently achieved, for Cu plating baths, in the following ways:

i. Chemical dissolution method. Cu metal slabs are plunged into the plating solution, which performs a corrosive action on the metal, this method is far too slow for an efficient industrial application.

ii. Addition of CuO powder. CuO powder can be poured directly into the working electrolyte and dissolves forming Cu^{2+} ed OH^-. This method is very handy and has the advantage of carrying out an alkalinising action (see Detailed description of the Invention in the following). Nevertheless dissolution is not quantitative (some very fine powder remains suspended in the plating bath and cannot be filtered out by standard continuous filtration plants, this powder can codeposit and spoil the properties of the plated layer). In addition, this reagent is generally too expensive for large-scale industrial applications.

[0005] A field were the need of plating processes with constant Cu^{2+} and Zn^{2+} is specially strong, is that relevant to the production of steel-wire reinforced rubber items for applications such as: tyres, pressure tubes, carrier- and drive-belts. Tyres are commonly reinforced with brass-coated high-strength steel plaits. In order to achieve an optimal behaviour of the reinforced system, it is necessary to guarantee a high adhesion between rubber and steelcord. The mechanism which ensures such adhesion is generally the chemical bonding obtained through the formation of sulphide bonds between a metal, which easily undergoes sulfidation, and the rubber; this reaction occurs mainly during the vulcanisation process. Alloys of interest for such applications are brass, Zn-Co and Zn-Mn. Such alloys also enhance the corrosion resistance of the steelcord. Such coatings are generally applied to steel wires whose diameter is larger than that of the final steelcord, such wires are therefore drawn after electroplating, the coating thus performs also a lubricating action during the drawing process.

[0006] The standard brass-coating process of steel wire typically consists in the following unit operations.

1) Hot water rinse at 140÷180°F.
2) Sulphuric or chloridric acid pickling, in order to dissolve surface oxides.
3) Water rinse.
4) Electrodeposition of the Cu layer (typical thickness 0.5 μm) from an alkaline pyrophosphate bath.
5) Electrodeposition of the Cu layer (typical thickness 0.5 μm) from an acid sulphate bath.
6) Water rinse.
7) Electrodeposition of the Zn layer (typical thickness 0.5 μm) from an acid sulphate bath.
8) Water rinse.
9) After the diffusion heat-treatment the brass-coated wire is pickled in a dilute phosphoric acid solution at room temperature.

[0007] Step # 5 could be omitted by having a thickness of Cu layer in step # 4 of about 1 arm.

[0008] In the baths for the electrodeposition of Cu and Zn, the concentration of the Cu^{2+} e Zn^{2+} cations is generally kept constant by the oxidation of soluble Cu and Zn anodes, respectively.

[0009] EP-A-0508212, in the name of The Goodyear Tyre and Rubber Co., discloses a process of keeping the Cu concentration constant with a system comprising insoluble anodes and an cation-exchange membrane-based replenishment device. According to this process, there is provided a replenishment, or enrichment, cell wherein a Cu anode is dissolved and the selective membrane avoids the Cu ions to migrate to the cathode, be reduced and redeposit at the cathode. The selective membrane acts as a chemical and selective separation means for Cu ions present in the enrichment bath.

[0010] The drawbacks of this process are that the membranes are expensive and lean to clog, and that they require maintenance and a pretreatment before they can be used in the process.

SUMMARY OF THE INVENTION

[0011] The present invention deals with a peculiar procedure for the supply of metal cations, and especially of Cu^{2+} and Zn^{2+}, for keeping the concentration of these cations constant in applications of alkaline pyrophosphate Cu and of acid sulphate Cu or Zn electroplating processes carried out with insoluble anodes.

[0012] The use of insoluble anodes shows marked advantages in comparison with the traditional soluble-anode process:

i. dimensional stability of current density distribution, with enhanced reproducibility of the product characteristics,
ii. savings of labour costs related to the substitution if soluble anodes,
iii. avoidance of reworking/recycling processes for partially dissolved anodes.

[0013] Cu^{2+} and Zn^{2+} supply to the working (i.e. deposition) cell is achieved by circulating a given amount of the working electrolyte from the working cell to the enrichment cell where dissolution of suitable anodes takes place: metal deposition at the cathode of the enrichment cell is reduced or substantially avoided, in the absence of the above disclosed selective membrane or of other cation chemical separation means located between anode and cathode of said enrichment cell, by carrying out cathodic reduction reactions that produce or consume a gas.

[0014] Said reduction reaction can be divided into two main groups.

<u>i. Anodic Cu or Zn dissolution with simultaneous limiting current density electrodeposition of Cu (cathodic efficiency less than 100%)</u>

[0015] The electrolyte in the enrichment cell is in contact with a large-area Cu or Zn anode and a small-area cathode (e.g., but with no limitation, a metal wire of suitable mechanical properties). These catodes and anodes are known in the art. The circulation of an electric current is imposed to the system. The anode tends to dissolve with an anodic efficiency close to 100% (the only technically relevant anodic reaction being the oxidation of Cu to Cu^{2+} and of Zn to Zn^{2+}), at the cathode the reduction of Cu^{2+} or Zn^{2+} to metallic Cu or Zn occurs under limiting-current conditions (the cathodic kinetics is controlled by mass-transport to the cathode) together with a side reaction: the reduction of H^+ to H_2 (cathodic current efficiency less that 100%). The difference between the cathodic and anodic current efficiencies is the enrichment factor for the solution. The enrichment factor can be optimized by acting on the cell geometry, the hydrodynamic conditions of the electrolyte and the current density imposed to the electrodic system. The limiting-current electrodeposition brings about the formation of an incoherent and powdery cathodic deposit, suitable means of powder removal will therefore be used. Notwithstanding the possibility of engineering optimisation, any feasible implementation of the process leads to an effective enrichment in Cu^{2+} of the solution.

<u>ii. Anodic Cu dissolution with an oxygen cathode</u>

[0016] The electrolyte in the enrichment cell is brought into contact with a Cu or Zn anode and a suitable cathode. Preferably the cathode is a porous electrode with a catalytic performance for the reaction of oxygen gas reduction to hydroxide anion in alkaline aqueous environment, such as an oxygen fuel-cell electrode; the alkaline environment is favourable in that most commercially available porous gas electrodes can be adopted. At the cathode triple contact is achieved among electrolyte, oxygen-rich gas (either pure oxygen or compressed air of the suitable pressure to achieve the required oxygen activity) and solid material which acts both as current-carrier and electrocatalyst for oxygen reduction. Alternatively - and especially with acid electrolytes - the reaction can be carried out in a packed bed cathode system made of catalytic spheroids (e.g. silver or graphite activated with platinum nuclei) through which the oxygen-rich gas flows in contact with the ion solution to be enriched.

[0017] Both the above-mentioned implementations (porous electrode and packed-sphere bed electrode) should be meant as examples and should not, in any way, be meant as limiting the applications of the combination of oxygen-reduction cathodic reaction and anodic dissolution of Cu or Zn. An electric current circulation is imposed to the system. The anode tends to dissolve with an anodic efficiency close to 100% (the only technologically relevant anodic reaction being the oxidation of Cu to Cu^{2+}), at the cathode the reduction of O_2 to OH^- occurs, this reaction is thermodynamically favoured over the reduction of Cu^{2+} to metallic Cu and of Zn^{2+} to Zn. The reduction of metal - which would be a loss term as far as cation-enrichment of the working solution is concerned and could damage the gas electrode - can occur only if O_2 reduction takes place under limiting current density conditions. The enrichment factor can be optimized by acting on the type of the cell (porous-electrode cell or packed sphere bed electrode) on the cell geometry, on the hydrodynamic conditions of the electrolyte and on the current density imposed to the cell. Even though engineering optimisations are possible, any feasible implementation of the process produces an efficient Cu^{2+} or Zn^{2+} enrichment of the solution.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The invention is further disclosed by reference to the following non-limiting drawings:

- Fig. 1 is a diagramic view of a device of the invention including working cell and enrichment cell;
- fig. 2 is a schematic view of the enrichment cell for a limiting current process;
- fig. 3 is a schematic view of an enrichment cell for the gas-cathode process;
- fig. 4 is a top view of the cell of fig. 2; and
- fig. 5 is a schematic sectional view of a gas cathode for the gas-cathode cell.

[0019] The hereinbelow disclosed process specifically refers to plating of steel wires, but this should not be intended to limit the invention scope to that use only.

[0020] In the application of this invention (see Figure 1) steel wire 1 is coated with a layer of a few µm (typically 0,5÷5 µm and preferably 1÷2 µm) in a deposition, or working, cell 2. Wire 1 is polarised cathodically by generator 3, generally operated in galvanostatic (current control) conditions (a successful application of potentiostatic, i.e. voltage control, conditions is possible too), via contact pulleys 4, known in the art. Steel wire 1 is contacting an aqueous solution of Cu^{2+}-pyrophosphate, or Cu^{2+} acid sulphate or Zn^{2+} acid sulphate 5 while flowing through the cell. Solution 5 is also in contact with an insoluble anode 6 and electrically connected to generator 3. Given the limited aggressivity of the electrolyte, most of the commercial insoluble anodes can be efficiently used (e.g. titanium-based and Pt, Pt/Ir coated, commonly commercially available, see above cited EP-A-0508212 for more details).

[0021] The working solution displays a cation concentration typically in the range 0.10÷0.25 ozs./gall. for Cu^{2+} in pyrophosphate baths, 9÷12 ozs/gall for Cu^{2+} in acid sulphate baths, and 10÷13 ozs/gall for Zn^{2+} in acid sulphate baths. Pyrophosphate anion concentration is typically in the range 0.80÷1.5 ozs./gall and sulfuric acid concentration in Cu and Zn cation solutions is typically in the range 8.0÷10.0 ozs/gall and the quantity necessary to reach a pH of about 3, respectively. The solution pH is generally controlled in the following intervals: Cu^{2+} pyrophosphate baths 7.5÷9.5 and preferably close to 8.5, Zn^{2+}- sulphate baths 2.75÷3.25 and preferably close to 3.0.

[0022] The temperature of working solution 5 is regulated in the range 100÷150°F and preferably close to 120°F. Generator 3 is controlled in such a way that it gives cathodic current densities in the interval 0.25÷1.5 A/sq.in.. The steel wire crosses the electrodeposition cell at a velocity suitable in order to guarantee - for a given cathodic current density - an optimal residence time of the wire in the cation solution according to the desired coating thickness.

[0023] As the electrodeposition process proceeds, the Cu^{2+} or Zn^{2+} concentration of working solution 5 diminishes (in an approximately linear way as a function of time) and it is necessary to replenish the solution with metal cations in order to keep the optimal concentration constant against time. This aim is achieved by recirculating ($Q=Q_1$) the working solution present in the cell 5, or, alternatively, blending ($Q>Q_1$) a portion of it with a suitably Cu^{2+} or Zn^{2+}-enriched solution produced in the enrichment device 7. The enrichment device is connected in series to the recirculation system (recirculation pumps 8, recirculation tubing 9, working electrolyte storage tank 10, the latter can be equipped with pH and Cu^{2+}/Zn^{2+} concentration controls), which is generally available in electrodeposition systems of this kind, allowing the treatment of a flow Q of electrolyte.

[0024] Usually, a portion Q_1 ($Q>Q_1$) is derived from the recirculation flow Q and is delivered to the enrichment device 7, comprising an enrichment cell 11 and possibly a storage and diluting tank for the treated electrolyte 12, a dilution system 13 supplying demineralised water to tank 12 and the relevant pumping systems 14 and pipelines 15. The treated flow Q_1 is added to the working electrolyte storage tank 10, from which the flow Q is pumped to the wire-coating cell.

[0025] As above mentioned, enrichment cell 11 can be implemented according to one of two embodiments of the process: i. (see Figure 2) anodic Cu or Zn dissolution with simultaneous limiting-current electrodeposition of Cu or Zn (cathodic efficiency less than 100%); ii. (see Figure 3) anodic dissolution of Cu or Zn with oxygen cathode.

[0026] In the limiting-current enrichment cell (Figure 2) the Cu^{2+} or Zn^{2+}-enriched solution is contacted with at least one Cu or Zn anode la whose surface area is much larger than the surface of cathode 3a. It is generally advisable to use Cu or Zn spheroids (nuggets) or scraps with typical dimension of a few inches which can be conveniently contained in one or two suitable commercial anode basket (e.g. made of Ti, see above cited EP application for details); if two anode baskets are present, the wire cathode is usually located between them. The anodic polarisation is obtained by connecting the Cu or Zn anode to the positive terminal of the generator 2a (of the same characteristics as the generator 3 of Figure 1). The anodic metal is oxidised to the relevant cation; as far as the material balance is concerned, it is a very good approximation to consider this as the only anodic reaction (100% anodic current efficiency) taking place in the enrichment cell. The anodic Cu or Zn is dissolved during the operation of the enrichment cell and it is therefore necessary to add Cu spheroids or scarps - typically batchwise - to the anode basket(s).

[0027] The thus enriched anolyte is in contact with a metal cathods 3a (e.g. a steel wire) whose surface area is much smaller than the anodic one. The cathodic polarisation is achieved by connecting the cathodic wire to the negative terminal of generator 2a (of the same characteristics as the generator 3 of Figure 1). The thermodynamically favoured cathodic reaction in the system at hand is Cu^{2+} or Zn^{2+} reduction to Cu metal or Zn metal. The rate of such reaction is limited by mass transport of the cations to the cathode.

[0028] A first approximation to the maximum reduction rate of Cu^{2+} to Cu and Zn^{2+} to Zn (a loss term for the enrichment process) - expressed as the maximum cathodic current density (A/sq.in.) for Cu discharge i_{max}^{Cu} and for Zn discharge i_{max}^{Zn} is given by the following equations:

$i_{max}^{Cu}=0.0154 \cdot [Cu^{2+}]/\delta$

$i_{max}^{Zn}=12.61 \cdot [Zn^{2+}]/\delta$

where $[Cu^{2+}]$ and $[Zn^{2+}]$ are the cation concentrations expressed in ozs./gall, i_{max} is expressed in A/sq.in and δ is the concentration boundary layer thickness (typically of the order of a few hundreds of μm), expressed in μm.

[0029] The imposed current density is larger than these values and the exceeding current density is used up for the next competitive side reaction of hydrogen evolution from water. It is worth noting that the loss term for electrodeposition of Cu or Zn can be limited to very low values.

[0030] Several technical features can be adopted, alone or combined together, to enhance the limiting current conditions.

[0031] A large area anode and a reduced area cathode can be used, as disclosed in figures 2 and 4.

[0032] Another feature is to minimize cation migration to the cathode by keeping the portion of electrolyte solution around the cathode in still conditions; to obtain this result, a porous container 16 is provided. Container 16 is made of porous ceramic, fabric or similar material suitable to let the electrolyte flow through its pores and reach the cathode: this will avoid the commotion due to pumping in and out the enrichment cell to reach the cathode area, while enabling the process to proceed. A further advantage is obtained through the use of container 16: the flow from the cell to within container 16 being reduced, a lesser amount of CU cations reach the cathode, thus enhancing the limiting current conditions.

[0033] It should be noticed that container 16 is not a cation exchange membrane as disclosed in prior art. In that case the membrane does not allow for Cu ions to flow through it: in present case porous container acts as a resistance to the flow of Cu ions, that is reduced but not impeded. The porous container can be dispensed with and a porous diaphragm, having analogous characteristics and defining a cathode area with respect to the anode(s) area(s), can be used. The overall effect of porous diaphragm or container is to reduce the effective diffusion coefficiency.

[0034] A further way of enhancing limiting current conditions is by controlling the electrolyte temperature; temperature should be lowered to the lowest acceptable value that does not jeopardize the cell efficiency.

[0035] The cathodic hydrogen-evolution reaction, besides allowing cation enrichment of the solution, brings about a beneficial alkalinising; as a matter of fact, the working electrolyte tends to acidify in the wire-coating cell because of the anodic reaction at the insoluble anodes bringing about the consumption of hydroxide anions supporting the anodic oxygen gas evolution; in the case of analyses performed under this research, it was observed that the alkalinisation in the enrichment cell can compensate for the electrolyte acidification in the wire-coating cell perfectly; it is anyway advisable to provide the system with an automatic pH-control device.

[0036] As far as the cathodic hydrogen gas evolution is concerned, also in the case of intensive industrial-scale applications, the amount of discharged hydrogen is relatively limited and cannot be judged a safety hazard if released to the atmosphere; nevertheless special care must be devoted in the design of industrial cells to avoid any hold-up of cathodic gas or build-up of hydrogen partial pressure in the plant. It is always advisable to avoid the use of free flames in the neighbourhood of the cathodic gas outlet of limiting-current enrichment cells.

[0037] As mentioned above, the limiting-current electrodeposition of Cu or Zn - necessary for the operation of the cathode of the limiting-current enrichment cell - can easily lead to the formation of dendritic or powdery deposits, it is therefore advisable to periodically clean the cathode. Such cleaning operation can be easily performed manually by simply wiping the cathode with a cloth. In the case of a cathodic wire, the cleaning operation can be very easily performed without interrupting the cell operation, e.g. with a device of the kind illustrated in Figure 4.

[0038] In this figure a top view of the limiting-current enrichment cell, shown in Figure 2, is given, one can note the large-surface-area anode 1a, the cathodic wire 3a and generator 2a. The cathodic wire forms a loop which is tensioned by two pulleys 19a and 19b and is connected to the cell through two seals 17 and 18 consisting of a disposable rigid plastic insert on the solution-side of the cell. The pulleys can be rotated periodically, e.g. by use of crank 20.

[0039] The movement of the wire through the plastic inserts can detach the loose deposit which falls in a suitable container, e.g. above mentioned porous container 16, or can be removed from the bottom of the cells as a mud.

[0040] In the enrichment cell with an oxygen cathode (Figure 3) the enriched Cu^{2+}-pyrophosphate, Cu^{2+}-sulphate or Zn^{2+}-sulphate solutions are in contact with at least one Cu or Zn anode 1b with the same properties mentioned with reference to the limiting-current enrichment cell, except the requirement of a high surface area. The anodic polarisation is obtained by connecting the Cu or Zn anode to the positive terminal of generator 2b (of the same characteristics as the generator 3 of Figure 1). Cu metal and Zn metal oxidise to Cu^{2+} and Zn^{2+} , respectively; it is a sound technical approximation to judge this reaction as the only relevant one at the anode of the enrichment cell.

[0041] The anolyte enriched in Cu^{2+} or Zn^{2+} is in contact with a bed of packed spheres or to some other sort of gas electrode 3b fed with a gas containing O_2 of suitable activity. The cathodic polarisation is achieved by connecting the gas electrode to the negative terminal of generator 2b (of the same characteristics as the generator 3 of Figure 1). The thermodynamically favoured cathodic reaction in the system of interest is the reduction of O_2 to OH^-. The rate of such reaction is limited by the mass transport of O_2 to the electroactive regions of the cathode.

[0042] Figure 5 shows a gas-cathode suitable for the invention process.

[0043] The cathode is made of Pyrex glass and is equipped with gas inlet 21 and outlet 22. The electrically active region of the electrode consists of a packed sphere bed of Ag beads 23 of average diameter 200 µm, placed on a bored plate 24 of Ag, fixed to the Pyrex cylinder.

[0044] Electrical contact is provided by a Pt wire 25 brazed to the glass in position 26. Pure oxygen is supplied with a low overpressure with respect to the atmosphere, in oredr to keep the solution level at a level which can guarantee the three-phase contact electrolyte - gas - Ag spheres. If air is used, it must be compressed to obtain the required oxygen activity.

[0045] Similarly to the limiting-current embodiment of the invention process, also the cathodic reaction of oxygen reduction of hydroxide anions, besides allowing Cu^{2+} or Zn^{2+} enrichment of the solution, brings about a beneficial alkalinising; as a matter of fact, the working electrolyte tends to acidify in the wire-coating cell because of the anodic reaction at the insoluble anodes bringing about the consumption of hydroxide anions supporting the anodic oxygen gas evolution; in the case of analyses performed under this research, it was observed that the alkalinisation in the enrichment cell can compensate for the electrolyte acidification in the wire-coating cell perfectly; it is anyway advisable to provide the system with an automatic pH-control device.

[0046] It ought to be noted that - in the present detailed description of the invention - typical implementations of the inventions were presented, such implementations, even though considerably flexible, must be meant as illustrative, any possibility of varying or optimising the design of the plant, by simplifying or complicating it, do not alter the scope and the nature of the invention. The present invention will be described from an application-oriented point of view in the following examples. These examples have a merely illustrative purpose and must not, in ant way, be judges as limiting the extension or the applicability of the invention or of the patented principles in devices showing a different composition or layout.

EXAMPLE 1 - EXPERIMENT SHOWING THE PROCESS OF COPPER ANODIC DISSOLUTION WITH SIMULTANEOUS LIMITING-CURRENT COPPER ELECTRODEPOSITION

[0047] In this experiment the enrichment of a Cu^{2+}-pyrophosphate solution is described, with the limiting-current process, object of the present invention. The cell consists in a PVC tank of dimensions 8 × 8 × 16 cu.in., equipped with a temperature-control system with plunged resistance and thermocouple and a recirculation system (magnetic PTFE pump) providing a maximum recirculation flow of Q=7 gall./h and a limited agitation of the electolyte (as far as the hydrodynamics of the cell are concerned, a stagnant electrolyte is optimal close to the cathode); the solution is removed from the upper part of the cell (1.5 in. below the free surface of the solution) and fed to the enrichment cell in the lower part (3 in. from the bottom of the cell). The anode consists in two Ti anode baskets of dimensions 1 × 6 × 12 cu.in. hanging from opposite walls of the cell. The anode baskets contains Cu spheroids of diameter 0.5 in.. The cathode is a fixed steel wire of of diameter 0.02 in., placed 8 in. above the bottom of the cell and centrally with respect to the two anodes, about 1.5 in. from each one of them. The cell is powered with a laboratory generator, the experiments were carried out under current control. The analysis of Cu concentration was performed by atomic absorption on discontinuously sampled portions of the electrolyte. The pH was monitored continuously with a glass-electrode pH-meter. The experimental results are reported in Table 1 for tests carried out with a starting Cu^{2+} concentration of 0.1155 ozs./gall., starting pyrophosphate 0.99 ozs./gall., starting pH 8.0, temperature 122°F.

Table 1 -

Variations of Cu^{2+} concentrations and pH for a demonstration run of a limiting-current pilot-plant enrichment cell (†pH corrected with discontinuous additions of H_2SO_4 in order to avoid basic-salt precipitations)

time (hours)	I=1 A Cu^{2+} ozs/gall	I=1 A pH	I=5 A Cu^{2+} ozs/gall	I=5 A pH	I=7,5 A Cu^{2+} ozs/gall	I=7,5 A pH
1	0.1157	8,02	0.1154	8,08	0.1307	8,07
2	0.1212	8,03	0.1289	8,15	0.1352	8,32
5	0.1185	8,08	0.1387	8,35	0.1434	8,80
10	0.1307	8,16	0.1434	8,78	0.1592	9,51
24	0.1359	8,30	0.1563	9,48	0.2141	∼10,00†
48	0.1457	8,78	0.2045	∼10,00†	0.2871	∼10,00†

EXAMPLE 2 - EXPERIMENT SHOWING THE PROCESS OF COPPER ANODIC DISSOLUTION WITH OXYGEN CATHODE

[0048] In this experiment the enrichment of a Cu^{2+}-pyrophosphate solution is described, with the oxygen-cathode process, object of the present invention. The cell was the same as described in Example 1. The anode was only one of the anode baskets used in Example 1. The gas cathode used in this Example is shown in Figure 6. This cathode was placed vertically in a central position in the enrichment cell. The cell is electrically connected as in Example 1, the experiment was carried out under current control. The analysis of Cu concentration and of pH were performed as in Example 1. The experimental results are reported in Table 2 for tests carried out with a starting Cu^{2+} concentration of 0.1155 ozs./gall., starting pyrophosphate 0.99 ozs./gall., starting pH 8.0, temperature 122°F.

Table 2 -

Variations of Cu^{2+} concentrations and pH for a demonstration run of a oxygen-cathode pilot-plant enrichment cell

time (hours)	I=1 A Cu^{2+} ozs/gall	I=1 A pH	I=1 A Cu^{2+} ozs/gall	I=1 A pH
1	0.1137	8,02	0.1179	8,06
2	0.1163	8,02	0.1197	8,15
5	0.1179	8,09	0.1216	8,22
10	0.1175	8,14	0.1274	8,39
24	0.1252	8,35	0.1371	8,88
48	0.1382	8,92	0.1598	9,53

EXAMPLE 3 - EXPERIMENT SHOWING THE PROCESS OF COPPER ANODIC DISSOLUTION IN A Cu^{2+}-SULPHATE SOLUTION WITH SIMULTANEOUS LIMITING-CURRENT COPPER ELECTRODEPOSITION

[0049] In this experiment the enrichment of a Cu^{2+}-sulphate solution is described, with the limiting-current process, object of the present invention.

[0050] The same cell described in Example 1 is adopted. The experimental results are reported in Table 3 for tests carried out with a starting Cu^{2+} concentration of 10.25ozs./gall., H_2SO_4 concentration of 9 ozs./gall., starting conductivity of 0.1912 S, temperature 120°F.

Table 3 -

Variations of Cu^{2+} concentrations and conductivity for a demonstration run of a limiting-current pilot-plant enrichment cell with an acidic copper sulphate electrolyte						
time (hours)	I=1 A Cu^{2+} ozs/gall	I=1 A conduct. S	I=2 A Cu^{2+} ozs/gall	I=2 A conduct. S	I=5 A Cu^{2+} ozs/gall	I=5 A conduct. S
1	10.42	0.1887	10.61	0.1876	11.06	0.1815
2	10.59	0.1872	10.88	0.1854	11.85	0.1784
5	11.07	0.1861	11.66	0.1804	precipitation	-
10	11.34	0.1757	precipitation	-	-	-
24	precipitation	-	-	-	-	-

EXAMPLE 4 - EXPERIMENT SHOWING THE PROCESS OF COPPER ANODIC DISSOLUTION IN A Cu^{2+}-SULPHATE SOLUTION WITH OXYGEN CATHODE

[0051] In this experiment the enrichment of a Cu^{2+}-sulphate solution is described, with the oxygen-cathode process, object of the present invention. The experimental system was the same as described in Example 2. The experimental results are reported in Table 4 for tests carried out with a starting Cu^{2+} concentration of 10.25 ozs./gall., H_2SO_4 concentration of 9 ozs./gall., starting conductivity of 0.1912 S, temperature 120 °F,

Table 4 -

Variations of Cu^{2+} concentrations and conductivity for a demonstration run of a oxygen-cathode pilot-plant enrichment cell with an acidic copper sulphate electrolyte				
time (hours)	I=1 A Cu^{2+} ozs/gall	I=1 A conduct. S	I=2 A Cu^{2+} ozs/gall	I=2 A conduct. S
1	10.40	0.1899	10.72	0.1885
2	10.47	0.1886	11.03	0.1865
5	10.95	0.1851	11.70	0.1807
10	12.35	0.1787	precipitation	-

EXAMPLE 5 - EXPERIMENT SHOWING THE PROCESS OF ZINC DISSOLUTION IN A Zn^{2+}-SULPHATE SOLUTION WITH SIMULTANEOUS LIMITING-CURRENT ZINC ELECTRODEPOSITION

[0052] In this experiment the enrichment of a Zn^{2+}-sulphate solution is described, with the limiting-current process, object of the present invention.

[0053] The same cell described in Example 1 is adopted. The experimental results are reported in Table 5 for tests carried out with a starting Zn^{2+} concentration of 11.85 ozs./gall., starting pH 3, room temperature.

Table 5 -

Variations of Zn^{2+} concentrations and pH for a demonstration run of a limiting-current pilot-plant enrichment cell with an acidic zinc sulphate electrolyte						
time (hours)	I=1 A Zn^{2+} ozs/gall	I=1 A pH	I=2 A Zn^{2+} ozs/gall	I=2 A pH	I=5 A Zn^{2+} ozs/gall	I=5 A pH
1	12.04	3.02	12.25	3.04	12.87	3.10
2	12.24	3.05	12.65	3.08	14.04	3.27
5	12.84	3.15	13.93	3.31	16.91	3.69
10	13.87	3.32	15.97	3.52	22.67	4.43
24	16.62	3.85	21.70	4.23	precipitation	-

Table 5 - (continued)

Variations of Zn^{2+} concentrations and pH for a demonstration run of a limiting-current pilot-plant enrichment cell with an acidic zinc sulphate electrolyte						
time (hours)	I=1 A Zn^{2+} ozs/gall	I=1 A pH	I=2 A Zn^{2+} ozs/gall	I=2 A pH	I=5 A Zn^{2+} ozs/gall	I=5 A pH
48	21.41	4.30	29.46	5.40	-	-

EXAMPLE 6 - EXPERIMENT SHOWING THE PROCESS OF ZINC ANODIC DISSOLUTION IN A Zn^{2+}-SULPHATE SOLUTION WITH OXYGEN CATHODE

[0054] In this experiment the enrichment of a Zn^{2+}-sulphate solution is described, with the oxygen-cathode process, object of the present invention. The experimental system was the same as described in Example 2. The experimental results are reported in Table 6 for tests carried out with a starting Zn^{2+} concentration of 11.85 ozs./gall., starting pH 3, room temperature.

Table 6 -

Variations of Zn^{2+} concentrations and pH for a demonstration run of a oxygen-cathode pilot-plant enrichment cell with an acidic zinc sulphate electrolyte				
time (hours)	I=1 A Zn^{2+} ozs/gall	I=1 A pH	I=2 A Zn^{2+} ozs/gall	I=2 A pH
1	11.98	3.01	12.16	3.02
2	12.09	3.06	12.71	3.07
5	12.96	3.12	13.92	3.29
10	13.99	3.39	15.82	3.63
24	16.19	4.12	21.49	4.15
48	22.35	4.42	29.18	5.10

Claims

1. A process of replenishing the concentration of a metal cation in an electrolyte solution in an electroplating process, wherein said solution is circulated from a working bath to an enrichment bath in an enrichment cell, a dissolution of metal anodes taking place in said enrichment cell, characterized in that metal deposition at the cathode of said enrichment cell is reduced or substantially avoided, in the absence of chemical ion separation means located between anode and cathode of said enrichment cell, by carrying out cathodic reduction reactions that produce or consume a gas.

2. A process according to claim 1, wherein said enrichment cell is kept at limiting current conditions and hydrogen gas is produced.

3. A process according to claim 2, wherein a cathode portion of said electrolyte in said enrichment cell is kept substantially still to enhance said limiting current conditions.

4. A process according to any claim 1 to 3, wherein flow of electrlolyte to the enrichment cell in controlled by means of a porous container or diaphragm to enhance said limiting current conditions.

5. A process according to claim 1, wherein said enrichment cell cathode is a gas cathode and gas is fed to said cathode to be reduced.

6. A process according to claim 5, wherein said gas cathode is an oxygen cathode and oxygen or compressed air is fed to said oxygen cathode to be reduced.

7. A process according to any previous claims, wherein said metal ions are selected from Cu^{2+} and Zn^{2+}.

8. An electroplating device, comprising a working cell, an enrichment cell, and means for circulating a metal ion electrolyte solution from said working cell to said enrichment cell and vice versa, characterized in that said enrichment cell is free from means of chemical ion separation located between anode and cathode of said enrichment cell.

9. A device according to claim 8, wherein said enrichment cell comprises a porous diaphragm or container defining an anode portion and a cathode portion, said porous diaphragm or container being at least in part permeable to said electrolyte including said metal cations.

10. A device according to claim 8 or 9, further comprising means to remove deposits from said cathode.

11. A device according to claim 8, wherein said enrichment cell comprises a gas cathode.

12. A device according to claim 11, wherein said gas cathode is selected between an oxygen fuel-cell cathode and a packed-sphere bed electrode.

13. A process for applying a copper or/and zinc layer to a metal filament by passing said filament into a working cell provided with insoluble anodes and containing a Cu or Zn cation electrolyte solution, characterized in that the concentration of Cu or Zn cations in said solution is replenished by means of an enrichment process according to any claim 1 to 7.

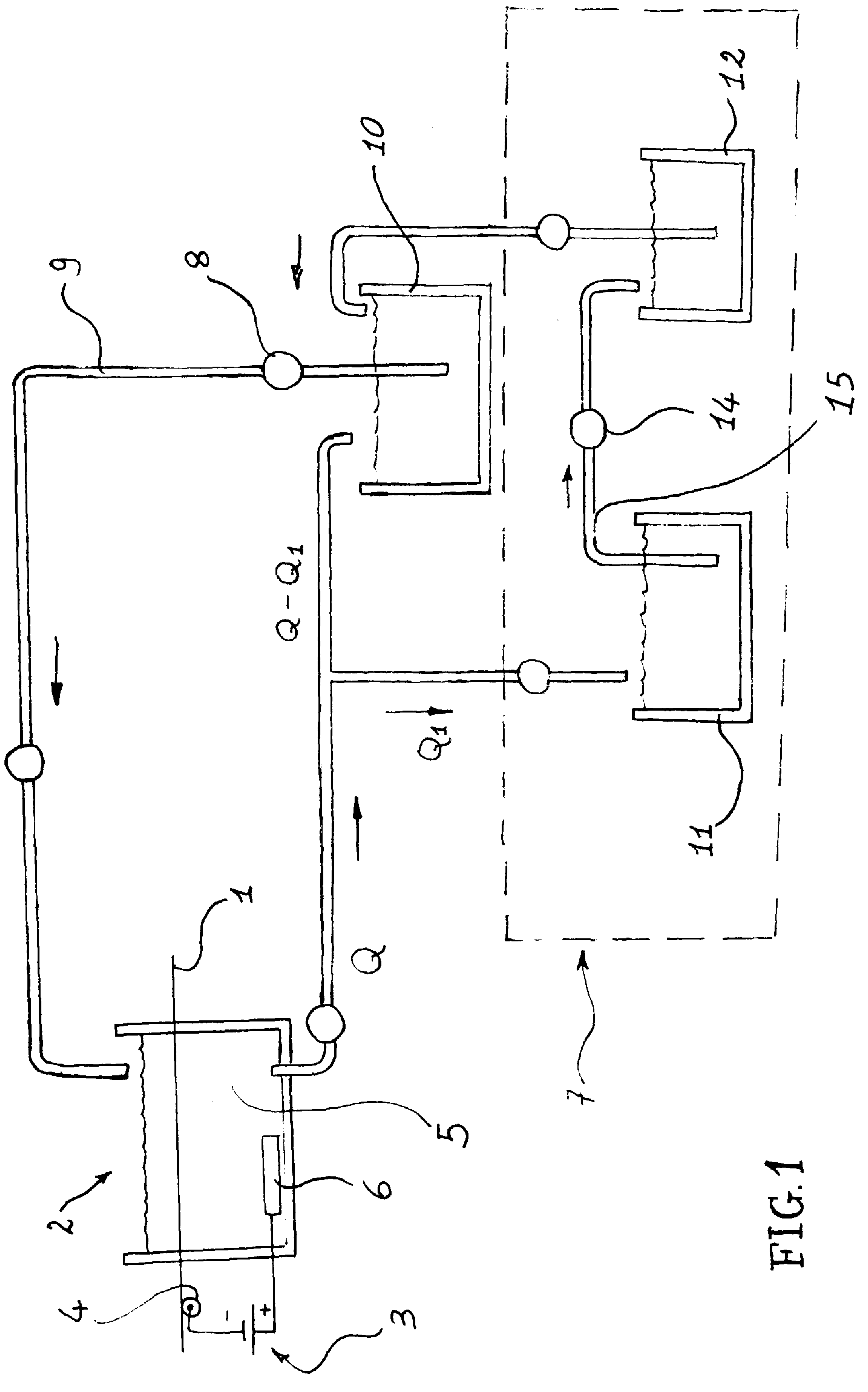

FIG.1

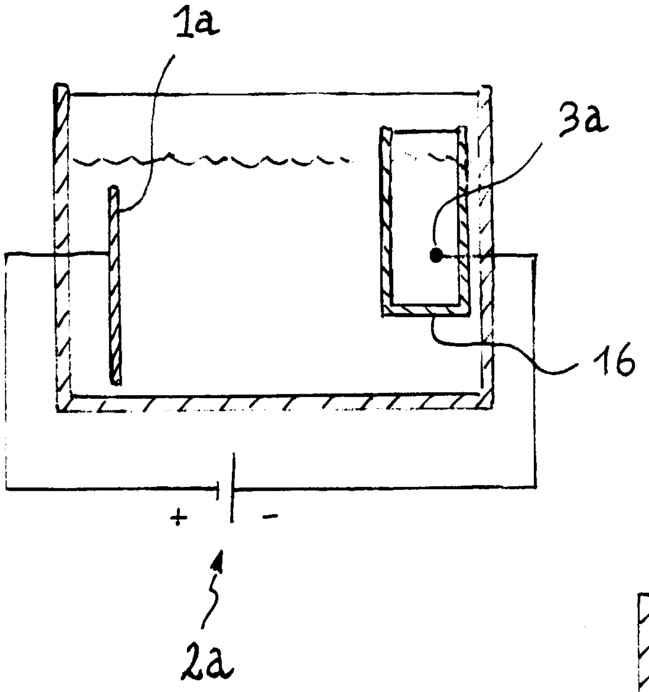

FIG. 2

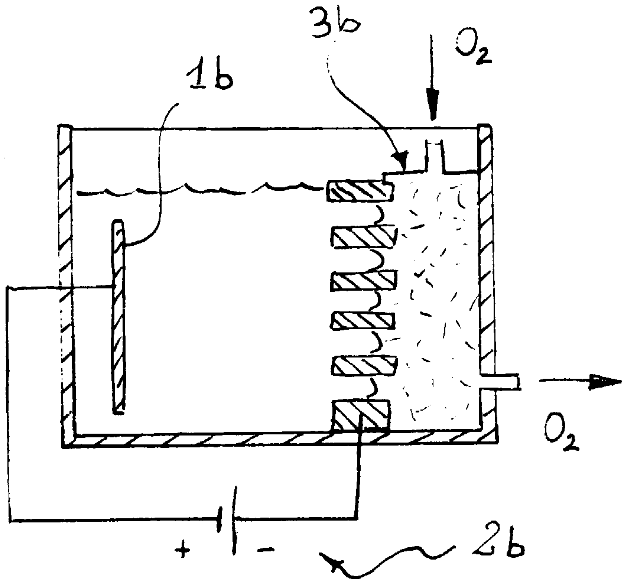

FIG. 3

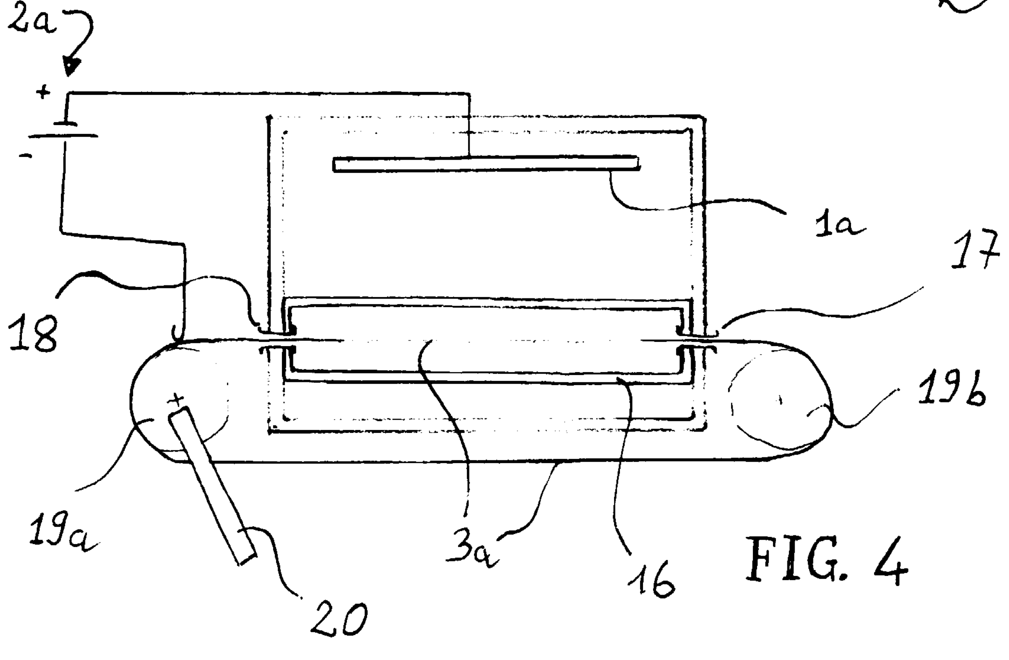

FIG. 4

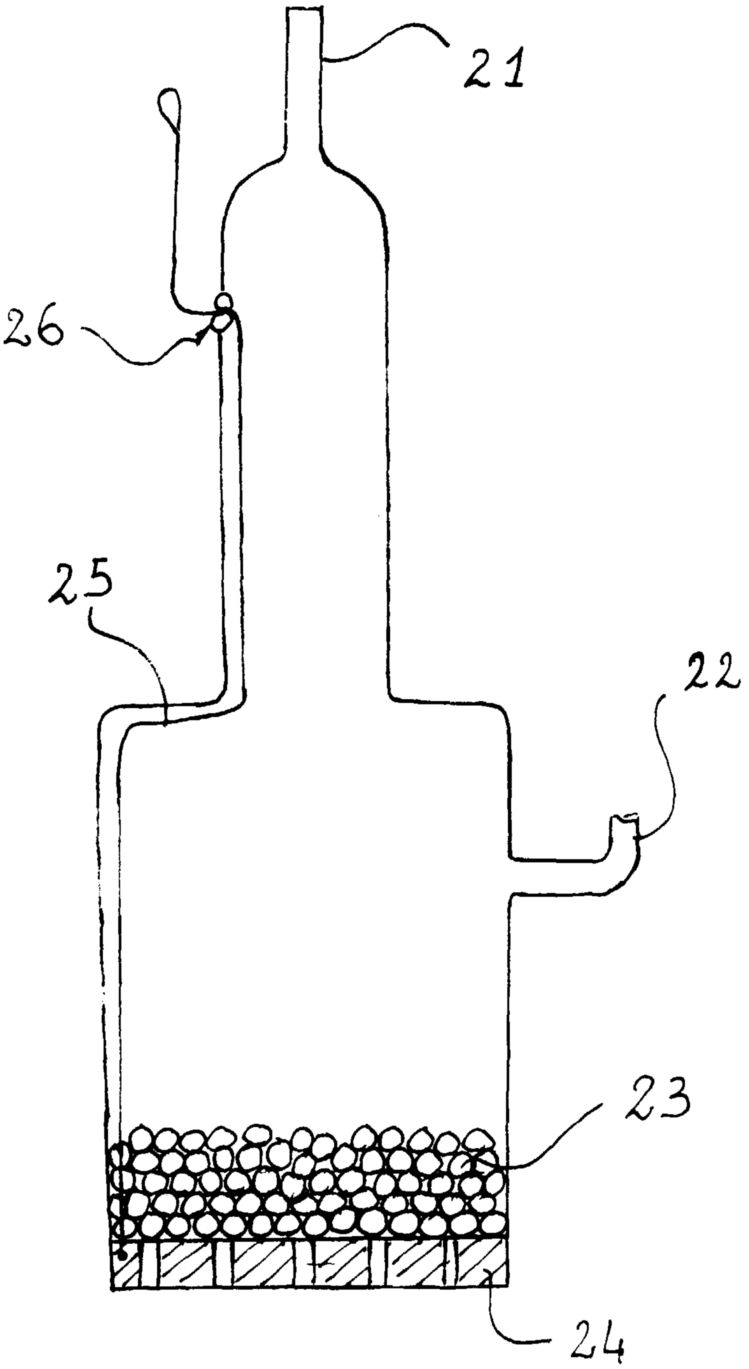

FIG. 5

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 99 11 7902

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.7)
X	EP 0 550 002 A (NKK CORPORATION) 7 July 1993 (1993-07-07) * page 3, line 46 - page 5, line 10 * * page 8 - page 9; claims 1-12 *	1,2,8,10	C25D21/14
X	US 5 082 538 A (D.L. DERESPIRIS) 21 January 1992 (1992-01-21) * column 2, line 31 - line 38 * * column 2, line 58 - line 64 * * column 4, line 19 - line 48 * * column 4, line 60 - line 61 * * column 6, line 58 - column 7, line 35 * * figure 1 *	1,5-9, 11,12	
X	PATENT ABSTRACTS OF JAPAN vol. 006, no. 257 (C-140), 16 December 1982 (1982-12-16) & JP 57 149498 A (DIPSOL KK), 16 September 1982 (1982-09-16) * abstract *	1,2,7,8	
A	EP 0 524 748 A (C. UYEMURA & CO, LTD) 27 January 1993 (1993-01-27) * page 6; claim 1 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C25D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 February 2000	Groseiller, P

CATEGORY OF CITED DOCUMENTS

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EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 99 11 7902

29-02-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 550002 A	07-07-1993	JP 5179497 A	20-07-1993
		JP 5179498 A	20-07-1993
		DE 69204644 D	12-10-1995
		DE 69204644 T	21-03-1996
US 5082538 A	21-01-1992	AU 635697 B	25-03-1993
		AU 8811591 A	16-07-1992
		CA 2054252 A	10-07-1992
		EP 0494434 A	15-07-1992
		JP 4268099 A	24-09-1992
JP 57149498 A	16-09-1982	JP 1619459 C	30-09-1991
		JP 2042919 B	26-09-1990
EP 524748 A	27-01-1993	JP 2546089 B	23-10-1996
		JP 5009800 A	19-01-1993
		DE 69208172 D	21-03-1996
		DE 69208172 T	05-09-1996
		US 5234572 A	10-08-1993

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82