

TRANSLATION

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PROCESS AND ARRANGEMENT FOR THE ELECTROLYTIC DEPOSITION OF METAL LAYERS

The present invention relates to a process and an apparatus for the electrolytic deposition of uniform metal layers, preferably of copper, having given physical-mechanical properties.

The electrolytic metallization, for instance with copper, of workpieces which are electrically conductive at least on their surface, has been known for a long time. For this purpose, the workpieces which are to be coated are connected as cathode and, together with anodes, brought into contact with the electrolytic plating solution. For the deposition, a flow of electric current is produced between anode and cathode.

Ordinarily, anodes of the material which is deposited from the plating solution are used. In that case, the amount of metal deposited from the solution is returned to the plating solution by dissolving at the anodes. In the case of copper, the amount deposited and the amount which is anodically dissolved are approximately the same for a given charge flow. This process is easy to carry out since, at least in the case of copper, only sporadic measurement and control of the metal-ion concentration of the plating solution is necessary.

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However, disadvantages have been encountered when carrying out the process with these soluble anodes. If the thickness of the metal layers deposited is to be very uniform at all places on the surface of the workpiece, then the soluble anodes are only conditionally suitable for this purpose, since the latter change shape with time due to the dissolving, so that the distribution of the lines of force in the electrolytic bath also changes. The use of smaller, for instance spherical, pieces of metal as anodes in insoluble metal baskets is also only conditionally suitable for solving the problem, since the metal parts frequently wedge against one another and as a result of the dissolving process gaps are frequently formed upon the sliding down in the pile of metal parts.

Therefore, attempts have frequently been made to use insoluble, and therefore dimensionally stable anodes, rather than soluble metal anodes. As materials, titanium or high-grade steel, for instance, enter into consideration for this. By the use of these anode materials, gases, such as for instance oxygen or chlorine, are formed upon the electrolytic deposition since the anodic dissolving of metal no longer takes place. The gases produced attack the anode materials and gradually dissolve them.

German Patent DD 215 589 D5, describes a process for the electrolytic deposition of metal with the use of insoluble

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metal anodes in which reversibly electrochemically convertible substances are added as addition to the plating solution, they being transported by intense positive convection with the plating solution to the anodes of a plating apparatus, converted electrochemically there by the electrolysis current, conducted, after their conversion, by intense positive convection away from the anodes into a regeneration space, returned electrochemically to their initial condition in the regeneration space on regeneration metal present in it with simultaneous electroless dissolving without external current of the regeneration metal, and fed in this initial condition again to the separation apparatus by intensive positive convection. By this process, the above-indicated disadvantages with the use of insoluble anodes are avoided. Instead of the corrosive gases, the substances added to the plating solution are oxidized at the anode, so that the anodes are not attacked.

The dissolving of the metal in the regeneration space is in this case independent of the process of the deposition of metal on the material being treated. Therefore, the concentration of the metal ions which are to be deposited is controlled by the effective metal surface in the regeneration space and by the velocity of flow in the circuit. In the case of a deficiency of metal ions, the effective metal surface and/or the velocity of flow from the deposition space

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to the regeneration space is increased or, in case of an excess of metal ions, correspondingly reduced. This process therefore presupposes that a high concentration of the reversibly electrochemically convertible substance is present in the plating solution. This has the result that the oxidized compounds of the addition substances (redox system) are again reduced at the cathode, so that the current efficiency is decreased.

In German Unexamined Application for Patent DE 31 10 320 A1, a process is described for cation reduction by anode-supported electrolysis of cations in the cathode space of a cell, the anode space containing ferrous ions as reducing agent and anodes being moved relative to the anolyte which surrounds the anodes.

In German Unexamined Application for Patent DE 31 00 635 A1, a process and an apparatus are described for supplementing an electroplating solution with a metal to be precipitated in an electroplating apparatus, wherein the metal which is to be galvanically precipitated is provided in an electroplating solution which is contained in an electroplating container and a supply of the metal to be precipitated is provided within an enclosed space, the gases produced in the electroplating container upon the advance of the electroplating process are conducted, together with the electroplating solution, into said enclosed space and applied

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there to said supply of metal in order to dissolve the latter, whereupon the dissolved supply of metal is again added to the electroplating solution in the electroplating container. The apparatus required for the carrying out of the process is, however, very expensive, since, among other things, it must be gas-tight.

Said processes have the disadvantage that the plating solutions to be regenerated contain no addition compounds, which, however, are ordinarily required in order to control the physical-mechanical properties of the metal layers to be deposited. Such substances are predominantly organic substances.

It is only by these addition compounds that the required physical-mechanical properties of the layers such as, for instance sufficient brightness, high elongation upon rupture, and resistance of the layer to cracks upon soldering shock tests are obtained. Without the addition of these compounds, the layers are dark, dull, and rough.

DD 261 613 A1 describes a process for the electrolytic deposition of copper from acid electrolytes with dimensionally stable anode using certain additions for the production of layers of copper having specific physical-mechanical properties, the plating electrolyte also containing the aforementioned electrochemically reversibly convertible addition substances.

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It has been found that, although the quality of the metal layers precipitated from such plating solutions initially satisfy the requirements, in particular with regard to the physical-mechanical properties, nevertheless, after a longer period of deposition, layers of poorer quality are obtained even if the substances in the plating solution whose concentration was decreased by consumption upon the deposition are supplemented. Copper coatings which are only poorly ductile are obtained from aged plating solutions, so that such layers tear on printed circuits in the region of the holes when they are subjected to a soldering shock test. Furthermore the surface of the metal layer then changes in disadvantageous manner, in that it becomes dull and rough.

The present invention therefore proceeds from the problem of avoiding the disadvantages of the processes and arrangements of the prior art and of finding an economical process, and suitable apparatus, for the electrolytic deposition of layers of metal, particularly of copper, in which the metal layers deposited by the process and the apparatus have predetermined physical-mechanical properties, in the manner that addition compounds are added to the plating solution in order to control the properties of the metal layers, and the properties of the metal layers do not change in disadvantageous manner even after a lengthy period of deposition. Furthermore, the thicknesses of the metal

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layers are to be approximately the same at all places on the surface of the material treated, and the deposition is to be possible with high current efficiency.

This problem is solved by Claims 1, 8, and 16.

Preferred embodiments of the invention are set forth in the dependent claims.

In order to obtain sufficiently uniform layer thicknesses on the surface of the material being treated, insoluble, dimensionally stable, anodes are used. In order to supplement the metal ions consumed by deposition, namely in a preferred use copper ions, a metal-ion generator is used in which parts consisting of the metal to be deposited are contained. The plating solution contains, in addition to the metal ions, compounds of an electrochemically reversible redox system. For the regeneration of the plating solution which has become impoverished by consumption of metal ions, it is passed by the anodes, whereby the oxidizing compounds of the redox system are formed. Thereupon, the solution is conducted through the metal-ion generator, the oxidizing compounds reacting with the metal parts, with the formation of metal ions. At the same time, the oxidizing compounds of the redox system are converted into the reduced form. By the formation of the metal ions, the total concentration of the metal-ion concentration contained in the plating solution is maintained constant. From the metal-ion generator, the

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plating solution passes back again into the electrolyte space which is in contact with the cathodes and anodes.

The solution furthermore contains addition compounds for controlling the physical-mechanical properties of the layer. In order to maintain the properties of the layer even after a lengthy period of deposition from the plating solution, means are provided in accordance with the invention by which the concentration of the oxidizing compounds of the redox system in the direct vicinity of the cathode can be minimized, preferably to a value below about 0.015 mole/liter.

Obviously, the addition compounds can be decomposed by the oxidizing compounds of the redox system. In this way, the concentration of the addition compounds would, on the one hand, be reduced in uncontrolled fashion. Since the determination of the concentration of these compounds is in general very cumbersome, while the content of the compounds is very sensitive to the physical-mechanical properties of the layers, only layers having varying properties could necessarily be deposited, since a sufficiently rapidly acting and precise technique of analysis for such requirements is not available.

This problem would furthermore be intensified by the fact that upon the decomposition of the addition compounds reaction products are formed which have a detrimental effect on the properties of the layer, so that, after lengthy

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duration of the electrolysis, even if the content of the addition compounds is maintained by enrichment of the injurious reaction products, only layers the properties of which would not satisfy the requirements made could still be deposited.

The means in accordance with the invention by which the concentration of the oxidizing compounds in the vicinity of the cathode can be minimized, preferably to a value less than about 0.015 mole/liter, are described below:

The total amount of the compounds of the redox system added to the plating solution is so determined that substantially the entire amount of the oxidizing compounds of the redox system fed to the metal-ion generator with the plating solution is required for the dissolving there of the metal parts with the formation of metal ions.

The amount of metal ions provided by the dissolving must just supplement the portion which is lost in the plating solution by the deposition. In order to maintain the metal-ion concentration and for the complete reduction of the amount of oxidizing compounds introduced into the metal-ion generator, a minimum size of the surface of the metal parts in the metal-ion generator is therefore required. This surface can be increased in upward direction as far as desired and, in particular, however, need not be variable. Thus, the further filling of the metal parts into the metal-

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ion generator can be effected in a technically simple manner in any desired amounts above said minimum amount.

The spatial distance between the anodes and the metal-ion generator must be small, and the connections for transferring the plating solution which has reached the anodes to the metal-ion generator and from the metal-ion generator back into the electrolyte space must be short. In this way, the result is obtained that the dwell time of the oxidizing compounds in the electrolyte space is short. By the rapid transfer of the plating solution containing the oxidizing compounds into the metal-ion generator, these compounds also have only a short life until they are converted into the reduced compounds of the redox system.

Furthermore, the velocity of flow of the plating solution must be as high as possible, particularly upon the transfer from the anodes to the metal-ion generator.

In order to keep the concentration of the oxidizing compounds as small as possible, it is furthermore possible to introduce another oxidizing agent directly into the metal-ion generator. Atmospheric oxygen is particularly suitable for this purpose. Upon the reaction of oxygen with the metal parts, only water is produced, it having no effect on the deposition process.

For the introduction of air into the metal-ion generator, means for the blowing-in of atmospheric oxygen are

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provided in the lower region of the generator.

Another possibility for supplementing the metal ions removed by deposition from the plating solution consists, in principle, of adding the metal ions in the form of their compounds or salts to the plating solution. However, in this case, the concentration of the anionic portions of the compounds or salts necessarily added with the metal ions cannot be prevented from increasing continuously due to the continuing addition of the compound, so that, after a certain amount of time, the solution must be discarded. If, in the present case, only a small part of the metal ions to be supplemented by addition of the corresponding compounds or salts, then the time until the discarding of the solution can be rather long. By combining the supplementing of the metal ions by addition of the salt with the regenerating of the solution in the metal-ion generator, the addition of the compounds or salts can be decreased to a few per cent of the necessary supplementation.

In this case, the possibility of controlling the metal-ion concentration in the plating solution in a simple and rapid manner from a control standpoint constitutes an advantage.

By the reduction in the life of the oxidizing compounds of the redox system which are formed on the anode which is obtained by means of said measures, and the minimizing of the

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concentration of the compounds, possible decomposition of the addition compounds is avoided, or at least definitely reduced.

The metal-ion concentration in the electrolyte space can also be controlled by a special manner of circulation of the plating solution. The reduced compounds of the redox system which are converted electrochemically at the anodes by the electrolysis current back into the oxidizing compounds are present in the cathode space. The quantity of the oxidizing compounds and thus the metal-ion concentration can be reduced if only a part of the plating solution is conducted from the space present in the vicinity of the cathode to the anodes and from there into the metal-ion generator. The other part of this solution which does not contain the oxidizing compounds is, on the other hand, conducted directly into the metal-ion generator. For this purpose, separate outlets are provided for the plating solution, they being located in the vicinity of the cathode. The solution which is branched off over the outlets passes through suitable pipelines into the metal-ion generator.

The surface of the metal to be dissolved is, in its turn, dimensioned so amply that all oxidizing compounds introduced into the metal-ion generator can be converted electrochemically.

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By this measure, a simple control of the metal-ion concentration in the plating solution and thus an automating of the control which is simple technically to achieve is made possible. By controlling the volumetric flows of the plating solution from the cathode via the anode into the metal-ion generator, on the one hand, and from the cathode directly into the metal-ion generator, on the other hand, the metal-ion concentration can be easily adjusted.

For the control, the velocity of flow of the plating solution in the circuit and the voltage between cathode and anode can also be adjusted.

The conditions of flow in the electrolyte space are to be such that, on the one hand, a flow of the plating solution is directed from the cathode to the anode and, on the other hand, the plating solution, however, first acts directly on the cathode. This latter is necessary in order to be able economically to produce uniform layers with sufficiently high current densities and predetermined physical-mechanical properties. These flows are produced by direct flow against the cathode by means of nozzle assemblies or surge nozzles and by subsequent deflection of this flow towards the anodes.

The preferred arrangement for the carrying out of the process of the invention comprises, in addition to the cathodes, insoluble, preferably perforated, dimensionally stable anodes, devices for the flow of the plating solution

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against the cathodes and anodes (nozzle assemblies, or surge nozzles), means of deflecting the flow to the anodes and connecting lines for transferring the plating solution which has been fed to the anode to the metal-ion generator as well as for transferring the plating solution emerging at the metal-ion generator back into the electrolyte space. In a preferred embodiment, means for drawing off the plating solution can also be provided in order to increase the velocity of flow upon the transfer of the plating solution from the anodes to the metal-ion generator.

In order to avoid the mixing of the parts of the plating solution which are located in the vicinity of the cathode and/or the anode, the electrolyte space can also be subdivided into several compartments by ion-pervious partition walls (ion-exchanger, diaphragms).

The metal-ion generator is preferably a tubular device which can be filled from above and which is provided with a bottom and, for the entrance of the electrolyte, with at least one pipe socket with lateral openings and also, in its upper region, with an overflow which debouches into an electrolyte container. In one particularly favorable embodiment, oblique, preferably perforated, plates are arranged within the metal-ion generator.

The process is particularly suitable for the metallizing of circuit boards. In this case, copper in particular is

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deposited on their surfaces and on the walls of the holes.

Ordinary dip devices can be used in which the circuit boards are dipped from above into the plating solution, or else horizontal installations in which the circuit boards are grasped horizontally and moved by suitable means in horizontal direction through the installation.

In addition to copper, which can preferable be deposited with the process of the invention from the arrangement which is also described, other metals, for instance, nickel, can also, in principle, be deposited in accordance with the method of the invention.

The basic composition of a copper bath can vary within relatively wide limits when using the process of the invention. In general, an aqueous solution of the following composition will be used:

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	20 - 250 g/liter
preferably	80 - 140 g/liter or 180 - 220 g/liter
Sulfuric acid, concentrated	50 - 350 g/liter
preferably	180 - 280 g/liter or 50 - 90 g/liter
Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) 0	0.1 - 50 g/liter
preferably	5 - 15 g/liter
Chloride ions (added, for instance, as NaCl)	0.01 - 0.18 g/liter

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preferably

0.03 - 0.10 g/liter.

Instead of copper sulfate, other copper salts can also be used, at least in part. The sulfuric acid can also be replaced, in whole or in part, by fluoboric acid, methane sulfonic acid, or other acids. The chloride ions are added as alkali chloride, for instance sodium chloride, or in the form of hydrochloric acid, p.A. The addition of sodium chloride can be dispensed with, in whole or in part, if halogen ions are already present in the additions.

The active $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox system is formed from ferrous sulfate heptahydrate. It is excellently suited for the regenerating of the copper ions in aqueous acid copper baths. However, other water-soluble iron salts can also be used, in particular ferric sulfate nonahydrate, provided that the salts do not contain biologically non-degradable (hard) complex formers in the compound, since the latter result in problems in connection with the disposal of the flushing water (for example, iron-ammonium alum).

In addition to iron salts, compounds of the elements titanium, cerium, vanadium, manganese, chromium and the like are also suitable as further redox systems. Compounds which can be used are, in particular, titanyl sulfuric acid, ceric sulfate, sodium metavanadate, manganous sulfate, and sodium chromate. For special uses, combinations of the above redox systems can also be used.

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With the process of the invention, the other elements which are known and have proven themselves in electrolytic metal deposition can be retained. Thus, ordinary brightening agents, leveling agents and surface-active agents can, for instance, be added to the plating solution. In order to obtain copper precipitates having predetermined physical-mechanical properties, at least one water-soluble sulfur compound and an oxygen-containing high-molecular compound are added. Addition compounds such as nitrogen-containing sulfur compounds, polymeric nitrogen compounds, and/or polymeric phenazonium compounds can also be used.

The addition compounds are contained in the plating solution within the following concentration ranges:

ordinary oxygen-containing	
high-molecular compounds	0.005 - 20 g/liter
preferably	0.01 - 5 g/liter
ordinary water-soluble	
organic sulfur compounds	0.005 - 0.4 g/liter
preferably	0.001 - 0.15 g/liter

Thiourea derivatives and/or polymeric phenazonium compounds and/or polymeric nitrogen compounds as addition compounds are used in the following concentrations:

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preferably

0.0001 - 0.50 g/liter

0.005 - 0.04 g/liter

For the preparation of the plating solution, the addition compounds are added to the above-indicated basic composition. The conditions for the deposition of copper are indicated below:

pH

< 1

Temperature:

15°C - 50°C

preferably

25°C - 40°C

cathodic current density:

0.05 - 12 amp/dm²

preferably

3 - 7 amp/dm²

A few oxygen-containing high-molecular compounds are listed in the following Table 1:

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Table 1: Oxygen-Containing, High-Molecular Compounds.

Carboxymethyl cellulose
Nonylphenol-polyglycolether
Octanediol-bis-(polyalkylene glycol ether)
Octanolpolyalkylene glycol ether
Oleic acid-polyglycol ester
Polyethylene-propylene glycol + polyethylene glycol
Polyethylene glycol-dimethylether
Polyoxypropylene glycol
Polypropylene glycol
Polyvinyl alcohol
Stearic acid polyglycol ester
Stearyl alcohol polyglycol ether
 β -Naphthol polyglycol ether

Table 2: Sulfur Compounds

3-benzthiazolyl-2-thio)-propylsulfonic acid, sodium salt
3-mercaptopropane-1-sulfonic acid, sodium salt
Ethylenedithiodipropyl sulfonic acid, sodium salt
Bis-(p-sulfophenyl)-disulfide, disodium salt
Bis-(ω -sulfobutyl)-disulfide, disodium salt
Bis-(ω -sulfohydroxypropyl)-disulfide, disodium salt
Bis-(ω -sulfopropyl)-disulfide, disodium salt
Bis-(ω -sulfopropyl)-sulfide, disodium salt

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Methyl-(ω -sulfopropyl)-disulfide, disodium salt

Methyl-(ω -sulfopropyl)-trisulfide, disodium salt

O-ethyl-dithiocarbonic acid-S-(ω -sulfopropyl)-ester,
potassium salt

Thioglycolic acid

Thiophosphoric acid-O-ethyl-bis-(ω -sulfopropyl)-ester,
disodium salt

Thiophosphoric acid-tris-(ω -sulfopropyl)-ester, trisodium
salt

A few sulfur compounds having functional groups suitable for the production of water solubility are set forth in the above Table 2.

By blowing air into the electrolyte space, the plating solution is moved. By addition action of air on the anode and/or the cathode, the convection in the region of their surfaces is increased. In this way, the mass transport in the vicinity of the cathode and/or anode is optimized, so that higher current densities can be obtained. Corrosive oxidizing agents which are possibly produced in a small amount, such as for instance oxygen and chlorine, are thereby led away from the anodes. Movement of the anodes and cathodes also results in an improved mass transport on the corresponding surfaces. In this way, a constant diffusion-controlled deposition is obtained. The movements can take place horizontally, vertically, in uniformly lateral

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movement, and/or by vibration. A combination with the action of air is particularly effective.

Inert material is used for the anodes. Anode materials which are chemically and electrochemically stable to the plating solution and the redox system used are suitable, for instance titanium or tantalum as base material, coated with platinum, iridium, ruthenium, or their oxides or mixed oxides. Titanium anodes having an iridium-oxide surface which are blasted with spherical bodies and thereby compacted so as to be free of pores were sufficiently resistant, and therefore had a long life. By the anodic current density or the anode potentials adjusted via the voltage between cathode and anode, the quantity of the corrosive reactions produced on the anode is determined. Below 2 amp/dm² their rate of formation is very small. In order, therefore, not to exceed this value, large effective anode surfaces are desirable. Therefore, in the case of limited three-dimensional dimensions, perforated anodes are preferred, for instance, anode nets or expanded metal having a suitable coating are used. In this way, the advantage of a large effective surface is combined with the simultaneous possibility of intensive flow through the anode by the plating solution, so that any corrosive reaction produced can be led away. Anode nets and/or expanded metal can, in addition, be used in several layers. In this way, the effective surface is

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correspondingly increased, so that the anodic current density with a predetermined electroplating current is reduced.

Metal is supplemented in a separate container, the metal-ion generator, which is passed through by the plating solution. In the case of copper deposition, metallic copper parts, for instance in the form of pieces, balls or pellets, are present in the metal-ion generator. The metallic copper used for the regeneration need not contain phosphorus, but phosphorus is not disturbing. Upon the additional use of soluble copper anodes, the composition of the anode material, on the other hand, is of great importance. In that case, the copper anodes must contain about 0.05% phosphorus. Such materials are expensive, and the addition of phosphorus causes residues in the electrolytic cell which must be removed by additional filtration.

Since, in accordance with the method of the invention, it is also possible to use metallic copper parts which contain no additions, electrolytic copper, including copper scrap, is as a rule used. An interesting variant consists therein that the circuit board waste which is coated with copper, such as obtained in large quantities upon the production of printed circuit boards, can also be used for this, provided that it does not contain further metals. This waste, consisting of the polymeric base material and the copper layers applied thereto, can be disposed of in

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traditional manner only at high expense due to the firm bond between the two materials. After the profitable dissolving of the copper of this waste in a metal-ion generator suitable for this, a sorted disposal of the base material is possible. In similar fashion, reject circuit boards can also be used.

Furthermore, filters for the removal of mechanical and/or chemical residues can also be inserted in the circulation of the plating solution. However, the need for them is less than with electrolytic cells having soluble anodes, since the anode sludge produced by the mixture of phosphorus to the anodes is not present.

For the further explanation of the invention, and further preferred embodiments, reference is had to the following diagrammatic figures.

- Fig. 1 shows the principle of an apparatus for the dip treatment;
- Fig. 2 shows the principle of an apparatus without and with diaphragm;
- Fig. 3 shows the principle of an apparatus with serial conducting of the plating solution;
- Fig. 4 shows the principle of an apparatus for the horizontal transport of the material being treated;
- Fig. 5 shows a metal-ion generator on an apparatus for dip treatment;

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Fig. 6 shows a metal-ion generator on an apparatus for the horizontal transport of the material being treated.

In Fig. 1, the process of the invention is shown on basis of a diagrammatically shown apparatus. The electrolyte space 1 is located in the container 3. The metal-ion generator 2 is so constructed and arranged with respect to the container 3 as to result in short paths for the feeding of the plating solution from the anodes 5 to the metal-ion generator and from there back again into the electrolyte space. For this reason, in the present case, the metal-ion generator is divided into two parts arranged in the vicinity of the insoluble anodes. This division in two is, however, not necessary. Thus, for instance, it can also be arranged as a single unit to the side of or below the bath container. The copper parts to be dissolved are introduced in a loose pile into the metal-ion generator in order to permit easy passage of the plating solution through the generator. On the other hand, however, a minimum loading with copper parts must be maintained therein. The pump 11 pumps the plating solution in a closed circuit through the arrangement. It is essential that the material 6 being treated, which is connected as cathode, be acted upon by the plating solution which is enriched in copper ions, as indicated by the arrows 14, via nozzle assemblies or surge nozzles, not shown here. In this way, the result is obtained that the copper layers

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are deposited on the surface of the material being treated with the necessary quality and the necessary speed. Furthermore, a further flow takes place within the electrolyte space from the space 15 present in the vicinity of the material being treated in the direction towards the space 16 present in the vicinity of the anodes. The plating solution which has been brought to the anodes passes through them, in the case of perforated anode, and arrives, with the advance of the flow, into the outlet 4 which leads to the metal-ion generator. In this way, the result is obtained that a transport of anodically formed oxidizing compounds of the redox system (ferric ions) into the cathode space 15 is minimized. This, in turn, prevents the injurious decomposition of the addition compounds, with simultaneous increase of the cathodic current efficiency.

Along the transport path from the anodes via the outlet into the metal-ion generator, the addition compounds are probably decomposed via a chemical decomposition reaction with the participation of the oxidizing compounds of the redox system. Therefore, the shortest possible connection with high velocity of the plating solution to the metal-ion generator is desirable outside the electrolyte space 1.

The minimum loading of the metal-ion generator with copper parts provides assurance that the oxidizing compounds formed are completely converted within the metal-ion

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generator and the concentration of these compounds at the outlet of the metal-ion generator is lowered to a value of about zero. This means that the copper surface which is in contact with the plating solution in the metal-ion generator leads to the complete reduction of the oxidizing compound to the reduced compounds (ferrous ions), with simultaneous electroless dissolving of copper with the formation of copper ions. The reduced compounds of the redox system do not contribute to the decomposition of the addition compounds.

By targeted flow onto the cathode surfaces, the anodes, for a given total circulation, are subjected to less electrolyte exchange. In this way, the corrosive gases possibly produced at the anodes are led away correspondingly slower, so that, on the one hand, the corrosion of the anodes increases while, on the other hand, it is limited by the following measures:

- low anodic current density
- inert base material of the anodes
- inert coating of the anodes
- surface compacting of the anodes
- liquid-pervious anode geometry.

By these measures, the result is obtained that the addition compounds which are added to the plating solution in order to control the physical-chemical properties of the layer of metal can be used also in arrangements with

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insoluble, dimensionally-stable anodes. Special mixtures of the addition compounds are not necessary for this. A high cathodic current efficiency and a long life of the insoluble anodes is obtained.

Fig. 2 shows another apparatus in accordance with the invention. It differs, on the one hand, from the arrangement shown in Fig. 1 by a difference in the guidance of the plating solution within the electrolyte space, which consists of a space 15 present in the vicinity of the material being treated, namely the cathode space, and of the spaces 16 present in the vicinity of the anodes, namely the anode spaces. These spaces are separated by the dashed lines 17 in the drawing. The plating solution, which was enriched with copper ion in the metal-ion generator 2 upon the reduction of ferric to ferrous ions, flows separately into each space and passes through nozzle assemblies or surge nozzles (not shown) as shown by the arrows 12 and 14 to the anodes 5 and the cathodic treatment material 6. Mixing of the plating solution in the anode space 16 with the solution in the cathode space 15 can take place only to a slight extent, in particular for the reason that the plating solution has its own outlets 4 from the anode space and, separately therefrom, the plating solution has an outlet 18 in the cathode space. In this embodiment, the ferric ion concentration is kept small in the cathode space, which is connected directly with

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the inlet to the metal-ion generator 2, so that a short conduction path from the anode space to the metal-ion generator results. On the other hand, the transport paths from the cathode space via the outlet 18 to the generators can be long, since there are no injurious interactions between the reduced compound which is contained in the plating solution present in the cathode space and the addition compounds. In order to avoid even a slight electrolyte mixing of the plating solutions in the cathode and anode spaces, these spaces can be separated along the lines 17 by, in each case, an ion-pervious partition wall (diaphragm) which, in its turn, is not chemically changed by the plating solution. The partition walls are pervious for the plating solution only to a very slight extent, if at all, so that they permit possibly only a slow equalization of different hydrostatic pressures in the spaces 15 and 16. Polypropylene fabrics or other membranes with a permeability for metal ions and their corresponding gegenions (for instance the Nafion of DuPont de Nemours, Inc., Wilmington, Del., USA) are, for instance, suitable. By separation of the spaces by partition walls, assurance is had that the plating solution cannot pass, for instance, by eddying from the anode space into the cathode space. This measure leads also to a further decrease in the concentration of the oxidizing compounds of the redox system in the vicinity of the cathode.

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Therefore, advantageous effects with respect to the resistance to aging of the plating solution result also from these measures.

The plating solution which is present in the anode space and which contains the ferric ions formed there is, in its turn, transferred, over the shortest path, into the metal-ion generator and enriched there again with copper, with the formation of ferrous ions. In practical operation, a condition of equilibrium between the copper solution in the metal-ion generator and the deposition of copper on the material being treated is established.

Fig. 3 shows another embodiment of the invention, having a two-part metal-ion generator. The plating solution which is enriched in copper ions in the metal-ion generator 2, is introduced only into the cathode space 15. This solution contains, furthermore, only ferrous ions and no ferric ions. The plating solution is conducted in succession from the cathode space 15 to the anode space 16. The ferrous ions formed in the metal-ion generator therefore, after passing through the cathode space, enter with the plating solution via a pump into the anode space. The feeding of the plating solution into the cathode space is effected by another pump 11. A hydrodynamic constancy and the constant transport conditions resulting therefrom are advantageous for the electrochemically active additions of the redox system.

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Furthermore, this serial conducting of the plating solution permits a dividing up of the plating solution withdrawn from the cathode space. In order to control the concentration of the copper ions in the electrolyte space 1, comprising the cathode and anode spaces, a part of the solution is conducted via the lines 43 indicated in dashed line, directly into the metal-ion generator. This partial quantity contains practically no oxidizing compounds of the redox system, so that the copper dissolving rate is reduced by admixture of this portion into the stream of solution which is introduced from the anode space into the metal-ion generator. By control and/or regulation of the partial quantities of the two streams by means of three-way valves (not shown), the copper ion concentration in the plating solution can be adjusted. In the arrangement shown in Fig. 2, these possibilities are not used, although, in that case also, two separate outlets 4 and 18 are present for the plating solutions from the cathode and anode spaces. The solutions of the two spaces are brought together there and conducted jointly into the metal-ion generators. The regenerated solutions coming from the metal-ion generators are fed to the spaces 15 and 16. The manner of procedure in accordance with Fig. 3 is advantageous when the plating solutions of the anode and cathode spaces cannot be mixed together in the electrolyte space, but a complete separation

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of the discharging solutions is not assured in the outlets 4 and 18 from the anode and cathode spaces.

In Figs. 1 to 3, the introduction of the plating solution enriched in copper ions into the container 3 is shown, by way of example, to be effected from below and the introduction into the metal-ion generator from above. In corresponding manner, the off lines from outlets 4 and 18 from the container 3 are shown at the top and those from the metal-ion generator 2 at the bottom. Circulation of the plating solution in other directions is also possible, such as, for instance, the introduction of the solution into the metal-ion generator from below.

Another embodiment of the invention, particularly for the electrolytic metallizing of plate-shaped treatment material, preferably circuit boards, in horizontal passage through the arrangement, is shown in Fig. 4. The system, part of which is shown in side view, consists of the electrolytic part 20 and a metal-ion generator 21 filled with copper, shown below it. The electrolytic part 20 consists of a plurality of individual electrolytic cells. Four of these individual cells are designed by the reference numerals 22, 40, 41, 42 in Fig. 4, with an insoluble anode 23 in each case for the top side and the bottom side of the treatment material 24. The treatment material is electrically connected to a rectifier (not shown) and is cathodically

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polarized. It is transported through the installation, in the direction of the arrow 25, by means of rollers or disks 26. The transport elements 26 are uniformly distributed along the entire installation. For reasons of simplification of the drawing, they have been shown here only at the beginning and end of the transport path. Surge nozzles or flood pipes 27, 39 are also present, uniformly distributed in the electrolytic cells. They correspond to the nozzle assemblies already mentioned above.

Plating solution coming from the metal-ion generator 24 is fed by pumps 29 to the flood pipes 27, 39 via the pipelines 28. The plating solution flows through the outlet openings of the flood pipes or surge nozzles onto the surfaces of the treatment material 24. In this connection, copper ions are reduced to metallic copper and deposited as a metallic layer on the material to be treated, and the ferrous ions, also present, are conveyed with the discharging electrolyte in the direction towards the anodes 23. In order to avoid a return flow from the anodes to the cathodes, various methods are provided the effecting of which is shown diagrammatically in Fig. 4. The plating solution which is enriched with copper is used for flow to the cathode (treatment material). From the plate-shaped treatment material, the stream of solution is then so deflected that, as indicated by arrows 30, it continues in the direction

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towards the anodes. In the case of perforated anodes, which are preferably used, the solution passes through them and then passes via suction pipes 31 and pipelines 32 back into the metal-ion generator. The anodes can consist, for instance, of expanded metal or netting. Openings 33 support the flow process. In order to avoid the formation of eddying, baffle walls 34 extending in the direction towards the material being treated can be arranged on the suction pipes. The slot 35 remaining between the baffle walls and the treatment material can amount to a few millimeters. From the standpoint of fluid mechanics, this forms practically closed electrolytic cells having favorable flow conditions. The flood pipes 27 can also be provided with baffle walls 36 in order to prevent further possible eddies.

Different flood pipes in different number are shown, by way of example, in the electrolytic cells of the arrangement shown in Fig. 4. The circulation of the plating solution is such that the level 37, which is above the suction pipes, is present in the electrolytic part of the installation. In the electrolytic cell 42 shown on the right, partition walls 38 are shown between each of the anodes 23 and the treatment material 24. In this way, the exchange of the plating solutions in the cathode and anode spaces over a direct path is minimized. By the use of ion-pervious partition walls, on the other hand, an ion-exchange between the chambers is made

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possible. The solution in the cathode space can emerge at the end side. In the anode space further flood pipes 39 are provided. The solution of this chamber passes out via the suction pipes 31. For such a cell, the serial flow path such as already described on the basis of Fig. 3 is again suitable.

The leading away of the plating solution from the anode space via the suction pipes 31 into the metal-ion generator 21 can take place over the shortest path in order to keep the life of the ferric ions as short as possible. Therefore, the metal-ion generator 21 is arranged here also as close as possible to the electrolytic part 20. In this way, short connection paths and short transport times result. The principle of construction can advantageously also be so selected that the parts 20 and 21 form a complete system. Each of several flood pipes 27 is fed by a pump 29 in the manner shown in Fig. 4. However, a single pump can also be used. This would lead to longer connecting paths between the flood pipes 27, 39 and the metal-ion generator 21. The plating solution in these connecting lines contains practically no oxidizing compounds of the redox system. Thus, the protection of the addition compounds is assured in this region also.

The electroplating installation is shown in side view in Fig. 4. The parts shown (anodes, pipes) extend in length

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into the depth of the drawing, and therefore transverse to the direction of transport over the material to be treated. The parts present in the electrical field between anode and cathode, such as, for instance, the flood pipes 27, consist of electrically non-conductive plastic. Their electric screening action is not disturbing here, since the material to be treated moves slowly through the installation and thus is continuously exposed to the different electrical fields.

Fig. 5 shows an arrangement in accordance with the invention having two metal-ion generators 44, an electrolyte space 1, and two additional electrolyte containers 45. This arrangement is operated in the dip process. In this case, the cell is developed symmetrically for the electroplating of the front and rear sides of the treatment material 6. The two metal-ion generators 44 shown in the figure and the electrolyte containers 45 can in each case also be provided individually and in such case arranged on both sides of the material being treated.

The metal-ion generator 44 consists of a preferably round tubular body 46 having an upper opening 47. All materials used for this are resistant to the plating solution and the additions contained in the solution. At least one pipe socket 49 extends through the bottom 48 of the metal-ion generator into the inside of the metal-ion generator. This pipe socket has lateral openings 50. They form a screen

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which, on the one hand, prevents penetration of metallic copper into the pipeline system and, on the other hand, permits the passage of the plating solution into the metal-ion generator. A small roof on top closes the top of the pipe socket. The roof at the same time holds the lateral openings 50 free of fine copper granulate which is present in this region of the metal-ion generator. Below the bottom, there is a mixing and collection chamber 51. Copper particles and impurities which were able to pass through the screen are collected in it. After opening the base plate 52, the chamber is accessible for cleaning purposes. Upon operation, the plating solution pumped out of the anode space 16, which solution is enriched in copper-dissolving ferric ions, enters. In addition, air which contains oxidizing oxygen can also be blown into the metal-ion generator via lines 56. In this case, the chamber 51 serves at the same time as mixing chamber. Through the holes 50 in the pipe socket 49, the plating solution and possibly air enter into the inside of the metal-ion generator. In the lower region of the generator there is predominantly fine copper granulate which has been formed by the dissolving of the metallic copper. It has a very large specific surface, which offers itself immediately for the dissolving of copper to the incoming plating solution which is enriched in ferric ions. The ferric ions are therefore rapidly reduced to ferrous

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ions, with the simultaneous dissolving of copper. Within the metal-ion generator, the quantity of ferric ions decreases rapidly towards the top. This has the result that the electrolytic copper which has been introduced as granulate or sections 53 is dissolved in upward direction to a continuously lesser extent. The dimensions of the granulate remain large in the upper region of the metal-ion generator. Thus, the permeability for the plating solution is also retained. Through the overflow 54, the solution discharges without pressure from the metal-ion generator into the electrolyte container 45. Within the metal-ion generator, the overflow 54 bends downward in such a manner that copper granulate 53 which slides downward from above cannot lead to the clogging of the generator. As a result of the sufficiently large dwell times, adapted to each other, of the plating solution which has entered into the generator, and which, at the same time, is sufficiently long for the dissolving of the copper surface offered, the plating solution which flows over the overflow 54 into the electrolyte container 45 contains practically no ferric ions any longer. Such an over-dimensioning of the regeneration unit thus provides assurance that the attack of the ferric ions on the addition compounds of the plating solution is complete already in the middle region of the generator.

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The filling and refilling of the metal-ion generator with metallic copper 53 is effected from above, through the opening 47 of, for instance, hopper shape. It can be closed by a cover. The region above the overflow 54, in which no plating solution is present, serves for the storing of metallic copper which is to be dissolved in the metal-ion generator. The filling and refilling can be effected manually. The arrangement is excellently suited for the automating of the filling process due to the absence of pressure at the filling opening 47 and the vertical or oblique arrangement. The filling can take place continuously or batchwise. Transport belts or vibratory conveyors (not shown here) which are known from the conveyance art transport the metallic copper into the openings 47 of the generators.

The invention has the advantage that copper parts of different geometrical shape can be dissolved in the metal-ion generator. Different shapes, however, have a different piling behavior. In order to maintain the permeability of the pile for the plating solution and to assure a sufficiently large copper surface which is accessible to the solution, additional individual measures are possible:

Downwardly inclined plates 55 within the generator prevent too great a compacting of the copper in the lower region. The plates are provided with holes the dimensions of which are adapted to the size of the metallic copper parts

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introduced. The holes are selected from plate to plate smaller from top to bottom corresponding to the dissolving of the copper. Similarly, the dimensions of the plates can increase from the top to the bottom. The angle of inclination can also be adapted to the circumstances of the pieces of copper introduced into the metal-ion generator.

The inclined position of the metal-ion generator itself can have the same result. By the blowing of air 56 into the lower region of the metal-ion generator or into the mixing and collecting chamber 51, a copper-dissolving substance, in this case oxygen, can also be introduced. In addition to this, the eddying of the copper granulate in the metal-ion generator connected therewith increases the reduction of the ferric ions and the dissolving of the copper. At the same time, the permeability for the plating solution through the copper parts is increased. With copper fillings which hook on to each other, it may be advisable to shake the metal-ion generator at times or continuously. The shaking movement can preferably be obtained from a vibrating conveyor, with which the automatic filling can at the same time be effected. All the measures described above for disturbance-free continuous operation of the metal-ion generator can also be combined with each other.

The electrolyte containers 45, 67 shown in Figs. 5 and 6 serve to reduce the dependence of the flow of the plating

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solution along the treatment material 6, 69 on the flow through the metal-ion generator 44, 66. This has the advantage that, in both circuits, the quantity of plating solution and its speed can be adjusted individually. These processes are described below with reference to Fig. 5.

The plating solution is conveyed by a pump 57 from the electrolyte container 45 into the electrolyte space 1. The solution flows through the flood pipes 58 arranged there onto the treatment material 6 and from the flow pipes 59 onto the liquid-pervious insoluble anodes 5. The division of the stream of solution over the flow pipes 58 and 59 is effected by adjustable valves, not shown in the drawing. From the cathode space 15, the plating solution flows via the outlet 8 through pipelines 60 and the outlet 61 back into the electrolyte container 45. Closely behind the anodes 5 there are suction pipes 62 through which the plating solution enriched with ferric ions is drawn off by means of the pump 63 and conveyed with high speed into the metal-ion generator. From there, the solution enriched with ferrous and cupric ions then returns again into the electrolyte container 45.

The division of the streams over the flood pipes 58 and 59 is so adjusted that an excess results in the cathode space 15. This equalizes itself with the anode space 16. If the two spaces are separated by a partition wall 17, as shown in Fig. 5, then at least one opening 64 in the partition wall

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sees to it that the equalizing of the plating solutions in the two spaces can take place in the direction indicated by the arrow. In order to avoid a mixing of the solutions in the electrolyte space 1 and a convective transport of ferric ions from the anode space to the cathode space, it therefore need merely be seen to it that a higher hydrostatic pressure is present in the plating solution in the cathode space 15 than in the anode space 16. This is assured by a corresponding adjustment of the partial streams through the flood pipe 58 and the flood pipes 59 of the circuit of the pump 57. In addition, the circuits of the pumps 57 and 63 are independent of each other.

Within the metal-ion generator, all ferric ions introduced with the feed stream are reduced to ferrous ions. Nevertheless, it cannot be excluded that a very small, scarcely measurable number of ferric ions pass through the metal-ion generator and enter into the electrolyte container 45. In order to reduce the ferric ions which have entered into said container to ferrous ions, copper parts 65 are introduced also into this container. In this case, copper scrap may also be used.

Another embodiment of the apparatus in accordance with the invention for the carrying out of the process is shown in Fig. 6. There is concerned here a horizontal circuit board electroplating installation shown in cross section. The

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figure shows the metal-ion generator 66, an electrolyte container and an electroplating cell 68. The circuit board 69 which is to be metallized is gripped in the arrangement by clamps 70 and conveyed horizontally through the installation. The contacting of the circuit board with the negative pole of a rectifier (not shown) is also effected via these clamps. In another embodiment, the contacting could also be effected by contact wheels. A pump 71 pumps the plating solution via flood pipes 72, 73 to the circuit boards and to the insoluble perforated anodes 74. Via outlets 75, the plating solution is conducted out of the cathode space back into the electrolyte container 67. From the anode space, the pump 86 conducts the plating solution which has been enriched with ferric ions through suction pipes 76 at high speed into the metal-ion generator. An outlet 77, which is developed as overflow for regulating the level, sees to it that excess plating solution passes from the upper region of the anode space also into circuit to the metal-ion generator 66 and not into the electrolyte container 67. The metal-ion generator is constructed in the manner which was described with reference to Fig. 5. Via the overflow 78, the plating solution passes back into the electrolyte container 67. In the latter, there are also contained copper parts 79 which effect a reduction to ferrous ions of stray ferric ions which are possibly present in this region. Furthermore, partition

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walls 80 are provided between the anode and cathode spaces. Openings 81 in these partition walls see, here also, to an equalization of the streams of the plating solution from the cathode space into the anode space. These directions of flow are also established if no partition walls are present.

Horizontally operating continuous installations such as shown in Figs. 4 and 6, and vertically operating electroplating installations have dimensions of several meters in length of the electrolytic cells. Therefore, in practice, preferably several metal-ion generators are arranged along the installation. This makes it possible to set them up in close spatial vicinity to the electrolytic cell or effect a partial or complete placing of electrolytic cell, electrolyte container, and metal-ion generator one within the other.

During the passage of a circuit board through the electroplating installation, the clamps 70 are also metallized in the region of their contacts 82. This layer must be removed again before the clamps are again used. This is done, in known manner, during the return of the clamps to the start of the electroplating installation. In this connection, the returning clamps 83 pass through a separate compartment 84 which is connected with the plating solution in the electrolytic cell 68. For the demetallization, the clamps 83 are connected via wiper contacts with the positive

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pole of a rectifier, not shown. The negative pole of this rectifier is connected to a cathode plate 85. During the electrolytic demetallization process, copper deposits on the insulating layers of the clamps 83 lose electric contact with the current supply before they are completely dissolved. Therefore, disturbing deposits of copper on these regions remain back. In accordance with the invention, therefore, the parameters for the demetallization, namely current and time, are so adjusted that, for instance, only 70% of the demetallization path is required for the removal of the metal layer. In the remaining path, Fe^{3+} ions are produced by the electrolysis current on the metallic contacted parts of the clamps. These ions are present precisely at the place where contact-less copper deposits are possibly still present. They dissolve this copper electroless. No noticeable increase in ferric ions in the electrolytic cell occurs as a result of this since, as compared with the metallizing of the treatment material, only very small currents and surfaces are concerned.

In order to maintain an operable deposition of metal, the copper content in the plating solution must be kept within given limits. This presupposes that the consumption rate and the rate of addition of copper ions correspond. In order to check the copper content, the absorption power of the plating solution can be measured at a wavelength of for

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instance 700 nm. The use of an ion-sensitive electrode has also proven suitable. The measured value obtained serves as actual value of a controller the control value of which is used to maintain the copper-ion concentration in the specific embodiments of the invention described.

For the analytical noting of the concentrations of the compounds of the redox system, a potential measurement can be carried out. For this purpose, a measurement cell is used which is formed of a platinum electrode and a reference electrode. By suitable calibration of the measured potential with the concentration ratio of the oxidizing and reduced compounds of the redox system for a given total concentration of the compounds, the corresponding concentration ratio can be determined. The measurement electrodes can be installed both in the anode and cathode spaces as well as in the pipelines of the arrangement.

In order to verify the anode processes, such as, for instance, the oxidation of the redox system required for the production of copper and a possible anodic decomposition of the addition compounds, a further measuring device can be provided with which the cathode potential is measured with respect to a reference electrode. For this purpose, the anode is connected via a potential measuring instrument with the corresponding reference electrode.

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The continuous or discontinuous measurement of further galvanotechnical parameters is advisable, such as, for instance the determination of the content of addition compounds by means of cyclic voltametrics. Thus, after lengthy pauses in operation, temporary changes in the concentration can occur. Knowledge of the instantaneous values can be utilized in order to avoid improper dosaging of the chemicals to be added.

The following examples serve for further explanation of the invention:

Example 1

In an arrangement in accordance with Fig. 2, using the measures in accordance with the invention (large specific surface of the copper parts in the metal-ion generator, high velocity of flow in the entire arrangement, conducting of the flow in such a manner that the oxidizing compounds of the redox compounds formed by oxidation at the anode cannot reach the cathode), a copper bath having the following composition was used:

80 g/liter copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

180 g/liter sulfuric acid, conc.

10 g/liter iron as ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)

0.08 g/liter sodium chloride

with the following brighteners:

1.5 g.liter polypropylene glycol

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0.006 g/liter 3-mercaptopropane-1-sulfonic acid, sodium salt

0.001 g/liter N-acetylthiourea

A current efficiency of 84% was determined. The consumption was determined over 100 amp hours/liter as:

propyleneglycol 3.3 g/kAh

3-mercaptopropane-1-sulfonic acid

sodium salt 0.3 g/kAh

N-acetylthiourea 0.04 g/kAh

The elongation upon rupture of the deposited layers amounted to 17% at the end of the test.

Example 2

The test of Example 1 was repeated in the arrangement shown in Fig. 3, the plating solution being conducted serially through the cathode and anode spaces. A current efficiency of 92% was obtained. The consumption, again determined over 100 amp hours/liter, was:

propyleneglycol 2.0 g/kAh

3-mercaptopropane-1-sulfonic acid

sodium salt 0.2 g/kAh

N-acetylthiourea 0.02 g/kAh

The elongation upon rupture was improved to 20%. In this test, the coated circuit boards passed a second soldering shock test (10 seconds at 288°C soldering

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temperature) without cracks in the region of the holes. The deposition was uniformly shiny.

Example 3

In a horizontal installation in accordance with Fig. 4, circuit boards were copper-plated in a plating solution of the following composition:

80 g/liter copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

200 g/liter sulfuric acid, conc.

8 g/liter iron as ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$)

0.06 g/liter sodium chloride

As brighteners there were added:

1.0 g/liter polypropylene glycol

0.01 g/liter 3-(benzthiazolyl-2-thio)-

propylsulfonic acid, sodium salt

0.05 g/liter acetamide

With an electrolyte temperature 34°C , bright metal layers were obtained on a scratched copper laminate with a current density of 6 amps/dm^2 . The circuit board metallized in this manner withstood five soldering shock tests (10 seconds at a soldering temperature of 288°C). The current efficiency was 91.%. No problems arose in the handling (making up of the addition substances consumed) of the plating solution.

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Example 4 (Comparison Example)

The test described in Example 1 was carried out in an electrolysis cell. The measures in accordance with the invention were not used, in particular not the feeding of the stream to the cathodes and anode in accordance with the invention.

At a temperature of the plating solution of 30°C, bright metal layers were obtained on scratched copper laminate surface with a current density of 4 map/dm². The cathodic current efficiency was only 68%. The consumption of the addition compounds without entrainment of the plating solution by lifting the treatment material out of the bath container amounted, averaged over 100 amp hours/liter, was:

propyleneglycol	5 g/kAh
3-mercaptopropane-1-sulfonic acid	
sodium salt	1.6 g/kAh
N-acetylthiourea	0.2 g/kAh

The elongation upon rupture of the deposited layers was only 14% at the end of the test.

Example 5 (Comparison Example)

Copper layers were deposited on circuit boards in accordance with Example 1 after a substrate of copper had been previously deposited from the solution for a lengthy period of time (2000 amp hours/liter).

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The circuit boards no longer withstood two soldering shock tests (10 seconds at a soldering temperature of 288°C) without cracks. Furthermore, non-uniform copper layers were obtained. In Examples 1 to 3, copper layers with good to very good elongation upon rupture were, to be sure, deposited. The cathodic current efficiency and the consumption of the addition compounds which were added to the plating solution in order to control the physical-mechanical layer properties, were satisfactory. The appearance of the copper layers was excellent and withstood the use tests.

After lengthy loading of the plating solution upon the electrolytic deposition of copper, on the other hand, no suitable results were obtained any longer.

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CLAIMS

1. A process for the electrolytic deposition of uniform metal layers of given physical-mechanical properties, in particular layers of copper, with high current efficiency from a plating solution containing ions of the deposited metal, compounds of a electrochemically reversible redox system, and addition compounds for controlling the physical-mechanical properties of the metal layers, in which
 - cathodes;
 - insoluble, dimensionally stable anodes;
 - a metal-ion generator by means of which the metal ions are formed by the dissolving of suitable metal parts upon passage of the plating solution containing oxidizing compounds of the redox system formed by anodic oxidation; and
 - means by which the concentration of the oxidizing compounds in the direct vicinity of the cathode is minimized, preferably to a value of less than about 0.015 moles/literare used.
2. A process according to Claim 1, characterized by the fact that the concentration of the compounds of the redox system is held slightly below a value which is

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necessary in order to maintain the metal-ion concentration.

3. A process according to any of the preceding claims, characterized by the fact that the surface of the metal parts is selected so large that the concentration of the oxidizing compounds is lowered to a value of about zero upon passage through the metal-ion generator.
4. A process according to any of the preceding claims, characterized by the fact that the plating solution passes to the anodes with a high velocity of flow and is transferred from there to the metal-ion generator with high velocity.
5. A process according to any of the preceding claims, characterized by the fact that at least one second oxidizing compound, preferably oxygen, is furthermore introduced into the metal-ion generator.
6. A process according to any of the preceding claims, characterized by the fact that a part of the solution present in the cathode space is conducted directly to the metal-ion generator without being fed to the anodes.
7. A process according to any of the preceding claims, characterized by the fact that the plating solution which is conducted through the metal-ion generator flows

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directly to the cathode and then, by deflection of the direction of flow, to the anodes.

8. An apparatus for the electrolytic deposition of uniform layers of metal of given physical-mechanical properties, in particular copper, with high current density, from a plating solution which is in contact with cathodes (6, 24, 69) and with insoluble, preferably perforated, dimensionally stable anodes (5, 23, 74), comprising an electrolyte space (1) arranged between the cathodes and the anodes, means for feeding the plating solution to the cathode and anode, a metal-ion generator (2, 21, 44, 66), a first means for transferring the plating solution fed to the anodes to the metal-ion generator, and a second means for transferring the plating solution emerging from the metal-ion generator into the electrolyte space, said means bridging over a distance of small space between the anodes and the metal-ion generator.
9. An apparatus according to Claim 8, characterized by the fact that means (31, 62, 76) are provided by which the plating solution present in the vicinity of the anodes is drawn off with high velocity or is removed via outlets (4, 61, 77) and transferred to the metal-ion generator (2, 21, 44, 66).

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10. An apparatus according to either of Claims 8 or 9, characterized by the fact that the electrolyte space (1) is divided into several compartments by ion-permeable partition walls (17, 38, 80).
11. An apparatus according to any of Claims 8 to 10, characterized by the fact that outlets (18, 75) are provided by which the plating solution present in the vicinity of the cathodes is removed from the electrolyte space (1) and brought to the metal-ion generator (2, 21, 44, 66).
12. An apparatus according to any of Claims 8 to 11, characterized by the fact that as metal-ion generator (2, 21, 44, 66) there is provided a tubular apparatus which can be filled from the top and is provided with a bottom (48) in its lower region and, for the entrance of the plating solution, with at least one pipe connection (49) having lateral openings (50), and, in its upper region, with an overflow (54, 78) which discharges into an electrolyte container (45, 67),
13. An apparatus according to any of Claims 8 to 12, characterized by oblique, preferably perforated, plates (55) within the metal-ion generator (2, 21, 44, 66).

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14. An apparatus according to any of Claims 8 to 13, characterized by means for the blowing-in of air (56) arranged in the lower region of the metal-ion generator (2, 21, 44, 66).
15. An apparatus according to any of Claims 8 to 14, characterized by means (26, 70, 82) for the horizontal grasping, electrical contacting, and movement of the cathodes in horizontal direction.
16. The use of the process according to any of Claims 1 to 7 for the metallizing of circuit boards.
17. A process for the electrolytic deposition of metals, characterized by some or all of the new features or by combinations of the features disclosed.
18. An apparatus for the electrolytic deposition of metals, characterized by some or all of the new features or by combinations of the features disclosed.

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PROCESS AND ARRANGEMENT FOR THE ELECTROLYTIC DEPOSITION OF METAL LAYERS

ABSTRACT OF THE DISCLOSURE

For the electrolytic deposition of uniform layers of metal having given physical-mechanical properties, particularly of copper, soluble anodes are not used, since their geometrical shape is changed by the deposition and therefore the distribution of the lines of force in the electrolytic cell are continuously changed.

In order to solve the problems occurring in this connection, a process has been proposed in which compounds of a redox system added to the plating solution are converted during the deposition on the insoluble anodes. The compounds produced in this connection dissolve new metal ions from a reservoir which contains parts of the metal to be deposited, so as again to supplement the metal ions removed from the solution by deposition.

The present invention describes a procedure in which, differing from the prior art, the addition compounds are not destroyed.

Fig. 6

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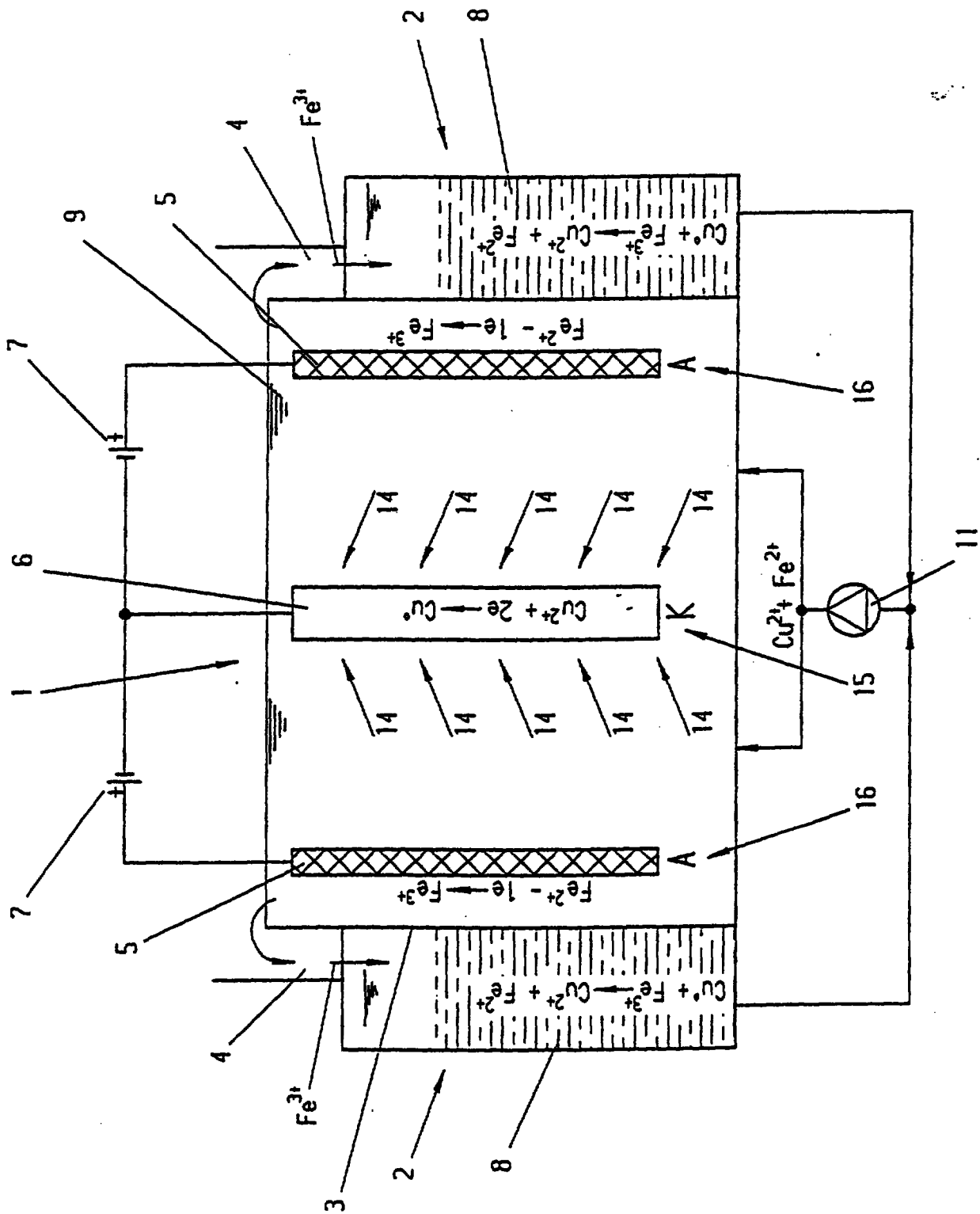


Fig. 1

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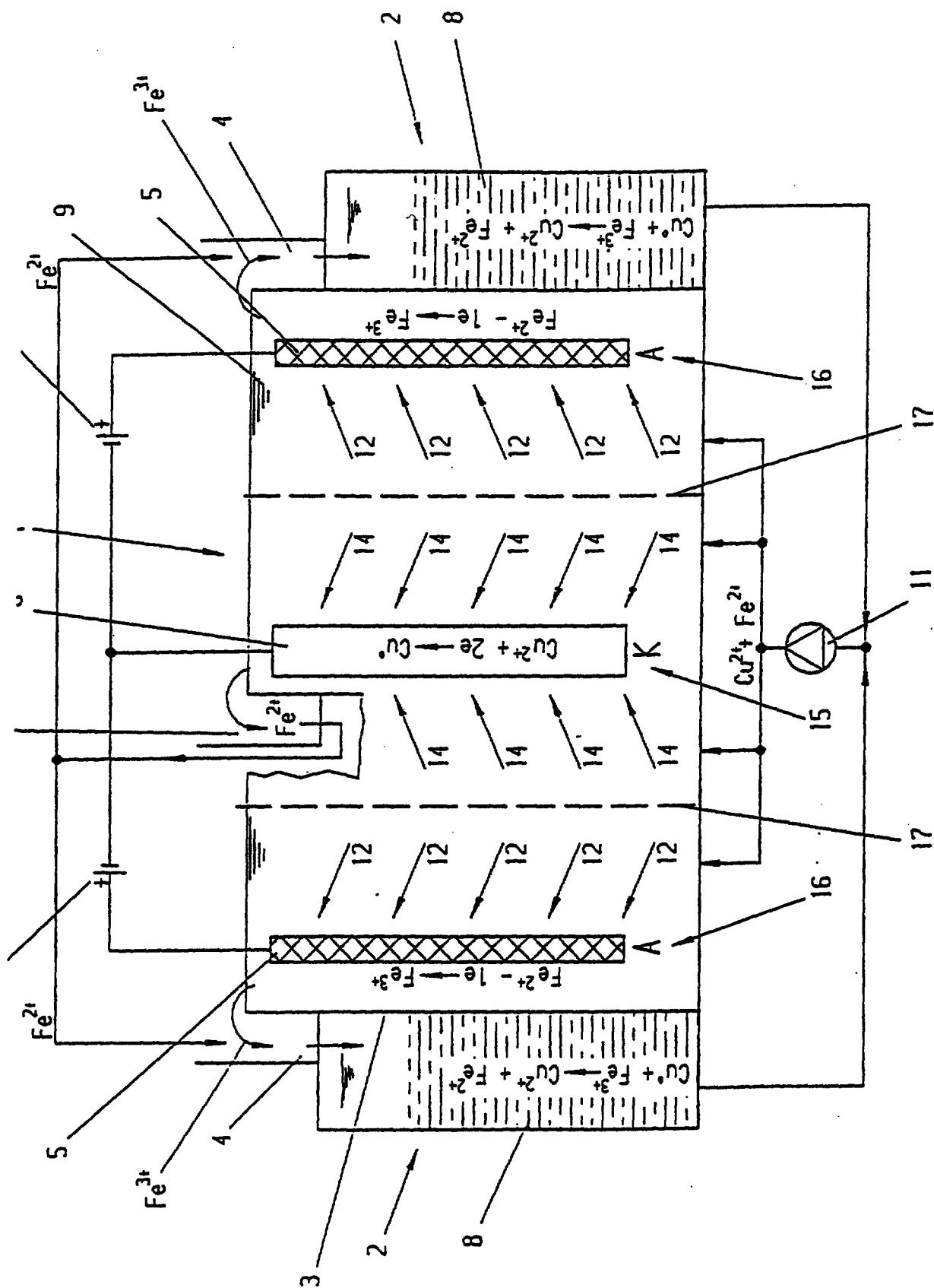


Fig. 2

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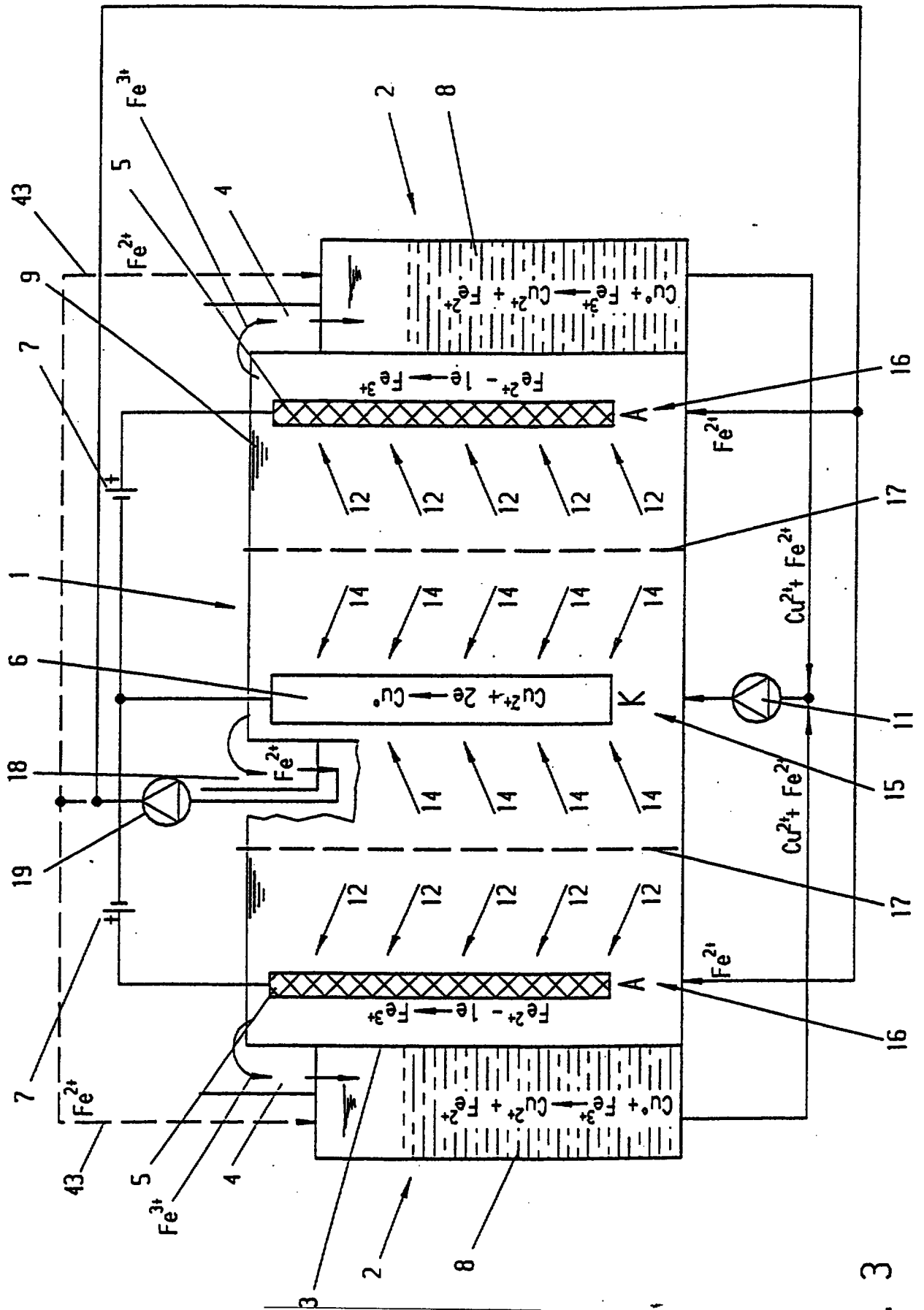


Fig. 3

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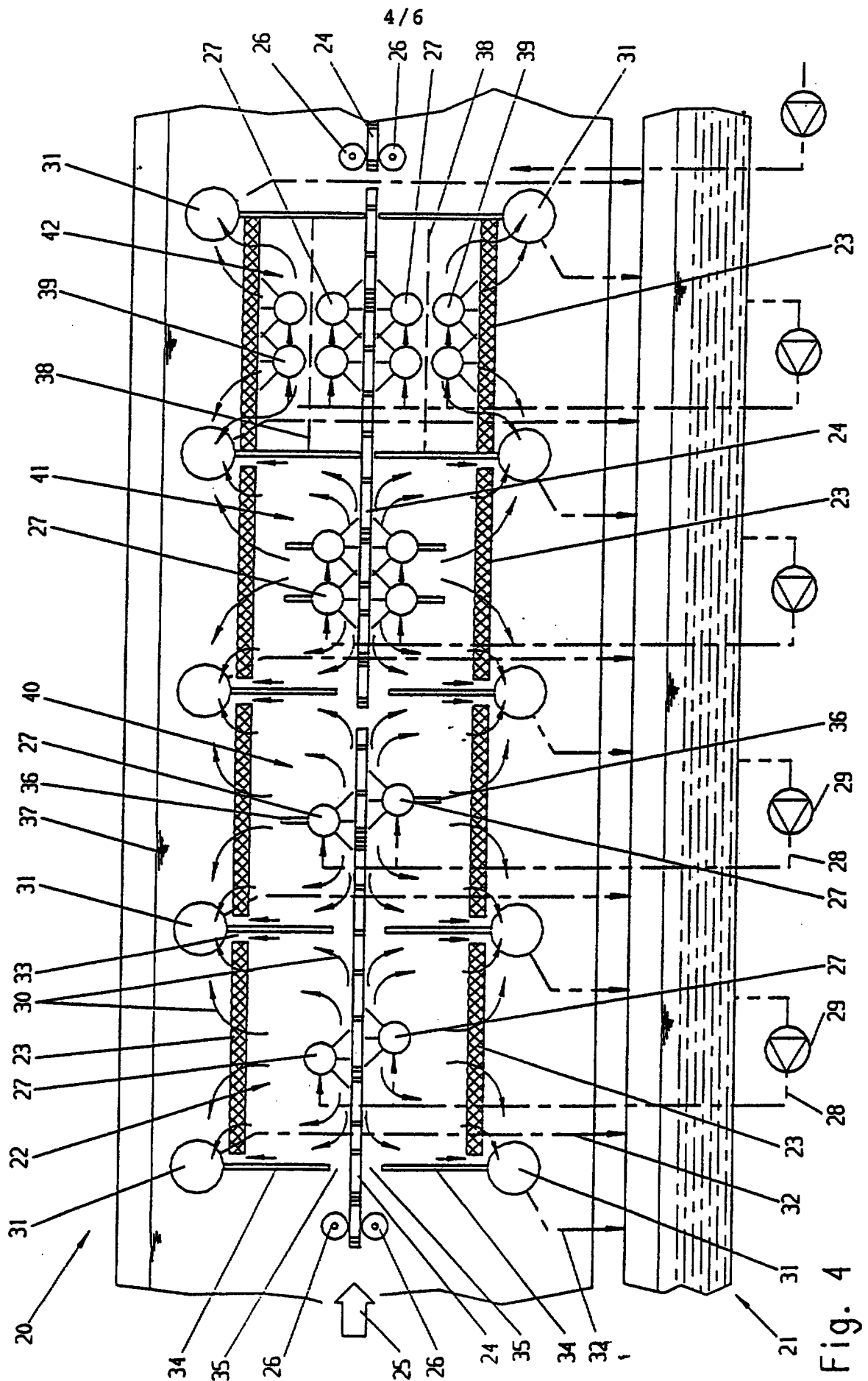
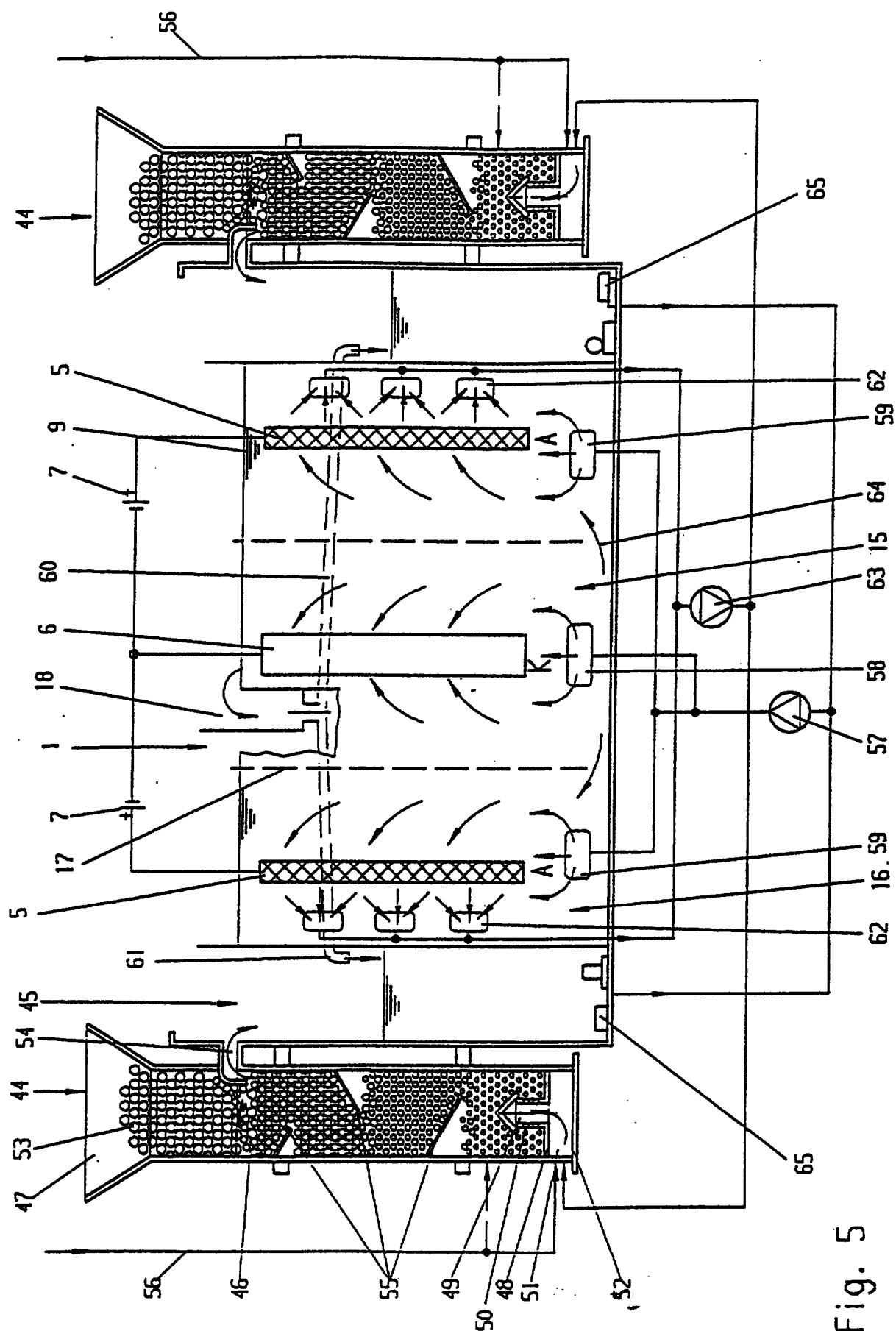


Fig. 4





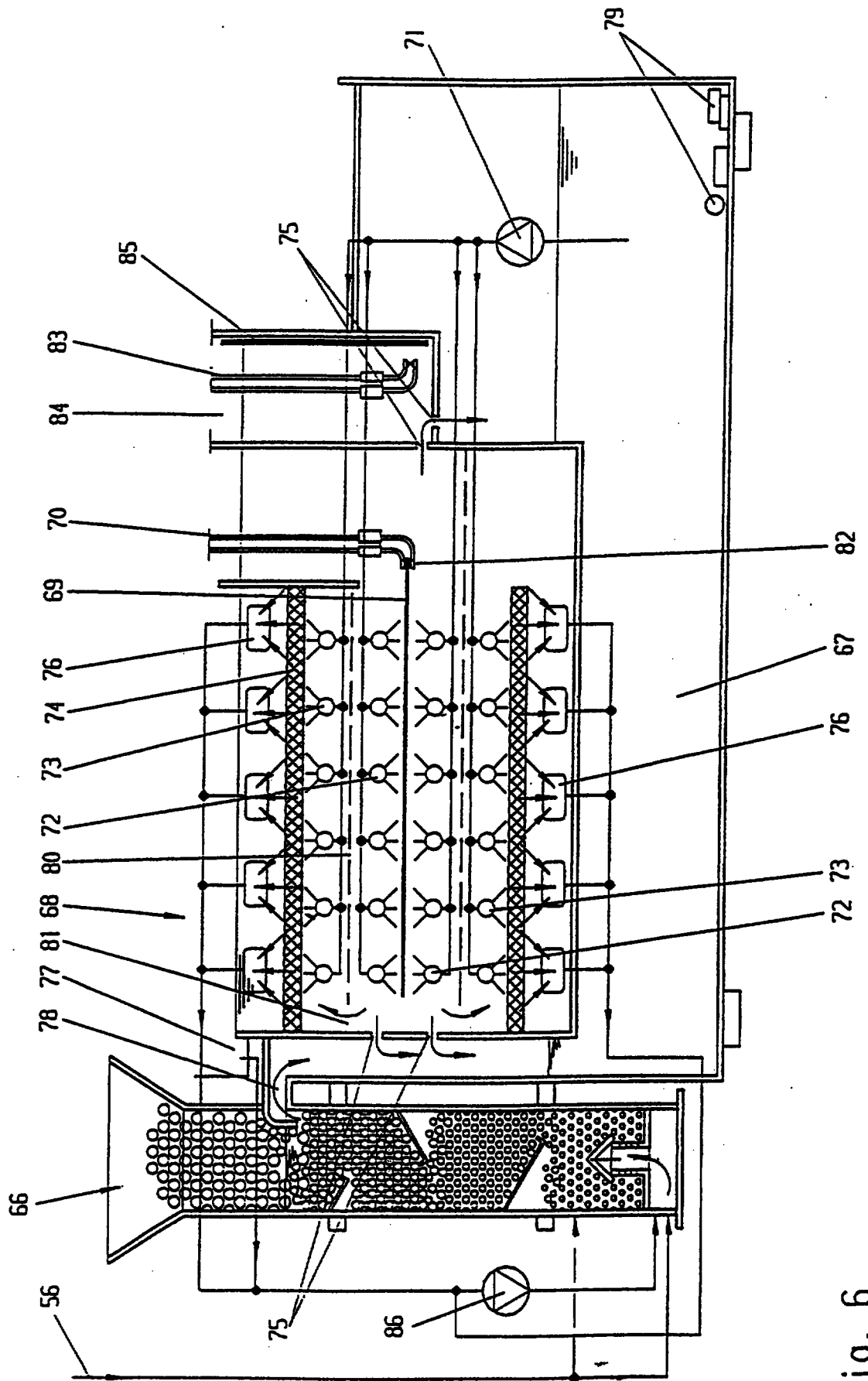


Fig. 6

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PROCESS AND DEVICE FOR ELECTROLYTIC PRECIPITATION
OF METALLIC LAYERS

The present invention relates to a process and an apparatus for the electrolytic deposition of uniform metal layers, preferably of copper, having given physical-mechanical properties.

The electrolytic metallization, for instance with copper, of workpieces which are electrically conductive at least on their surface, has been known for a long time. For this purpose, the workpieces which are to be coated are connected as cathode and, together with anodes, brought into contact with the electrolytic plating solution. For the deposition, a flow of electric current is produced between anode and cathode.

Ordinarily, anodes of the material which is deposited from the plating solution are used. In that case, the amount of metal deposited from the solution is returned to the plating solution by dissolving at the anodes. In the case of copper, the amount deposited and the amount which is anodically dissolved are approximately the same for a given charge flow. This process is easy to carry out since, at least in the case of copper, only sporadic measurement and control of the metal-ion concentration of the plating solution is necessary.

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However, disadvantages have been encountered when carrying out the process with these soluble anodes. If the thickness of the metal layers deposited is to be very uniform at all places on the surface of the workpiece, then the soluble anodes are only conditionally suitable for this purpose, since the latter change shape with time due to the dissolving, so that the distribution of the lines of force in the electrolytic bath also changes. The use of smaller, for instance spherical, pieces of metal as anodes in insoluble metal baskets is also only conditionally suitable for solving the problem, since the metal parts frequently wedge against one another and as a result of the dissolving process gaps are frequently formed upon the sliding down in the pile of metal parts.

Therefore, attempts have frequently been made to use insoluble, and therefore dimensionally stable anodes, rather than soluble metal anodes. As materials, titanium or high-grade steel, for instance, enter into consideration for this. By the use of these anode materials, gases, such as for instance oxygen or chlorine, are formed upon the electrolytic deposition since the anodic dissolving of metal no longer takes place. The gases produced attack the anode materials and gradually dissolve them.

German Patent DD 215 589 D5, describes a process for the electrolytic deposition of metal with the use of insoluble

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metal anodes in which reversibly electrochemically convertible substances are added as addition to the plating solution, they being transported by intense positive convection with the plating solution to the anodes of a plating apparatus, converted electrochemically there by the electrolysis current, conducted, after their conversion, by intense positive convection away from the anodes into a regeneration space, returned electrochemically to their initial condition in the regeneration space on regeneration metal present in it with simultaneous electroless dissolving without external current of the regeneration metal, and fed in this initial condition again to the separation apparatus by intensive positive convection. By this process, the above-indicated disadvantages with the use of insoluble anodes are avoided. Instead of the corrosive gases, the substances added to the plating solution are oxidized at the anode, so that the anodes are not attacked.

The dissolving of the metal in the regeneration space is in this case independent of the process of the deposition of metal on the material being treated. Therefore, the concentration of the metal ions which are to be deposited is controlled by the effective metal surface in the regeneration space and by the velocity of flow in the circuit. In the case of a deficiency of metal ions, the effective metal surface and/or the velocity of flow from the deposition space

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to the regeneration space is increased or, in case of an excess of metal ions, correspondingly reduced. This process therefore presupposes that a high concentration of the reversibly electrochemically convertible substance is present in the plating solution. This has the result that the oxidized compounds of the addition substances (redox system) are again reduced at the cathode, so that the current efficiency is decreased.

In German Unexamined Application for Patent DE 31 10 320 A1, a process is described for cation reduction by anode-supported electrolysis of cations in the cathode space of a cell, the anode space containing ferrous ions as reducing agent and anodes being moved relative to the anolyte which surrounds the anodes.

In German Unexamined Application for Patent DE 31 00 635 A1, a process and an apparatus are described for supplementing an electroplating solution with a metal to be precipitated in an electroplating apparatus, wherein the metal which is to be galvanically precipitated is provided in an electroplating solution which is contained in an electroplating container and a supply of the metal to be precipitated is provided within an enclosed space, the gases produced in the electroplating container upon the advance of the electroplating process are conducted, together with the electroplating solution, into said enclosed space and applied

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there to said supply of metal in order to dissolve the latter, whereupon the dissolved supply of metal is again added to the electroplating solution in the electroplating container. The apparatus required for the carrying out of the process is, however, very expensive, since, among other things, it must be gas-tight.

Said processes have the disadvantage that the plating solutions to be regenerated contain no addition compounds, which, however, are ordinarily required in order to control the physical-mechanical properties of the metal layers to be deposited. Such substances are predominantly organic substances.

It is only by these addition compounds that the required physical-mechanical properties of the layers such as, for instance sufficient brightness, high elongation upon rupture, and resistance of the layer to cracks upon soldering shock tests are obtained. Without the addition of these compounds, the layers are dark, dull, and rough.

DD 261 613 A1 describes a process for the electrolytic deposition of copper from acid electrolytes with dimensionally stable anode using certain additions for the production of layers of copper having specific physical-mechanical properties, the plating electrolyte also containing the aforementioned electrochemically reversibly convertible addition substances.

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It has been found that, although the quality of the metal layers precipitated from such plating solutions initially satisfy the requirements, in particular with regard to the physical-mechanical properties, nevertheless, after a longer period of deposition, layers of poorer quality are obtained even if the substances in the plating solution whose concentration was decreased by consumption upon the deposition are supplemented. Copper coatings which are only poorly ductile are obtained from aged plating solutions, so that such layers tear on printed circuits in the region of the holes when they are subjected to a soldering shock test. Furthermore the surface of the metal layer then changes in disadvantageous manner, in that it becomes dull and rough.

The present invention therefore proceeds from the problem of avoiding the disadvantages of the processes and arrangements of the prior art and of finding an economical process, and suitable apparatus, for the electrolytic deposition of layers of metal, particularly of copper, in which the metal layers deposited by the process and the apparatus have predetermined physical-mechanical properties, in the manner that addition compounds are added to the plating solution in order to control the properties of the metal layers, and the properties of the metal layers do not change in disadvantageous manner even after a lengthy period of deposition. Furthermore, the thicknesses of the metal

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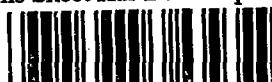
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layers are to be approximately the same at all places on the surface of the material treated, and the deposition is to be possible with high current efficiency.

This problem is solved by Claims 1, 8, and 16. Preferred embodiments of the invention are set forth in the dependent claims.

In order to obtain sufficiently uniform layer thicknesses on the surface of the material being treated, insoluble, dimensionally stable, anodes are used. In order to supplement the metal ions consumed by deposition, namely in a preferred use copper ions, a metal-ion generator is used in which parts consisting of the metal to be deposited are contained. The plating solution contains, in addition to the metal ions, compounds of an electrochemically reversible redox system. For the regeneration of the plating solution which has become impoverished by consumption of metal ions, it is passed by the anodes, whereby the oxidizing compounds of the redox system are formed. Thereupon, the solution is conducted through the metal-ion generator, the oxidizing compounds reacting with the metal parts, with the formation of metal ions. At the same time, the oxidizing compounds of the redox system are converted into the reduced form. By the formation of the metal ions, the total concentration of the metal-ion concentration contained in the plating solution is maintained constant. From the metal-ion generator, the

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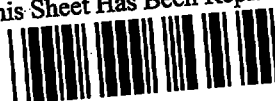
plating solution passes back again into the electrolyte space which is in contact with the cathodes and anodes.

The solution furthermore contains addition compounds for controlling the physical-mechanical properties of the layer. In order to maintain the properties of the layer even after a lengthy period of deposition from the plating solution, means are provided in accordance with the invention by which the concentration of the oxidizing compounds of the redox system in the direct vicinity of the cathode can be minimized, preferably to a value below about 0.015 mole/liter.

Obviously, the addition compounds can be decomposed by the oxidizing compounds of the redox system. In this way, the concentration of the addition compounds would, on the one hand, be reduced in uncontrolled fashion. Since the determination of the concentration of these compounds is in general very cumbersome, while the content of the compounds is very sensitive to the physical-mechanical properties of the layers, only layers having varying properties could necessarily be deposited, since a sufficiently rapidly acting and precise technique of analysis for such requirements is not available.

This problem would furthermore be intensified by the fact that upon the decomposition of the addition compounds reaction products are formed which have a detrimental effect on the properties of the layer, so that, after lengthy

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duration of the electrolysis, even if the content of the addition compounds is maintained by enrichment of the injurious reaction products, only layers the properties of which would not satisfy the requirements made could still be deposited.

The means in accordance with the invention by which the concentration of the oxidizing compounds in the vicinity of the cathode can be minimized, preferably to a value less than about 0.015 mole/liter, are described below:

The total amount of the compounds of the redox system added to the plating solution is so determined that substantially the entire amount of the oxidizing compounds of the redox system fed to the metal-ion generator with the plating solution is required for the dissolving there of the metal parts with the formation of metal ions.

The amount of metal ions provided by the dissolving must just supplement the portion which is lost in the plating solution by the deposition. In order to maintain the metal-ion concentration and for the complete reduction of the amount of oxidizing compounds introduced into the metal-ion generator, a minimum size of the surface of the metal parts in the metal-ion generator is therefore required. This surface can be increased in upward direction as far as desired and, in particular, however, need not be variable. Thus, the further filling of the metal parts into the metal-

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ion generator can be effected in a technically simple manner in any desired amounts above said minimum amount.

The spatial distance between the anodes and the metal-ion generator must be small, and the connections for transferring the plating solution which has reached the anodes to the metal-ion generator and from the metal-ion generator back into the electrolyte space must be short. In this way, the result is obtained that the dwell time of the oxidizing compounds in the electrolyte space is short. By the rapid transfer of the plating solution containing the oxidizing compounds into the metal-ion generator, these compounds also have only a short life until they are converted into the reduced compounds of the redox system.

Furthermore, the velocity of flow of the plating solution must be as high as possible, particularly upon the transfer from the anodes to the metal-ion generator.

In order to keep the concentration of the oxidizing compounds as small as possible, it is furthermore possible to introduce another oxidizing agent directly into the metal-ion generator. Atmospheric oxygen is particularly suitable for this purpose. Upon the reaction of oxygen with the metal parts, only water is produced, it having no effect on the deposition process.

For the introduction of air into the metal-ion generator, means for the blowing-in of atmospheric oxygen are

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provided in the lower region of the generator.

Another possibility for supplementing the metal ions removed by deposition from the plating solution consists, in principle, of adding the metal ions in the form of their compounds or salts to the plating solution. However, in this case, the concentration of the anionic portions of the compounds or salts necessarily added with the metal ions cannot be prevented from increasing continuously due to the continuing addition of the compound, so that, after a certain amount of time, the solution must be discarded. If, in the present case, only a small part of the metal ions to be supplemented by addition of the corresponding compounds or salts, then the time until the discarding of the solution can be rather long. By combining the supplementing of the metal ions by addition of the salt with the regenerating of the solution in the metal-ion generator, the addition of the compounds or salts can be decreased to a few per cent of the necessary supplementation.

In this case, the possibility of controlling the metal-ion concentration in the plating solution in a simple and rapid manner from a control standpoint constitutes an advantage.

By the reduction in the life of the oxidizing compounds of the redox system which are formed on the anode which is obtained by means of said measures, and the minimizing of the

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concentration of the compounds, possible decomposition of the addition compounds is avoided, or at least definitely reduced.

The metal-ion concentration in the electrolyte space can also be controlled by a special manner of circulation of the plating solution. The reduced compounds of the redox system which are converted electrochemically at the anodes by the electrolysis current back into the oxidizing compounds are present in the cathode space. The quantity of the oxidizing compounds and thus the metal-ion concentration can be reduced if only a part of the plating solution is conducted from the space present in the vicinity of the cathode to the anodes and from there into the metal-ion generator. The other part of this solution which does not contain the oxidizing compounds is, on the other hand, conducted directly into the metal-ion generator. For this purpose, separate outlets are provided for the plating solution, they being located in the vicinity of the cathode. The solution which is branched off over the outlets passes through suitable pipelines into the metal-ion generator.

The surface of the metal to be dissolved is, in its turn, dimensioned so amply that all oxidizing compounds introduced into the metal-ion generator can be converted electrochemically.

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By this measure, a simple control of the metal-ion concentration in the plating solution and thus an automating of the control which is simple technically to achieve is made possible. By controlling the volumetric flows of the plating solution from the cathode via the anode into the metal-ion generator, on the one hand, and from the cathode directly into the metal-ion generator, on the other hand, the metal-ion concentration can be easily adjusted.

For the control, the velocity of flow of the plating solution in the circuit and the voltage between cathode and anode can also be adjusted.

The conditions of flow in the electrolyte space are to be such that, on the one hand, a flow of the plating solution is directed from the cathode to the anode and, on the other hand, the plating solution, however, first acts directly on the cathode. This latter is necessary in order to be able economically to produce uniform layers with sufficiently high current densities and predetermined physical-mechanical properties. These flows are produced by direct flow against the cathode by means of nozzle assemblies or surge nozzles and by subsequent deflection of this flow towards the anodes.

The preferred arrangement for the carrying out of the process of the invention comprises, in addition to the cathodes, insoluble, preferably perforated, dimensionally stable anodes, devices for the flow of the plating solution

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against the cathodes and anodes (nozzle assemblies, or surge nozzles), means of deflecting the flow to the anodes and connecting lines for transferring the plating solution which has been fed to the anode to the metal-ion generator as well as for transferring the plating solution emerging at the metal-ion generator back into the electrolyte space. In a preferred embodiment, means for drawing off the plating solution can also be provided in order to increase the velocity of flow upon the transfer of the plating solution from the anodes to the metal-ion generator.

In order to avoid the mixing of the parts of the plating solution which are located in the vicinity of the cathode and/or the anode, the electrolyte space can also be subdivided into several compartments by ion-pervious partition walls (ion-exchanger, diaphragms).

The metal-ion generator is preferably a tubular device which can be filled from above and which is provided with a bottom and, for the entrance of the electrolyte, with at least one pipe socket with lateral openings and also, in its upper region, with an overflow which debouches into an electrolyte container. In one particularly favorable embodiment, oblique, preferably perforated, plates are arranged within the metal-ion generator.

The process is particularly suitable for the metallizing of circuit boards. In this case, copper in particular is

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deposited on their surfaces and on the walls of the holes.

Ordinary dip devices can be used in which the circuit boards are dipped from above into the plating solution, or else horizontal installations in which the circuit boards are grasped horizontally and moved by suitable means in horizontal direction through the installation.

In addition to copper, which can preferable be deposited with the process of the invention from the arrangement which is also described, other metals, for instance, nickel, can also, in principle, be deposited in accordance with the method of the invention.

The basic composition of a copper bath can vary within relatively wide limits when using the process of the invention. In general, an aqueous solution of the following composition will be used:

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	20 - 250 g/liter
preferably	80 - 140 g/liter or 180 - 220 g/liter
Sulfuric acid, concentrated	50 - 350 g/liter
preferably	180 - 280 g/liter or 50 - 90 g/liter
Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) 0	0.1 - 50 g/liter
preferably	5 - 15 g/liter
Chloride ions (added, for instance, as NaCl)	0.01 - 0.18 g/liter

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preferably

0.03 - 0.10 g/liter.

Instead of copper sulfate, other copper salts can also be used, at least in part. The sulfuric acid can also be replaced, in whole or in part, by fluoboric acid, methane sulfonic acid, or other acids. The chloride ions are added as alkali chloride, for instance sodium chloride, or in the form of hydrochloric acid, p.A. The addition of sodium chloride can be dispensed with, in whole or in part, if halogen ions are already present in the additions.

The active $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox system is formed from ferrous sulfate heptahydrate. It is excellently suited for the regenerating of the copper ions in aqueous acid copper baths. However, other water-soluble iron salts can also be used, in particular ferric sulfate nonahydrate, provided that the sales do not contain biologically non-degradable (hard) complex formers in the compound, since the latter result in problems in connection with the disposal of the flushing water (for example, iron-ammonium alum).

In addition to iron salts, compounds of the elements titanium, cerium, vanadium, manganese, chromium and the like are also suitable as further redox systems. Compounds which can be used are, in particular, titanyl sulfuric acid, ceric sulfate, sodium metavanadate, manganous sulfate, and sodium chromate. For special uses, combinations of the above redox systems can also be used.

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With the process of the invention, the other elements which are known and have proven themselves in electrolytic metal deposition can be retained. Thus, ordinary brightening agents, leveling agents and surface-active agents can, for instance, be added to the plating solution. In order to obtain copper precipitates having predetermined physical-mechanical properties, at least one water-soluble sulfur compound and an oxygen-containing high-molecular compound are added. Addition compounds such as nitrogen-containing sulfur compounds, polymeric nitrogen compounds, and/or polymeric phenazonium compounds can also be used.

The addition compounds are contained in the plating solution within the following concentration ranges:

ordinary oxygen-containing

high-molecular compounds

0.005 - 20 g/liter

preferably

0.01 - 5 g/liter

ordinary water-soluble

organic sulfur compounds

0.005 - 0.4 g/liter

preferably

0.001 - 0.15 g/liter

Thiourea derivatives and/or polymeric phenazonium compounds and/or polymeric nitrogen compounds as addition compounds are used in the following concentrations:

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0.0001 - 0.50 g/liter

preferably

0.005 - 0.04 g/liter

For the preparation of the plating solution, the addition compounds are added to the above-indicated basic composition. The conditions for the deposition of copper are indicated below:

pH < 1

Temperature: 15°C - 50°C

preferably 25°C - 40°C

cathodic current density: 0.05 - 12 amp/dm²

preferably 3 - 7 amp/dm²

A few oxygen-containing high-molecular compounds are listed in the following Table 1:

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Table 1: Oxygen-Containing, High-Molecular Compounds.

Carboxymethyl cellulose

Nonylphenol-polyglycolether

Octanediol-bis-(polyalkylene glycol ether)

Octanolpolyalkylene glycol ether

Oleic acid-polyglycol ester

Polyethylene-propylene glycol + polyethylene glycol

Polyethylene glycol-dimethylether

Polyoxypropylene glycol

Polypropylene glycol

Polyvinyl alcohol

Stearic acid polyglycol ester

Stearyl alcohol polyglycol ether

 β -Naphthol polyglycol etherTable 2: Sulfur Compounds

3-benzthiazolyl-2-thio)-propylsulfonic acid, sodium salt

3-mercaptopropane-1-sulfonic acid, sodium salt

Ethylenedithiodipropyl sulfonic acid, sodium salt

Bis-(p-sulfophenyl)-disulfide, disodium salt

Bis-(ω -sulfobutyl)-disulfide, disodium saltBis-(ω -sulfohydroxypropyl)-disulfide, disodium saltBis-(ω -sulfopropyl)-disulfide, disodium saltBis-(ω -sulfopropyl)-sulfide, disodium salt

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Methyl-(ω -sulfopropyl)-disulfide, disodium salt

Methyl-(ω -sulfopropyl)-trisulfide, disodium salt

O-ethyl-dithiocarbonic acid-S-(ω -sulfopropyl)-ester,
potassium salt

Thioglycolic acid

Thiophosphoric acid-O-ethyl-bis-(ω -sulfopropyl)-ester,
disodium salt

Thiophosphoric acid-tris-(ω -sulfopropyl)-ester, trisodium
salt

A few sulfur compounds having functional groups suitable for the production of water solubility are set forth in the above Table 2.

By blowing air into the electrolyte space, the plating solution is moved. By addition action of air on the anode and/or the cathode, the convection in the region of their surfaces is increased. In this way, the mass transport in the vicinity of the cathode and/or anode is optimized, so that higher current densities can be obtained. Corrosive oxidizing agents which are possibly produced in a small amount, such as for instance oxygen and chlorine, are thereby led away from the anodes. Movement of the anodes and cathodes also results in an improved mass transport on the corresponding surfaces. In this way, a constant diffusion-controlled deposition is obtained. The movements can take place horizontally, vertically, in uniformly lateral

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movement, and/or by vibration. A combination with the action of air is particularly effective.

Inert material is used for the anodes. Anode materials which are chemically and electrochemically stable to the plating solution and the redox system used are suitable, for instance titanium or tantalum as base material, coated with platinum, iridium, ruthenium, or their oxides or mixed oxides. Titanium anodes having an iridium-oxide surface which are blasted with spherical bodies and thereby compacted so as to be free of pores were sufficiently resistant, and therefore had a long life. By the anodic current density or the anode potentials adjusted via the voltage between cathode and anode, the quantity of the corrosive reactions produced on the anode is determined. Below 2 amp/dm² their rate of formation is very small. In order, therefore, not to exceed this value, large effective anode surfaces are desirable. Therefore, in the case of limited three-dimensional dimensions, perforated anodes are preferred, for instance, anode nets or expanded metal having a suitable coating are used. In this way, the advantage of a large effective surface is combined with the simultaneous possibility of intensive flow through the anode by the plating solution, so that any corrosive reaction produced can be led away. Anode nets and/or expanded metal can, in addition, be used in several layers. In this way, the effective surface is

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correspondingly increased, so that the anodic current density with a predetermined electroplating current is reduced.

Metal is supplemented in a separate container, the metal-ion generator, which is passed through by the plating solution. In the case of copper deposition, metallic copper parts, for instance in the form of pieces, balls or pellets, are present in the metal-ion generator. The metallic copper used for the regeneration need not contain phosphorus, but phosphorus is not disturbing. Upon the additional use of soluble copper anodes, the composition of the anode material, on the other hand, is of great importance. In that case, the copper anodes must contain about 0.05% phosphorus. Such materials are expensive, and the addition of phosphorus causes residues in the electrolytic cell which must be removed by additional filtration.

Since, in accordance with the method of the invention, it is also possible to use metallic copper parts which contain no additions, electrolytic copper, including copper scrap, is as a rule used. An interesting variant consists therein that the circuit board waste which is coated with copper, such as obtained in large quantities upon the production of printed circuit boards, can also be used for this, provided that it does not contain further metals. This waste, consisting of the polymeric base material and the copper layers applied thereto, can be disposed of in

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traditional manner only at high expense due to the firm bond between the two materials. After the profitable dissolving of the copper of this waste in a metal-ion generator suitable for this, a sorted disposal of the base material is possible. In similar fashion, reject circuit boards can also be used.

Furthermore, filters for the removal of mechanical and/or chemical residues can also be inserted in the circulation of the plating solution. However, the need for them is less than with electrolytic cells having soluble anodes, since the anode sludge produced by the mixture of phosphorus to the anodes is not present.

For the further explanation of the invention, and further preferred embodiments, reference is had to the following diagrammatic figures.

- Fig. 1 shows the principle of an apparatus for the dip treatment;
- Fig. 2 shows the principle of an apparatus without and with diaphragm;
- Fig. 3 shows the principle of an apparatus with serial conducting of the plating solution;
- Fig. 4 shows the principle of an apparatus for the horizontal transport of the material being treated;
- Fig. 5 shows a metal-ion generator on an apparatus for dip treatment;

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Fig. 6 shows a metal-ion generator on an apparatus for the horizontal transport of the material being treated.

In Fig. 1, the process of the invention is shown on basis of a diagrammatically shown apparatus. The electrolyte space 1 is located in the container 3. The metal-ion generator 2 is so constructed and arranged with respect to the container 3 as to result in short paths for the feeding of the plating solution from the anodes 5 to the metal-ion generator and from there back again into the electrolyte space. For this reason, in the present case, the metal-ion generator is divided into two parts arranged in the vicinity of the insoluble anodes. This division in two is, however, not necessary. Thus, for instance, it can also be arranged as a single unit to the side of or below the bath container. The copper parts to be dissolved are introduced in a loose pile into the metal-ion generator in order to permit easy passage of the plating solution through the generator. On the other hand, however, a minimum loading with copper parts must be maintained therein. The pump 11 pumps the plating solution in a closed circuit through the arrangement. It is essential that the material 6 being treated, which is connected as cathode, be acted upon by the plating solution which is enriched in copper ions, as indicated by the arrows 14, via nozzle assemblies or surge nozzles, not shown here. In this way, the result is obtained that the copper layers

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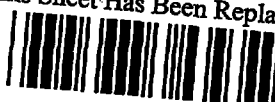
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are deposited on the surface of the material being treated with the necessary quality and the necessary speed. Furthermore, a further flow takes place within the electrolyte space from the space 15 present in the vicinity of the material being treated in the direction towards the space 16 present in the vicinity of the anodes. The plating solution which has been brought to the anodes passes through them, in the case of perforated anode, and arrives, with the advance of the flow, into the outlet 4 which leads to the metal-ion generator. In this way, the result is obtained that a transport of anodically formed oxidizing compounds of the redox system (ferric ions) into the cathode space 15 is minimized. This, in turn, prevents the injurious decomposition of the addition compounds, with simultaneous increase of the cathodic current efficiency.

Along the transport path from the anodes via the outlet into the metal-ion generator, the addition compounds are probably decomposed via a chemical decomposition reaction with the participation of the oxidizing compounds of the redox system. Therefore, the shortest possible connection with high velocity of the plating solution to the metal-ion generator is desirable outside the electrolyte space 1.

The minimum loading of the metal-ion generator with copper parts provides assurance that the oxidizing compounds formed are completely converted within the metal-ion

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generator and the concentration of these compounds at the outlet of the metal-ion generator is lowered to a value of about zero. This means that the copper surface which is in contact with the plating solution in the metal-ion generator leads to the complete reduction of the oxidizing compound to the reduced compounds (ferrous ions), with simultaneous electroless dissolving of copper with the formation of copper ions. The reduced compounds of the redox system do not contribute to the decomposition of the addition compounds.

By targeted flow onto the cathode surfaces, the anodes, for a given total circulation, are subjected to less electrolyte exchange. In this way, the corrosive gases possibly produced at the anodes are led away correspondingly slower, so that, on the one hand, the corrosion of the anodes increases while, on the other hand, it is limited by the following measures:

- low anodic current density
- inert base material of the anodes
- inert coating of the anodes
- surface compacting of the anodes
- liquid-pervious anode geometry.

By these measures, the result is obtained that the addition compounds which are added to the plating solution in order to control the physical-chemical properties of the layer of metal can be used also in arrangements with

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insoluble, dimensionally-stable anodes. Special mixtures of the addition compounds are not necessary for this. A high cathodic current efficiency and a long life of the insoluble anodes is obtained.

Fig. 2 shows another apparatus in accordance with the invention. It differs, on the one hand, from the arrangement shown in Fig. 1 by a difference in the guidance of the plating solution within the electrolyte space, which consists of a space 15 present in the vicinity of the material being treated, namely the cathode space, and of the spaces 16 present in the vicinity of the anodes, namely the anode spaces. These spaces are separated by the dashed lines 17 in the drawing. The plating solution, which was enriched with copper ion in the metal-ion generator 2 upon the reduction of ferric to ferrous ions, flows separately into each space and passes through nozzle assemblies or surge nozzles (not shown) as shown by the arrows 12 and 14 to the anodes 5 and the cathodic treatment material 6. Mixing of the plating solution in the anode space 16 with the solution in the cathode space 15 can take place only to a slight extent, in particular for the reason that the plating solution has its own outlets 4 from the anode space and, separately therefrom, the plating solution has an outlet 18 in the cathode space. In this embodiment, the ferric ion concentration is kept small in the cathode space, which is connected directly with

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the inlet to the metal-ion generator 2, so that a short conduction path from the anode space to the metal-ion generator results. On the other hand, the transport paths from the cathode space via the outlet 18 to the generators can be long, since there are no injurious interactions between the reduced compound which is contained in the plating solution present in the cathode space and the addition compounds. In order to avoid even a slight electrolyte mixing of the plating solutions in the cathode and anode spaces, these spaces can be separated along the lines 17 by, in each case, an ion-pervious partition wall (diaphragm) which, in its turn, is not chemically changed by the plating solution. The partition walls are pervious for the plating solution only to a very slight extent, if at all, so that they permit possibly only a slow equalization of different hydrostatic pressures in the spaces 15 and 16. Polypropylene fabrics or other membranes with a permeability for metal ions and their corresponding gegenions (for instance the Nafion of DuPont de Nemours, Inc., Wilmington, Del., USA) are, for instance, suitable. By separation of the spaces by partition walls, assurance is had that the plating solution cannot pass, for instance, by eddying from the anode space into the cathode space. This measure leads also to a further decrease in the concentration of the oxidizing compounds of the redox system in the vicinity of the cathode.

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Therefore, advantageous effects with respect to the resistance to aging of the plating solution result also from these measures.

The plating solution which is present in the anode space and which contains the ferric ions formed there is, in its turn, transferred, over the shortest path, into the metal-ion generator and enriched there again with copper, with the formation of ferrous ions. In practical operation, a condition of equilibrium between the copper solution in the metal-ion generator and the deposition of copper on the material being treated is established.

Fig. 3 shows another embodiment of the invention, having a two-part metal-ion generator. The plating solution which is enriched in copper ions in the metal-ion generator 2, is introduced only into the cathode space 15. This solution contains, furthermore, only ferrous ions and no ferric ions. The plating solution is conducted in succession from the cathode space 15 to the anode space 16. The ferrous ions formed in the metal-ion generator therefore, after passing through the cathode space, enter with the plating solution via a pump into the anode space. The feeding of the plating solution into the cathode space is effected by another pump 11. A hydrodynamic constancy and the constant transport conditions resulting therefrom are advantageous for the electrochemically active additions of the redox system.

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Furthermore, this serial conducting of the plating solution permits a dividing up of the plating solution withdrawn from the cathode space. In order to control the concentration of the copper ions in the electrolyte space 1, comprising the cathode and anode spaces, a part of the solution is conducted via the lines 43 indicated in dashed line, directly into the metal-ion generator. This partial quantity contains practically no oxidizing compounds of the redox system, so that the copper dissolving rate is reduced by admixture of this portion into the stream of solution which is introduced from the anode space into the metal-ion generator. By control and/or regulation of the partial quantities of the two streams by means of three-way valves (not shown), the copper ion concentration in the plating solution can be adjusted. In the arrangement shown in Fig. 2, these possibilities are not used, although, in that case also, two separate outlets 4 and 18 are present for the plating solutions from the cathode and anode spaces. The solutions of the two spaces are brought together there and conducted jointly into the metal-ion generators. The regenerated solutions coming from the metal-ion generators are fed to the spaces 15 and 16. The manner of procedure in accordance with Fig. 3 is advantageous when the plating solutions of the anode and cathode spaces cannot be mixed together in the electrolyte space, but a complete separation

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of the discharging solutions is not assured in the outlets 4 and 18 from the anode and cathode spaces.

In Figs. 1 to 3, the introduction of the plating solution enriched in copper ions into the container 3 is shown, by way of example, to be effected from below and the introduction into the metal-ion generator from above. In corresponding manner, the off lines from outlets 4 and 18 from the container 3 are shown at the top and those from the metal-ion generator 2 at the bottom. Circulation of the plating solution in other directions is also possible, such as, for instance, the introduction of the solution into the metal-ion generator from below.

Another embodiment of the invention, particularly for the electrolytic metallizing of plate-shaped treatment material, preferably circuit boards, in horizontal passage through the arrangement, is shown in Fig. 4. The system, part of which is shown in side view, consists of the electrolytic part 20 and a metal-ion generator 21 filled with copper, shown below it. The electrolytic part 20 consists of a plurality of individual electrolytic cells. Four of these individual cells are designated by the reference numerals 22, 40, 41, 42 in Fig. 4, with an insoluble anode 23 in each case for the top side and the bottom side of the treatment material 24. The treatment material is electrically connected to a rectifier (not shown) and is cathodically

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polarized. It is transported through the installation, in the direction of the arrow 25, by means of rollers or disks 26. The transport elements 26 are uniformly distributed along the entire installation. For reasons of simplification of the drawing, they have been shown here only at the beginning and end of the transport path. Surge nozzles or flood pipes 27, 39 are also present, uniformly distributed in the electrolytic cells. They correspond to the nozzle assemblies already mentioned above.

Plating solution coming from the metal-ion generator 24 is fed by pumps 29 to the flood pipes 27, 39 via the pipelines 28. The plating solution flows through the outlet openings of the flood pipes or surge nozzles onto the surfaces of the treatment material 24. In this connection, copper ions are reduced to metallic copper and deposited as a metallic layer on the material to be treated, and the ferrous ions, also present, are conveyed with the discharging electrolyte in the direction towards the anodes 23. In order to avoid a return flow from the anodes to the cathodes, various methods are provided the effecting of which is shown diagrammatically in Fig. 4. The plating solution which is enriched with copper is used for flow to the cathode (treatment material). From the plate-shaped treatment material, the stream of solution is then so deflected that, as indicated by arrows 30, it continues in the direction

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towards the anodes. In the case of perforated anodes, which are preferably used, the solution passes through them and then passes via suction pipes 31 and pipelines 32 back into the metal-ion generator. The anodes can consist, for instance, of expanded metal or netting. Openings 33 support the flow process. In order to avoid the formation of eddying, baffle walls 34 extending in the direction towards the material being treated can be arranged on the suction pipes. The slot 35 remaining between the baffle walls and the treatment material can amount to a few millimeters. From the standpoint of fluid mechanics, this forms practically closed electrolytic cells having favorable flow conditions. The flood pipes 27 can also be provided with baffle walls 36 in order to prevent further possible eddies.

Different flood pipes in different number are shown, by way of example, in the electrolytic cells of the arrangement shown in Fig. 4. The circulation of the plating solution is such that the level 37, which is above the suction pipes, is present in the electrolytic part of the installation. In the electrolytic cell 42 shown on the right, partition walls 38 are shown between each of the anodes 23 and the treatment material 24. In this way, the exchange of the plating solutions in the cathode and anode spaces over a direct path is minimized. By the use of ion-pervious partition walls, on the other hand, an ion-exchange between the chambers is made

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possible. The solution in the cathode space can emerge at the end side. In the anode space further flood pipes 39 are provided. The solution of this chamber passes out via the suction pipes 31. For such a cell, the serial flow path such as already described on the basis of Fig. 3 is again suitable.

The leading away of the plating solution from the anode space via the suction pipes 31 into the metal-ion generator 21 can take place over the shortest path in order to keep the life of the ferric ions as short as possible. Therefore, the metal-ion generator 21 is arranged here also as close as possible to the electrolytic part 20. In this way, short connection paths and short transport times result. The principle of construction can advantageously also be so selected that the parts 20 and 21 form a complete system. Each of several flood pipes 27 is fed by a pump 29 in the manner shown in Fig. 4. However, a single pump can also be used. This would lead to longer connecting paths between the flood pipes 27, 39 and the metal-ion generator 21. The plating solution in these connecting lines contains practically no oxidizing compounds of the redox system. Thus, the protection of the addition compounds is assured in this region also.

The electroplating installation is shown in side view in Fig. 4. The parts shown (anodes, pipes) extend in length

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into the depth of the drawing, and therefore transverse to the direction of transport over the material to be treated. The parts present in the electrical field between anode and cathode, such as, for instance, the flood pipes 27, consist of electrically non-conductive plastic. Their electric screening action is not disturbing here, since the material to be treated moves slowly through the installation and thus is continuously exposed to the different electrical fields.

Fig. 5 shows an arrangement in accordance with the invention having two metal-ion generators 44, an electrolyte space 1, and two additional electrolyte containers 45. This arrangement is operated in the dip process. In this case, the cell is developed symmetrically for the electroplating of the front and rear sides of the treatment material 6. The two metal-ion generators 44 shown in the figure and the electrolyte containers 45 can in each case also be provided individually and in such case arranged on both sides of the material being treated.

The metal-ion generator 44 consists of a preferably round tubular body 46 having an upper opening 47. All materials used for this are resistant to the plating solution and the additions contained in the solution. At least one pipe socket 49 extends through the bottom 48 of the metal-ion generator into the inside of the metal-ion generator. This pipe socket has lateral openings 50. They form a screen

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which, on the one hand, prevents penetration of metallic copper into the pipeline system and, on the other hand, permits the passage of the plating solution into the metal-ion generator. A small roof on top closes the top of the pipe socket. The roof at the same time holds the lateral openings 50 free of fine copper granulate which is present in this region of the metal-ion generator. Below the bottom, there is a mixing and collection chamber 51. Copper particles and impurities which were able to pass through the screen are collected in it. After opening the base plate 52, the chamber is accessible for cleaning purposes. Upon operation, the plating solution pumped out of the anode space 16, which solution is enriched in copper-dissolving ferric ions, enters. In addition, air which contains oxidizing oxygen can also be blown into the metal-ion generator via lines 56. In this case, the chamber 51 serves at the same time as mixing chamber. Through the holes 50 in the pipe socket 49, the plating solution and possibly air enter into the inside of the metal-ion generator. In the lower region of the generator there is predominantly fine copper granulate which has been formed by the dissolving of the metallic copper. It has a very large specific surface, which offers itself immediately for the dissolving of copper to the incoming plating solution which is enriched in ferric ions. The ferric ions are therefore rapidly reduced to ferrous

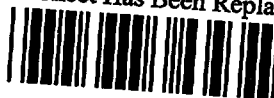
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ions, with the simultaneous dissolving of copper. Within the metal-ion generator, the quantity of ferric ions decreases rapidly towards the top. This has the result that the electrolytic copper which has been introduced as granulate or sections 53 is dissolved in upward direction to a continuously lesser extent. The dimensions of the granulate remain large in the upper region of the metal-ion generator. Thus, the permeability for the plating solution is also retained. Through the overflow 54, the solution discharges without pressure from the metal-ion generator into the electrolyte container 45. Within the metal-ion generator, the overflow 54 bends downward in such a manner that copper granulate 53 which slides downward from above cannot lead to the clogging of the generator. As a result of the sufficiently large dwell times, adapted to each other, of the plating solution which has entered into the generator, and which, at the same time, is sufficiently long for the dissolving of the copper surface offered, the plating solution which flows over the overflow 54 into the electrolyte container 45 contains practically no ferric ions any longer. Such an over-dimensioning of the regeneration unit thus provides assurance that the attack of the ferric ions on the addition compounds of the plating solution is complete already in the middle region of the generator.

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The filling and refilling of the metal-ion generator with metallic copper 53 is effected from above, through the opening 47 of, for instance, hopper shape. It can be closed by a cover. The region above the overflow 54, in which no plating solution is present, serves for the storing of metallic copper which is to be dissolved in the metal-ion generator. The filling and refilling can be effected manually. The arrangement is excellently suited for the automating of the filling process due to the absence of pressure at the filling opening 47 and the vertical or oblique arrangement. The filling can take place continuously or batchwise. Transport belts or vibratory conveyors (not shown here) which are known from the conveyance art transport the metallic copper into the openings 47 of the generators.

The invention has the advantage that copper parts of different geometrical shape can be dissolved in the metal-ion generator. Different shapes, however, have a different piling behavior. In order to maintain the permeability of the pile for the plating solution and to assure a sufficiently large copper surface which is accessible to the solution, additional individual measures are possible:

Downwardly inclined plates 55 within the generator prevent too great a compacting of the copper in the lower region. The plates are provided with holes the dimensions of which are adapted to the size of the metallic copper parts

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introduced. The holes are selected from plate to plate smaller from top to bottom corresponding to the dissolving of the copper. Similarly, the dimensions of the plates can increase from the top to the bottom. The angle of inclination can also be adapted to the circumstances of the pieces of copper introduced into the metal-ion generator.

The inclined position of the metal-ion generator itself can have the same result. By the blowing of air 56 into the lower region of the metal-ion generator or into the mixing and collecting chamber 51, a copper-dissolving substance, in this case oxygen, can also be introduced. In addition to this, the eddying of the copper granulate in the metal-ion generator connected therewith increases the reduction of the ferric ions and the dissolving of the copper. At the same time, the permeability for the plating solution through the copper parts is increased. With copper fillings which hook on to each other, it may be advisable to shake the metal-ion generator at times or continuously. The shaking movement can preferably be obtained from a vibrating conveyor, with which the automatic filling can at the same time be effected. All the measures described above for disturbance-free continuous operation of the metal-ion generator can also be combined with each other.

The electrolyte containers 45, 67 shown in Figs. 5 and 6 serve to reduce the dependence of the flow of the plating

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solution along the treatment material 6, 69 on the flow through the metal-ion generator 44, 66. This has the advantage that, in both circuits, the quantity of plating solution and its speed can be adjusted individually. These processes are described below with reference to Fig. 5.

The plating solution is conveyed by a pump 57 from the electrolyte container 45 into the electrolyte space 1. The solution flows through the flood pipes 58 arranged there onto the treatment material 6 and from the flow pipes 59 onto the liquid-pervious insoluble anodes 5. The division of the stream of solution over the flow pipes 58 and 59 is effected by adjustable valves, not shown in the drawing. From the cathode space 15, the plating solution flows via the outlet 8 through pipelines 60 and the outlet 61 back into the electrolyte container 45. Closely behind the anodes 5 there are suction pipes 62 through which the plating solution enriched with ferric ions is drawn off by means of the pump 63 and conveyed with high speed into the metal-ion generator. From there, the solution enriched with ferrous and cupric ions then returns again into the electrolyte container 45.

The division of the streams over the flood pipes 58 and 59 is so adjusted that an excess results in the cathode space 15. This equalizes itself with the anode space 16. If the two spaces are separated by a partition wall 17, as shown in Fig. 5, then at least one opening 64 in the partition wall

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sees to it that the equalizing of the plating solutions in the two spaces can take place in the direction indicated by the arrow. In order to avoid a mixing of the solutions in the electrolyte space 1 and a convective transport of ferric ions from the anode space to the cathode space, it therefore need merely be seen to it that a higher hydrostatic pressure is present in the plating solution in the cathode space 15 than in the anode space 16. This is assured by a corresponding adjustment of the partial streams through the flood pipe 58 and the flood pipes 59 of the circuit of the pump 57. In addition, the circuits of the pumps 57 and 63 are independent of each other.

Within the metal-ion generator, all ferric ions introduced with the feed stream are reduced to ferrous ions. Nevertheless, it cannot be excluded that a very small, scarcely measurable number of ferric ions pass through the metal-ion generator and enter into the electrolyte container 45. In order to reduce the ferric ions which have entered into said container to ferrous ions, copper parts 65 are introduced also into this container. In this case, copper scrap may also be used.

Another embodiment of the apparatus in accordance with the invention for the carrying out of the process is shown in Fig. 6. There is concerned here a horizontal circuit board electroplating installation shown in cross section. The

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figure shows the metal-ion generator 66, an electrolyte container and an electroplating cell 68. The circuit board 69 which is to be metallized is gripped in the arrangement by clamps 70 and conveyed horizontally through the installation. The contacting of the circuit board with the negative pole of a rectifier (not shown) is also effected via these clamps. In another embodiment, the contacting could also be effected by contact wheels. A pump 71 pumps the plating solution via flood pipes 72, 73 to the circuit boards and to the insoluble perforated anodes 74. Via outlets 75, the plating solution is conducted out of the cathode space back into the electrolyte container 67. From the anode space, the pump 86 conducts the plating solution which has been enriched with ferric ions through suction pipes 76 at high speed into the metal-ion generator. An outlet 77, which is developed as overflow for regulating the level, sees to it that excess plating solution passes from the upper region of the anode space also into circuit to the metal-ion generator 66 and not into the electrolyte container 67. The metal-ion generator is constructed in the manner which was described with reference to Fig. 5. Via the overflow 78, the plating solution passes back into the electrolyte container 67. In the latter, there are also contained copper parts 79 which effect a reduction to ferrous ions of stray ferric ions which are possibly present in this region. Furthermore, partition

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walls 80 are provided between the anode and cathode spaces. Openings 81 in these partition walls see, here also, to an equalization of the streams of the plating solution from the cathode space into the anode space. These directions of flow are also established if no partition walls are present.

Horizontally operating continuous installations such as shown in Figs. 4 and 6, and vertically operating electroplating installations have dimensions of several meters in length of the electrolytic cells. Therefore, in practice, preferably several metal-ion generators are arranged along the installation. This makes it possible to set them up in close spatial vicinity to the electrolytic cell or effect a partial or complete placing of electrolytic cell, electrolyte container, and metal-ion generator one within the other.

During the passage of a circuit board through the electroplating installation, the clamps 70 are also metallized in the region of their contacts 82. This layer must be removed again before the clamps are again used. This is done, in known manner, during the return of the clamps to the start of the electroplating installation. In this connection, the returning clamps 83 pass through a separate compartment 84 which is connected with the plating solution in the electrolytic cell 68. For the demetallization, the clamps 83 are connected via wiper contacts with the positive

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pole of a rectifier, not shown. The negative pole of this rectifier is connected to a cathode plate 85. During the electrolytic demetallization process, copper deposits on the insulating layers of the clamps 83 lose electric contact with the current supply before they are completely dissolved. Therefore, disturbing deposits of copper on these regions remain back. In accordance with the invention, therefore, the parameters for the demetallization, namely current and time, are so adjusted that, for instance, only 70% of the demetallization path is required for the removal of the metal layer. In the remaining path, Fe^{3+} ions are produced by the electrolysis current on the metallic contacted parts of the clamps. These ions are present precisely at the place where contact-less copper deposits are possibly still present. They dissolve this copper electroless. No noticeable increase in ferric ions in the electrolytic cell occurs as a result of this since, as compared with the metallizing of the treatment material, only very small currents and surfaces are concerned.

In order to maintain an operable deposition of metal, the copper content in the plating solution must be kept within given limits. This presupposes that the consumption rate and the rate of addition of copper ions correspond. In order to check the copper content, the absorption power of the plating solution can be measured at a wavelength of for

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instance 700 nm. The use of an ion-sensitive electrode has also proven suitable. The measured value obtained serves as actual value of a controller the control value of which is used to maintain the copper-ion concentration in the specific embodiments of the invention described.

For the analytical noting of the concentrations of the compounds of the redox system, a potential measurement can be carried out. For this purpose, a measurement cell is used which is formed of a platinum electrode and a reference electrode. By suitable calibration of the measured potential with the concentration ratio of the oxidizing and reduced compounds of the redox system for a given total concentration of the compounds, the corresponding concentration ratio can be determined. The measurement electrodes can be installed both in the anode and cathode spaces as well as in the pipelines of the arrangement.

In order to verify the anode processes, such as, for instance, the oxidation of the redox system required for the production of copper and a possible anodic decomposition of the addition compounds, a further measuring device can be provided with which the cathode potential is measured with respect to a reference electrode. For this purpose, the anode is connected via a potential measuring instrument with the corresponding reference electrode.

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The continuous or discontinuous measurement of further galvanotechnical parameters is advisable, such as, for instance the determination of the content of addition compounds by means of cyclic voltametrics. Thus, after lengthy pauses in operation, temporary changes in the concentration can occur. Knowledge of the instantaneous values can be utilized in order to avoid improper dosaging of the chemicals to be added.

The following examples serve for further explanation of the invention:

Example 1

In an arrangement in accordance with Fig. 2, using the measures in accordance with the invention (large specific surface of the copper parts in the metal-ion generator, high velocity of flow in the entire arrangement, conducting of the flow in such a manner that the oxidizing compounds of the redox compounds formed by oxidation at the anode cannot reach the cathode), a copper bath having the following composition was used:

80 g/liter copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

180 g/liter sulfuric acid, conc.

10 g/liter iron as ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)

0.08 g/liter sodium chloride

with the following brighteners:

1.5 g.liter polypropylene glycol

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0.006 g/liter 3-mercaptopropane-1-sulfonic acid, sodium
salt

0.001 g/liter N-acetylthiourea

A current efficiency of 84% was determined. The
consumption was determined over 100 amp hours/liter as:

propyleneglycol 3.3 g/kAh

3-mercaptopropane-1-sulfonic acid

sodium salt 0.3 g/kAh

N-acetylthiourea 0.04 g/kAh

The elongation upon rupture of the deposited layers
amounted to 17% at the end of the test.

Example 2

The test of Example 1 was repeated in the arrangement
shown in Fig. 3, the plating solution being conducted
serially through the cathode and anode spaces. A current
efficiency of 92% was obtained. The consumption, again
determined over 100 amp hours/liter, was:

propyleneglycol 2.0 g/kAh

3-mercaptopropane-1-sulfonic acid

sodium salt 0.2 g/kAh

N-acetylthiourea 0.02 g/kAh

The elongation upon rupture was improved to 20%. In
this test, the coated circuit boards passed a second
soldering shock test (10 seconds at 288°C soldering

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temperature) without cracks in the region of the holes. The deposition was uniformly shiny.

Example 3

In a horizontal installation in accordance with Fig. 4, circuit boards were copper-plated in a plating solution of the following composition:

80 g/liter copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

200 g/liter sulfuric acid, conc.

8 g/liter iron as ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$)

0.06 g/liter sodium chloride

As brighteners there were added:

1.0 g/liter polypropylene glycol

0.01 g/liter 3-(benzthiazolyl-2-thio)-

propylsulfonic acid, sodium salt

0.05 g/liter acetamide

With an electrolyte temperature 34°C , bright metal layers were obtained on a scratched copper laminate with a current density of 6 amps/dm². The circuit board metallized in this manner withstood five soldering shock tests (10 seconds at a soldering temperature of 288°C). The current efficiency was 91.%. No problems arose in the handling (making up of the addition substances consumed) of the plating solution.

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Example 4 (Comparison Example)

The test described in Example 1 was carried out in an electrolysis cell. The measures in accordance with the invention were not used, in particular not the feeding of the stream to the cathodes and anode in accordance with the invention.

At a temperature of the plating solution of 30°C, bright metal layers were obtained on scratched copper laminate surface with a current density of 4 map/dm². The cathodic current efficiency was only 68%. The consumption of the addition compounds without entrainment of the plating solution by lifting the treatment material out of the bath container amounted, averaged over 100 amp hours/liter, was:

propyleneglycol	5 g/kAh
3-mercaptopropane-1-sulfonic acid	
sodium salt	1.6 g/kAh
N-acetylthiourea	0.2 g/kAh

The elongation upon rupture of the deposited layers was only 14% at the end of the test.

Example 5 (Comparison Example)

Copper layers were deposited on circuit boards in accordance with Example 1 after a substrate of copper had been previously deposited from the solution for a lengthy period of time (2000 amp hours/liter).

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The circuit boards no longer withstood two soldering shock tests (10 seconds at a soldering temperature of 288°C) without cracks. Furthermore, non-uniform copper layers were obtained. In Examples 1 to 3, copper layers with good to very good elongation upon rupture were, to be sure, deposited. The cathodic current efficiency and the consumption of the addition compounds which were added to the plating solution in order to control the physical-mechanical layer properties, were satisfactory. The appearance of the copper layers was excellent and withstood the use tests.

After lengthy loading of the plating solution upon the electrolytic deposition of copper, on the other hand, no suitable results were obtained any longer.

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CLAIMS

1. A process for the electrolytic deposition of uniform metal layers of given physical-mechanical properties, in particular layers of copper, with high current efficiency from a plating solution containing ions of the deposited metal, compounds of a electrochemically reversible redox system, and addition compounds for controlling the physical-mechanical properties of the metal layers, in which
 - cathodes;
 - insoluble, dimensionally stable anodes;
 - a metal-ion generator by means of which the metal ions are formed by the dissolving of suitable metal parts upon passage of the plating solution containing oxidizing compounds of the redox system formed by anodic oxidation; and
 - means by which the concentration of the oxidizing compounds in the direct vicinity of the cathode is minimized, preferably to a value of less than about 0.015 moles/literare used.
2. A process according to Claim 1, characterized by the fact that the concentration of the compounds of the redox system is held slightly below a value which is

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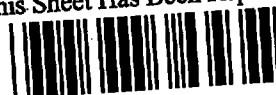
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necessary in order to maintain the metal-ion concentration.

3. A process according to any of the preceding claims, characterized by the fact that the surface of the metal parts is selected so large that the concentration of the oxidizing compounds is lowered to a value of about zero upon passage through the metal-ion generator.
4. A process according to any of the preceding claims, characterized by the fact that the plating solution passes to the anodes with a high velocity of flow and is transferred from there to the metal-ion generator with high velocity.
5. A process according to any of the preceding claims, characterized by the fact that at least one second oxidizing compound, preferably oxygen, is furthermore introduced into the metal-ion generator.
6. A process according to any of the preceding claims, characterized by the fact that a part of the solution present in the cathode space is conducted directly to the metal-ion generator without being fed to the anodes.
7. A process according to any of the preceding claims, characterized by the fact that the plating solution which is conducted through the metal-ion generator flows

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directly to the cathode and then, by deflection of the direction of flow, to the anodes.

8. An apparatus for the electrolytic deposition of uniform layers of metal of given physical-mechanical properties, in particular copper, with high current density, from a plating solution which is in contact with cathodes (6, 24, 69) and with insoluble, preferably perforated, dimensionally stable anodes (5, 23, 74), comprising an electrolyte space (1) arranged between the cathodes and the anodes, means for feeding the plating solution to the cathode and anode, a metal-ion generator (2, 21, 44, 66), a first means for transferring the plating solution fed to the anodes to the metal-ion generator, and a second means for transferring the plating solution emerging from the metal-ion generator into the electrolyte space, said means bridging over a distance of small space between the anodes and the metal-ion generator.
9. An apparatus according to Claim 8, characterized by the fact that means (31, 62, 76) are provided by which the plating solution present in the vicinity of the anodes is drawn off with high velocity or is removed via outlets (4, 61, 77) and transferred to the metal-ion generator (2, 21, 44, 66).

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10. An apparatus according to either of Claims 8 or 9, characterized by the fact that the electrolyte space (1) is divided into several compartments by ion-permeable partition walls (17, 38, 80).
11. An apparatus according to any of Claims 8 to 10, characterized by the fact that outlets (18, 75) are provided by which the plating solution present in the vicinity of the cathodes is removed from the electrolyte space (1) and brought to the metal-ion generator (2, 21, 44, 66).
12. An apparatus according to any of Claims 8 to 11, characterized by the fact that as metal-ion generator (2, 21, 44, 66) there is provided a tubular apparatus which can be filled from the top and is provided with a bottom (48) in its lower region and, for the entrance of the plating solution, with at least one pipe connection (49) having lateral openings (50), and, in its upper region, with an overflow (54, 78) which discharges into an electrolyte container (45, 67),
13. An apparatus according to any of Claims 8 to 12, characterized by oblique, preferably perforated, plates (55) within the metal-ion generator (2, 21, 44, 66).

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14. An apparatus according to any of Claims 8 to 13,
characterized by means for the blowing-in of air (56)
arranged in the lower region of the metal-ion generator
(2, 21, 44, 66).
15. An apparatus according to any of Claims 8 to 14,
characterized by means (26, 70, 82) for the horizontal
grasping, electrical contacting, and movement of the
cathodes in horizontal direction.
16. The use of the process according to any of Claims 1 to 7
for the metallizing of circuit boards.
17. A process for the electrolytic deposition of metals,
characterized by some or all of the new features or by
combinations of the features disclosed.
18. An apparatus for the electrolytic deposition of metals,
characterized by some or all of the new features or by
combinations of the features disclosed.

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PROCESS AND DEVICE FOR ELECTROLYTIC PRECIPITATION
OF METALLIC LAYERS

ABSTRACT OF THE DISCLOSURE

For the electrolytic deposition of uniform layers of metal having given physical-mechanical properties, particularly of copper, soluble anodes are not used, since their geometrical shape is changed by the deposition and therefore the distribution of the lines of force in the electrolytic cell are continuously changed.

In order to solve the problems occurring in this connection, a process has been proposed in which compounds of a redox system added to the plating solution are converted during the deposition on the insoluble anodes. The compounds produced in this connection dissolve new metal ions from a reservoir which contains parts of the metal to be deposited, so as again to supplement the metal ions removed from the solution by deposition.

The present invention describes a procedure in which, differing from the prior art, the addition compounds are not destroyed.

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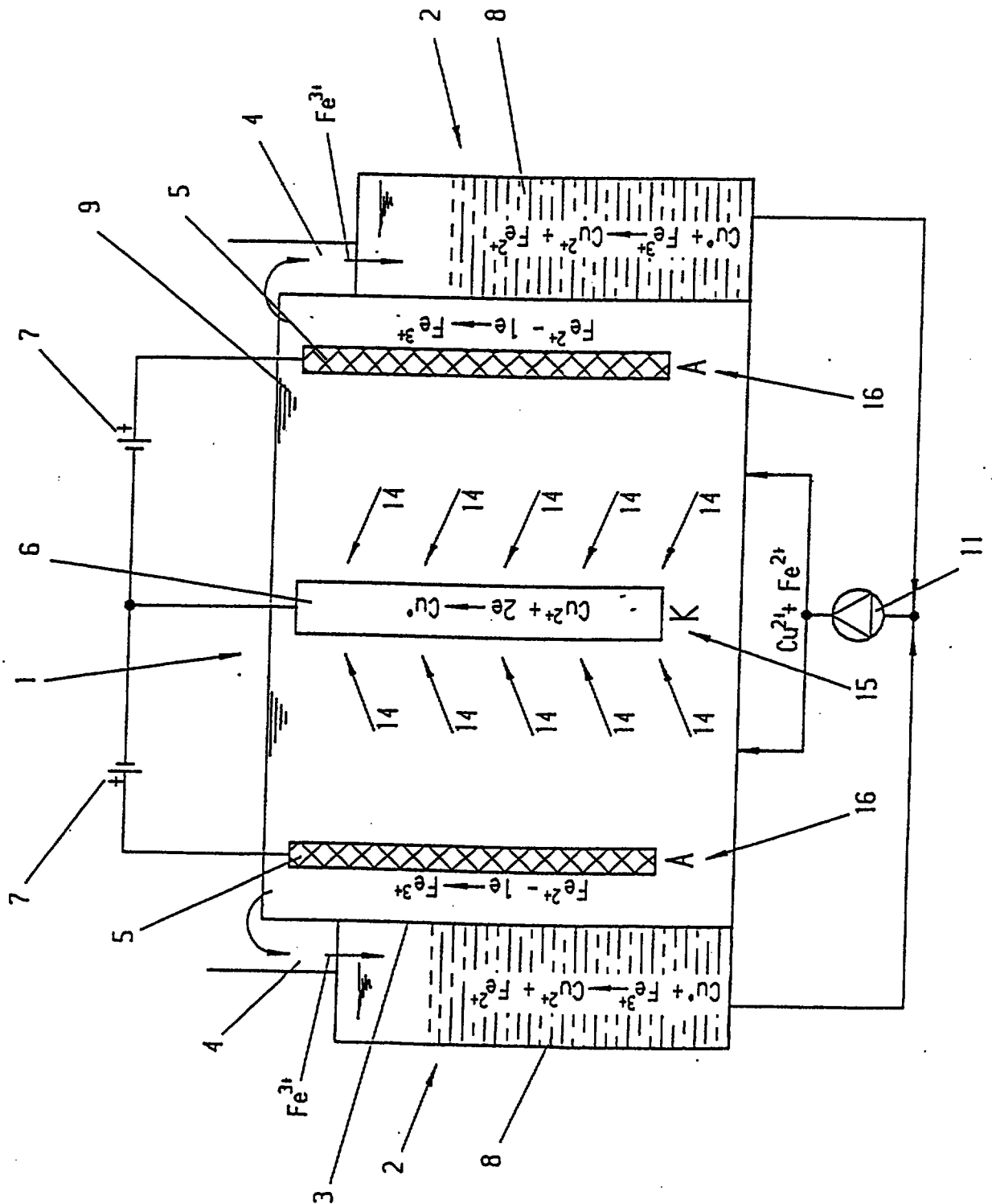


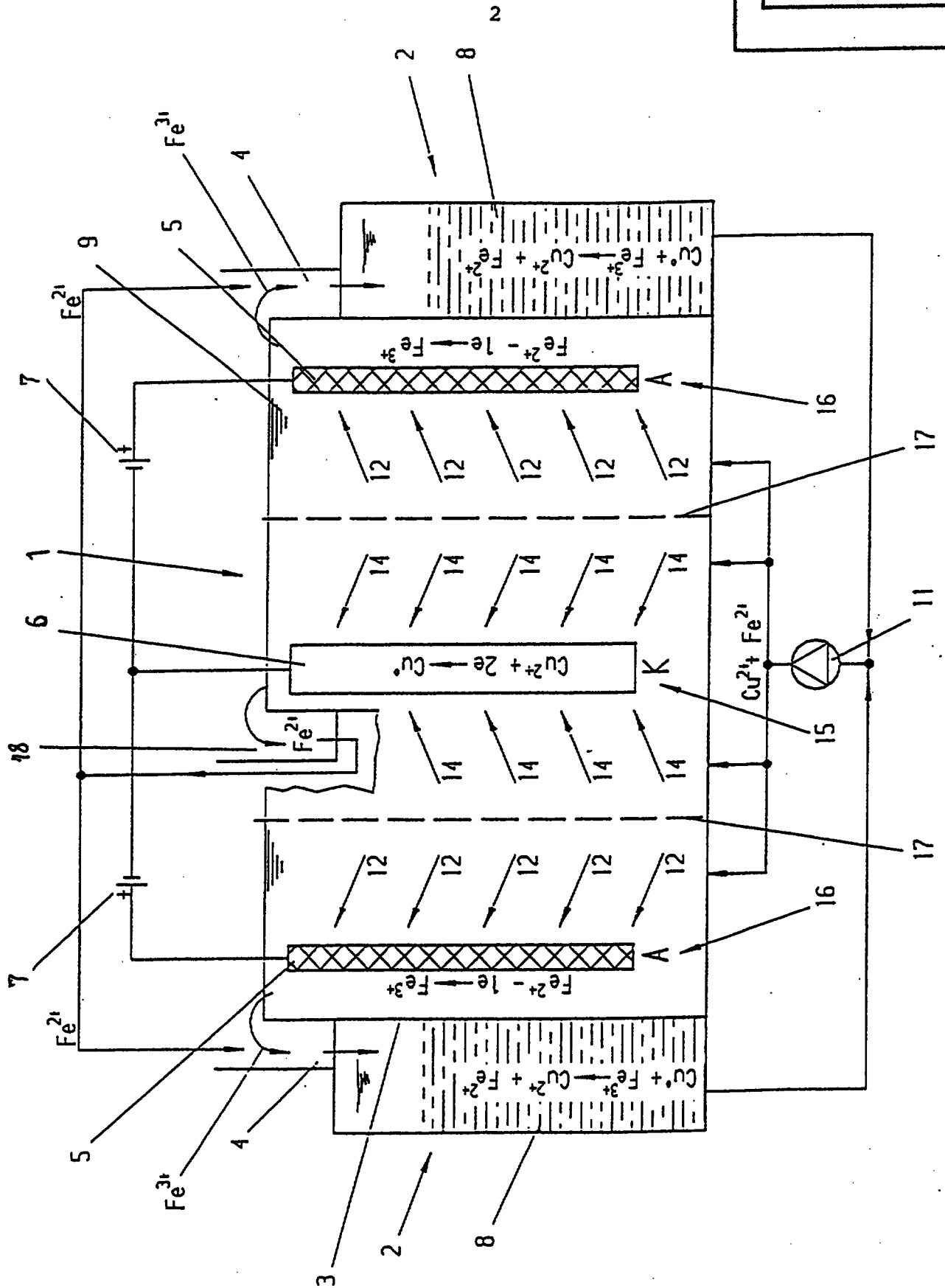
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Fig. 2

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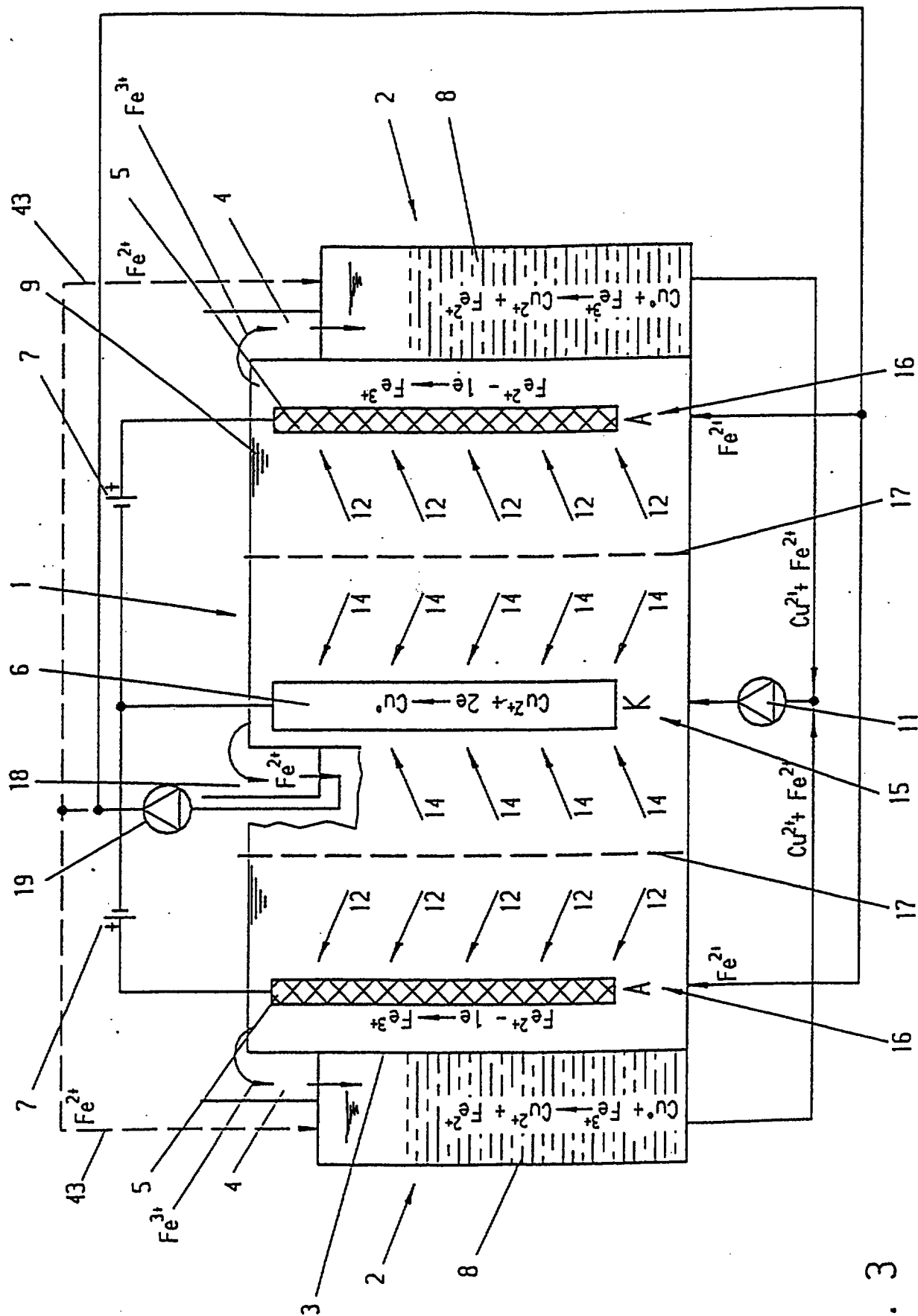


Fig. 3

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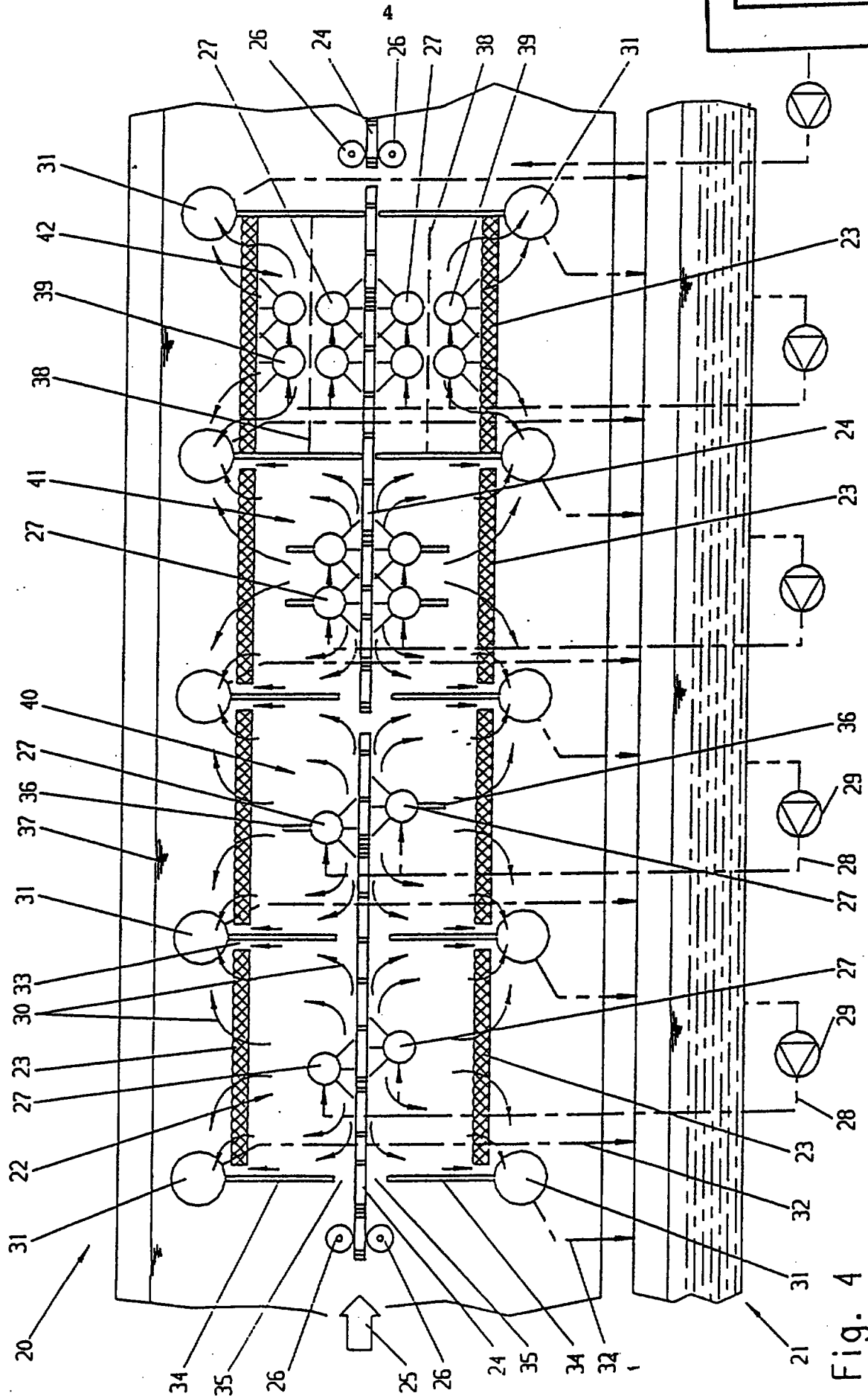


Fig. 4



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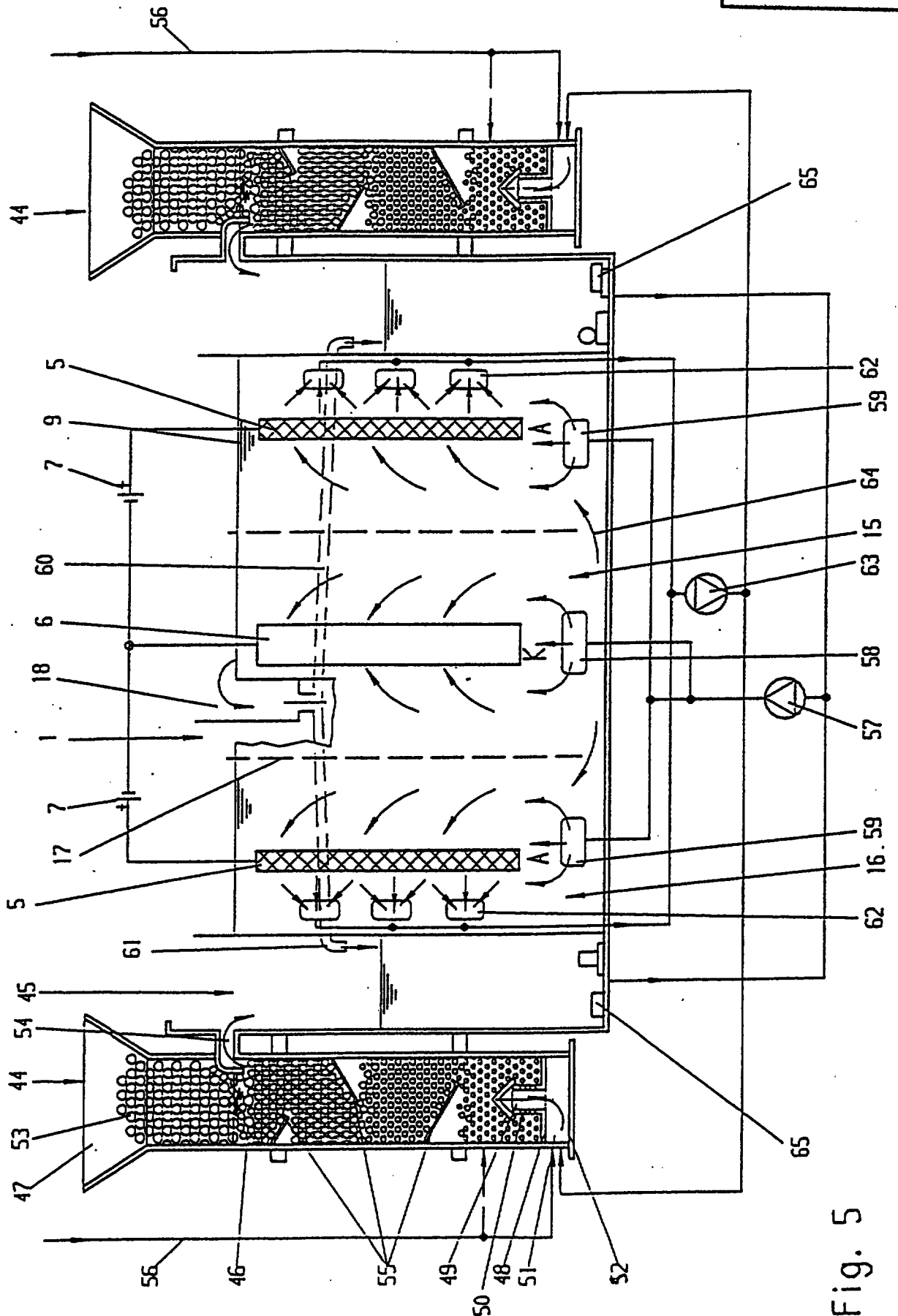
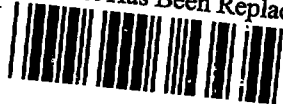


Fig. 5

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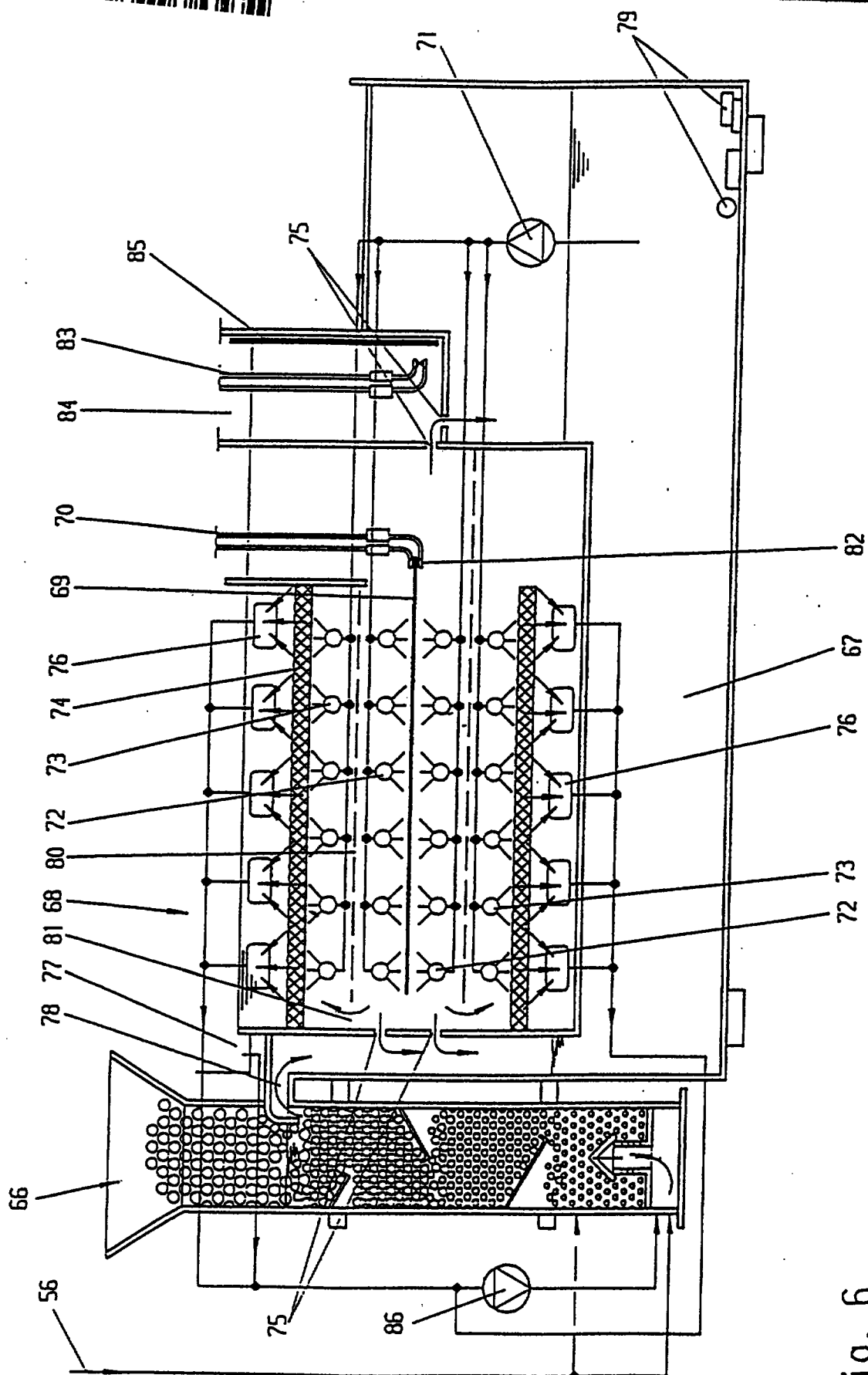


Fig. 6

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- PROCESS AND ARRANGEMENT FOR THE ELECTROLYTIC DEPOSITION
OF METAL LAYERS

The present invention relates to a process and an apparatus for the electrolytic deposition of uniform metal layers, preferably of copper, having given physical-mechanical properties.

The electrolytic metallization, for instance with copper, of workpieces which are electrically conductive at least on their surface, has been known for a long time. For this purpose, the workpieces which are to be coated are connected as cathode and, together with anodes, brought into contact with the electrolytic plating solution. For the deposition, a flow of electric current is produced between anode and cathode.

Ordinarily, anodes of the material which is deposited from the plating solution are used. In that case, the amount of metal deposited from the solution is returned to the plating solution by dissolving at the anodes. In the case of copper, the amount deposited and the amount which is anodically dissolved are approximately the same for a given charge flow. This process is easy to carry out since, at least in the case of copper, only sporadic measurement and control of the metal-ion concentration of the plating solution is necessary.

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However, disadvantages have been encountered when carrying out the process with these soluble anodes. If the thickness of the metal layers deposited is to be very uniform at all places on the surface of the workpiece, then the soluble anodes are only conditionally suitable for this purpose, since the latter change shape with time due to the dissolving, so that the distribution of the lines of force in the electrolytic bath also changes. The use of smaller, for instance spherical, pieces of metal as anodes in insoluble metal baskets is also only conditionally suitable for solving the problem, since the metal parts frequently wedge against one another and as a result of the dissolving process gaps are frequently formed upon the sliding down in the pile of metal parts.

Therefore, attempts have frequently been made to use insoluble, and therefore dimensionally stable anodes, rather than soluble metal anodes. As materials, titanium or high-grade steel, for instance, enter into consideration for this. By the use of these anode materials, gases, such as for instance oxygen or chlorine, are formed upon the electrolytic deposition since the anodic dissolving of metal no longer takes place. The gases produced attack the anode materials and gradually dissolve them.

German Patent DD 215 589 D5, describes a process for the electrolytic deposition of metal with the use of insoluble

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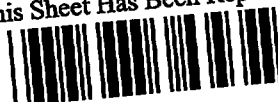
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metal anodes in which reversibly electrochemically convertible substances are added as addition to the plating solution, they being transported by intense positive convection with the plating solution to the anodes of a plating apparatus, converted electrochemically there by the electrolysis current, conducted, after their conversion, by intense positive convection away from the anodes into a regeneration space, returned electrochemically to their initial condition in the regeneration space on regeneration metal present in it with simultaneous electroless dissolving without external current of the regeneration metal, and fed in this initial condition again to the separation apparatus by intensive positive convection. By this process, the above-indicated disadvantages with the use of insoluble anodes are avoided. Instead of the corrosive gases, the substances added to the plating solution are oxidized at the anode, so that the anodes are not attacked.

The dissolving of the metal in the regeneration space is in this case independent of the process of the deposition of metal on the material being treated. Therefore, the concentration of the metal ions which are to be deposited is controlled by the effective metal surface in the regeneration space and by the velocity of flow in the circuit. In the case of a deficiency of metal ions, the effective metal surface and/or the velocity of flow from the deposition space

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to the regeneration space is increased or, in case of an excess of metal ions, correspondingly reduced. This process therefore presupposes that a high concentration of the reversibly electrochemically convertible substance is present in the plating solution. This has the result that the oxidized compounds of the addition substances (redox system) are again reduced at the cathode, so that the current efficiency is decreased.

In German Unexamined Application for Patent DE 31 10 320 A1, a process is described for cation reduction by anode-supported electrolysis of cations in the cathode space of a cell, the anode space containing ferrous ions as reducing agent and anodes being moved relative to the anolyte which surrounds the anodes.

In German Unexamined Application for Patent DE 31 00 635 A1, a process and an apparatus are described for supplementing an electroplating solution with a metal to be precipitated in an electroplating apparatus, wherein the metal which is to be galvanically precipitated is provided in an electroplating solution which is contained in an electroplating container and a supply of the metal to be precipitated is provided within an enclosed space, the gases produced in the electroplating container upon the advance of the electroplating process are conducted, together with the electroplating solution, into said enclosed space and applied

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there to said supply of metal in order to dissolve the latter, whereupon the dissolved supply of metal is again added to the electroplating solution in the electroplating container. The apparatus required for the carrying out of the process is, however, very expensive, since, among other things, it must be gas-tight.

Said processes have the disadvantage that the plating solutions to be regenerated contain no addition compounds, which, however, are ordinarily required in order to control the physical-mechanical properties of the metal layers to be deposited. Such substances are predominantly organic substances.

It is only by these addition compounds that the required physical-mechanical properties of the layers such as, for instance sufficient brightness, high elongation upon rupture, and resistance of the layer to cracks upon soldering shock tests are obtained. Without the addition of these compounds, the layers are dark, dull, and rough.

DD 261 613 A1 describes a process for the electrolytic deposition of copper from acid electrolytes with dimensionally stable anode using certain additions for the production of layers of copper, having specific physical-mechanical properties, the plating electrolyte also containing the aforementioned electrochemically reversibly convertible addition substances.

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It has been found that, although the quality of the metal layers precipitated from such plating solutions initially satisfy the requirements, in particular with regard to the physical-mechanical properties, nevertheless, after a longer period of deposition, layers of poorer quality are obtained even if the substances in the plating solution whose concentration was decreased by consumption upon the deposition are supplemented. Copper coatings which are only poorly ductile are obtained from aged plating solutions, so that such layers tear on printed circuits in the region of the holes when they are subjected to a soldering shock test. Furthermore the surface of the metal layer then changes in disadvantageous manner, in that it becomes dull and rough.

The present invention therefore proceeds from the problem of avoiding the disadvantages of the processes and arrangements of the prior art and of finding an economical process, and suitable apparatus, for the electrolytic deposition of layers of metal, particularly of copper, in which the metal layers deposited by the process and the apparatus have predetermined physical-mechanical properties, in the manner that addition compounds are added to the plating solution in order to control the properties of the metal layers, and the properties of the metal layers do not change in disadvantageous manner even after a lengthy period of deposition. Furthermore, the thicknesses of the metal

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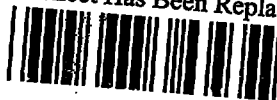
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layers are to be approximately the same at all places on the surface of the material treated, and the deposition is to be possible with high current efficiency.

This problem is solved by Claims 1, 8, and 16. Preferred embodiments of the invention are set forth in the dependent claims.

In order to obtain sufficiently uniform layer thicknesses on the surface of the material being treated, insoluble, dimensionally stable, anodes are used. In order to supplement the metal ions consumed by deposition, namely in a preferred use copper ions, a metal-ion generator is used in which parts consisting of the metal to be deposited are contained. The plating solution contains, in addition to the metal ions, compounds of an electrochemically reversible redox system. For the regeneration of the plating solution which has become impoverished by consumption of metal ions, it is passed by the anodes, whereby the oxidizing compounds of the redox system are formed. Thereupon, the solution is conducted through the metal-ion generator, the oxidizing compounds reacting with the metal parts, with the formation of metal ions. At the same time, the oxidizing compounds of the redox system are converted into the reduced form. By the formation of the metal ions, the total concentration of the metal-ion concentration contained in the plating solution is maintained constant. From the metal-ion generator, the

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plating solution passes back again into the electrolyte space which is in contact with the cathodes and anodes.

The solution furthermore contains addition compounds for controlling the physical-mechanical properties of the layer. In order to maintain the properties of the layer even after a lengthy period of deposition from the plating solution, means are provided in accordance with the invention by which the concentration of the oxidizing compounds of the redox system in the direct vicinity of the cathode can be minimized, preferably to a value below about 0.015 mole/liter.

Obviously, the addition compounds can be decomposed by the oxidizing compounds of the redox system. In this way, the concentration of the addition compounds would, on the one hand, be reduced in uncontrolled fashion. Since the determination of the concentration of these compounds is in general very cumbersome, while the content of the compounds is very sensitive to the physical-mechanical properties of the layers, only layers having varying properties could necessarily be deposited, since a sufficiently rapidly acting and precise technique of analysis for such requirements is not available.

This problem would furthermore be intensified by the fact that upon the decomposition of the addition compounds reaction products are formed which have a detrimental effect on the properties of the layer, so that, after lengthy

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duration of the electrolysis, even if the content of the addition compounds is maintained by enrichment of the injurious reaction products, only layers the properties of which would not satisfy the requirements made could still be deposited.

The means in accordance with the invention by which the concentration of the oxidizing compounds in the vicinity of the cathode can be minimized, preferably to a value less than about 0.015 mole/liter, are described below:

The total amount of the compounds of the redox system added to the plating solution is so determined that substantially the entire amount of the oxidizing compounds of the redox system fed to the metal-ion generator with the plating solution is required for the dissolving there of the metal parts with the formation of metal ions.

The amount of metal ions provided by the dissolving must just supplement the portion which is lost in the plating solution by the deposition. In order to maintain the metal-ion concentration and for the complete reduction of the amount of oxidizing compounds introduced into the metal-ion generator, a minimum size of the surface of the metal parts in the metal-ion generator is therefore required. This surface can be increased in upward direction as far as desired and, in particular, however, need not be variable. Thus, the further filling of the metal parts into the metal-

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ion generator can be effected in a technically simple manner in any desired amounts above said minimum amount.

The spatial distance between the anodes and the metal-ion generator must be small, and the connections for transferring the plating solution which has reached the anodes to the metal-ion generator and from the metal-ion generator back into the electrolyte space must be short. In this way, the result is obtained that the dwell time of the oxidizing compounds in the electrolyte space is short. By the rapid transfer of the plating solution containing the oxidizing compounds into the metal-ion generator, these compounds also have only a short life until they are converted into the reduced compounds of the redox system.

Furthermore, the velocity of flow of the plating solution must be as high as possible, particularly upon the transfer from the anodes to the metal-ion generator.

In order to keep the concentration of the oxidizing compounds as small as possible, it is furthermore possible to introduce another oxidizing agent directly into the metal-ion generator. Atmospheric oxygen is particularly suitable for this purpose. Upon the reaction of oxygen with the metal parts, only water is produced, it having no effect on the deposition process.

For the introduction of air into the metal-ion generator, means for the blowing-in of atmospheric oxygen are

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provided in the lower region of the generator.

Another possibility for supplementing the metal ions removed by deposition from the plating solution consists, in principle, of adding the metal ions in the form of their compounds or salts to the plating solution. However, in this case, the concentration of the anionic portions of the compounds or salts necessarily added with the metal ions cannot be prevented from increasing continuously due to the continuing addition of the compound, so that, after a certain amount of time, the solution must be discarded. If, in the present case, only a small part of the metal ions to be supplemented by addition of the corresponding compounds or salts, then the time until the discarding of the solution can be rather long. By combining the supplementing of the metal ions by addition of the salt with the regenerating of the solution in the metal-ion generator, the addition of the compounds or salts can be decreased to a few per cent of the necessary supplementation.

In this case, the possibility of controlling the metal-ion concentration in the plating solution in a simple and rapid manner from a control standpoint constitutes an advantage.

By the reduction in the life of the oxidizing compounds of the redox system which are formed on the anode which is obtained by means of said measures, and the minimizing of the

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concentration of the compounds, possible decomposition of the addition compounds is avoided, or at least definitely reduced.

The metal-ion concentration in the electrolyte space can also be controlled by a special manner of circulation of the plating solution. The reduced compounds of the redox system which are converted electrochemically at the anodes by the electrolysis current back into the oxidizing compounds are present in the cathode space. The quantity of the oxidizing compounds and thus the metal-ion concentration can be reduced if only a part of the plating solution is conducted from the space present in the vicinity of the cathode to the anodes and from there into the metal-ion generator. The other part of this solution which does not contain the oxidizing compounds is, on the other hand, conducted directly into the metal-ion generator. For this purpose, separate outlets are provided for the plating solution, they being located in the vicinity of the cathode. The solution which is branched off over the outlets passes through suitable pipelines into the metal-ion generator.

The surface of the metal to be dissolved is, in its turn, dimensioned so amply that all oxidizing compounds introduced into the metal-ion generator can be converted electrochemically.

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By this measure, a simple control of the metal-ion concentration in the plating solution and thus an automating of the control which is simple technically to achieve is made possible. By controlling the volumetric flows of the plating solution from the cathode via the anode into the metal-ion generator, on the one hand, and from the cathode directly into the metal-ion generator, on the other hand, the metal-ion concentration can be easily adjusted.

For the control, the velocity of flow of the plating solution in the circuit and the voltage between cathode and anode can also be adjusted.

The conditions of flow in the electrolyte space are to be such that, on the one hand, a flow of the plating solution is directed from the cathode to the anode and, on the other hand, the plating solution, however, first acts directly on the cathode. This latter is necessary in order to be able economically to produce uniform layers with sufficiently high current densities and predetermined physical-mechanical properties. These flows are produced by direct flow against the cathode by means of nozzle assemblies or surge nozzles and by subsequent deflection of this flow towards the anodes.

The preferred arrangement for the carrying out of the process of the invention comprises, in addition to the cathodes, insoluble, preferably perforated, dimensionally stable anodes, devices for the flow of the plating solution

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against the cathodes and anodes (nozzle assemblies, or surge nozzles), means of deflecting the flow to the anodes and connecting lines for transferring the plating solution which has been fed to the anode to the metal-ion generator as well as for transferring the plating solution emerging at the metal-ion generator back into the electrolyte space. In a preferred embodiment, means for drawing off the plating solution can also be provided in order to increase the velocity of flow upon the transfer of the plating solution from the anodes to the metal-ion generator.

In order to avoid the mixing of the parts of the plating solution which are located in the vicinity of the cathode and/or the anode, the electrolyte space can also be subdivided into several compartments by ion-pervious partition walls (ion-exchanger, diaphragms).

The metal-ion generator is preferably a tubular device which can be filled from above and which is provided with a bottom and, for the entrance of the electrolyte, with at least one pipe socket with lateral openings and also, in its upper region, with an overflow which debouches into an electrolyte container. In one particularly favorable embodiment, oblique, preferably perforated, plates are arranged within the metal-ion generator.

The process is particularly suitable for the metallizing of circuit boards. In this case, copper in particular is

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deposited on their surfaces and on the walls of the holes.

Ordinary dip devices can be used in which the circuit boards are dipped from above into the plating solution, or else horizontal installations in which the circuit boards are grasped horizontally and moved by suitable means in horizontal direction through the installation.

In addition to copper, which can preferably be deposited with the process of the invention from the arrangement which is also described, other metals, for instance, nickel, can also, in principle, be deposited in accordance with the method of the invention.

The basic composition of a copper bath can vary within relatively wide limits when using the process of the invention. In general, an aqueous solution of the following composition will be used:

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	20 - 250 g/liter
preferably	80 - 140 g/liter or 180 - 220 g/liter
Sulfuric acid, concentrated	50 - 350 g/liter
preferably	180 - 280 g/liter or 50 - 90 g/liter
Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	0.1 - 50 g/liter
preferably	5 - 15 g/liter
Chloride ions (added, for instance, as NaCl)	0.01 - 0.18 g/liter

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preferably

0.03 - 0.10 g/liter.

Instead of copper sulfate, other copper salts can also be used, at least in part. The sulfuric acid can also be replaced, in whole or in part, by fluoboric acid, methane sulfonic acid, or other acids. The chloride ions are added as alkali chloride, for instance sodium chloride, or in the form of hydrochloric acid, p.A. The addition of sodium chloride can be dispensed with, in whole or in part, if halogen ions are already present in the additions.

The active $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox system is formed from ferrous sulfate heptahydrate. It is excellently suited for the regenerating of the copper ions in aqueous acid copper baths. However, other water-soluble iron salts can also be used, in particular ferric sulfate nonahydrate, provided that the sales do not contain biologically non-degradable (hard) complex formers in the compound, since the latter result in problems in connection with the disposal of the flushing water (for example, iron-ammonium alum).

In addition to iron salts, compounds of the elements titanium, cerium, vanadium, manganese, chromium and the like are also suitable as further redox systems. Compounds which can be used are, in particular, titanyl sulfuric acid, ceric sulfate, sodium metavanadate, manganous sulfate, and sodium chromate. For special uses, combinations of the above redox systems can also be used.

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With the process of the invention, the other elements which are known and have proven themselves in electrolytic metal deposition can be retained. Thus, ordinary brightening agents, leveling agents and surface-active agents can, for instance, be added to the plating solution. In order to obtain copper precipitates having predetermined physical-mechanical properties, at least one water-soluble sulfur compound and an oxygen-containing high-molecular compound are added. Addition compounds such as nitrogen-containing sulfur compounds, polymeric nitrogen compounds, and/or polymeric phenazonium compounds can also be used.

The addition compounds are contained in the plating solution within the following concentration ranges:

ordinary oxygen-containing	
high-molecular compounds	0.005 - 20 g/liter
preferably	0.01 - 5 g/liter
ordinary water-soluble	
organic sulfur compounds	0.005 - 0.4 g/liter
preferably	0.001 - 0.15 g/liter

Thiourea derivatives and/or polymeric phenazonium compounds and/or polymeric nitrogen compounds as addition compounds are used in the following concentrations:

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preferably 0.0001 - 0.50 g/liter
0.005 - 0.04 g/liter

For the preparation of the plating solution, the addition compounds are added to the above-indicated basic composition. The conditions for the deposition of copper are indicated below:

pH	< 1
Temperature:	15°C - 50°C
preferably	25°C - 40°C
cathodic current density:	0.05 - 12 amp/dm ²
preferably	3 - 7 amp/dm ²

A few oxygen-containing high-molecular compounds are listed in the following Table 1:

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Table 1: Oxygen-Containing, High-Molecular Compounds.

Carboxymethyl cellulose

Nonylphenol-polyglycolether

Octanediol-bis-(polyalkylene glycol ether)

Octanolpolyalkylene glycol ether

Oleic acid-polyglycol ester

Polyethylene-propylene glycol + polyethylene glycol

Polyethylene glycol-dimethylether

Polyoxypropylene glycol

Polypropylene glycol

Polyvinyl alcohol

Stearic acid polyglycol ester

Stearyl alcohol polyglycol ether

 β -Naphthol polyglycol etherTable 2: Sulfur Compounds

3-benzthiazolyl-2-thio)-propylsulfonic acid, sodium salt

3-mercaptopropane-1-sulfonic acid, sodium salt

Ethylenedithiodipropyl sulfonic acid, sodium salt

Bis-(p-sulfophenyl)-disulfide, disodium salt

Bis-(ω -sulfobutyl)-disulfide, disodium saltBis-(ω -sulfohydroxypropyl)-disulfide, disodium saltBis-(ω -sulfopropyl)-disulfide, disodium saltBis-(ω -sulfopropyl)-sulfide, disodium salt

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Methyl-(ω -sulfopropyl)-disulfide, disodium salt
Methyl-(ω -sulfopropyl)-trisulfide, disodium salt
O-ethyl-dithiocarbonic acid-S-(ω -sulfopropyl)-ester,
potassium salt
Thioglycolic acid
Thiophosphoric acid-O-ethyl-bis-(ω -sulfopropyl)-ester,
disodium salt
Thiophosphoric acid-tris-(ω -sulfopropyl)-ester, trisodium
salt

A few sulfur compounds having functional groups suitable for the production of water solubility are set forth in the above Table 2.

By blowing air into the electrolyte space, the plating solution is moved. By addition action of air on the anode and/or the cathode, the convection in the region of their surfaces is increased. In this way, the mass transport in the vicinity of the cathode and/or anode is optimized, so that higher current densities can be obtained. Corrosive oxidizing agents which are possibly produced in a small amount, such as for instance oxygen and chlorine, are thereby led away from the anodes. Movement of the anodes and cathodes also results in an improved mass transport on the corresponding surfaces. In this way, a constant diffusion-controlled deposition is obtained. The movements can take place horizontally, vertically, in uniformly lateral

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movement, and/or by vibration. A combination with the action of air is particularly effective.

Inert material is used for the anodes. Anode materials which are chemically and electrochemically stable to the plating solution and the redox system used are suitable, for instance titanium or tantalum as base material, coated with platinum, iridium, ruthenium, or their oxides or mixed oxides. Titanium anodes having an iridium-oxide surface which are blasted with spherical bodies and thereby compacted so as to be free of pores were sufficiently resistant, and therefore had a long life. By the anodic current density or the anode potentials adjusted via the voltage between cathode and anode, the quantity of the corrosive reactions produced on the anode is determined. Below 2 amp/dm² their rate of formation is very small. In order, therefore, not to exceed this value, large effective anode surfaces are desirable. Therefore, in the case of limited three-dimensional dimensions, perforated anodes are preferred, for instance, anode nets or expanded metal having a suitable coating are used. In this way, the advantage of a large effective surface is combined with the simultaneous possibility of intensive flow through the anode by the plating solution, so that any corrosive reaction produced can be led away. Anode nets and/or expanded metal can, in addition, be used in several layers. In this way, the effective surface is

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correspondingly increased, so that the anodic current density with a predetermined electroplating current is reduced.

Metal is supplemented in a separate container, the metal-ion generator, which is passed through by the plating solution. In the case of copper deposition, metallic copper parts, for instance in the form of pieces, balls or pellets, are present in the metal-ion generator. The metallic copper used for the regeneration need not contain phosphorus, but phosphorus is not disturbing. Upon the additional use of soluble copper anodes, the composition of the anode material, on the other hand, is of great importance. In that case, the copper anodes must contain about 0.05% phosphorus. Such materials are expensive, and the addition of phosphorus causes residues in the electrolytic cell which must be removed by additional filtration.

Since, in accordance with the method of the invention, it is also possible to use metallic copper parts which contain no additions, electrolytic copper, including copper scrap, is as a rule used. An interesting variant consists therein that the circuit board waste which is coated with copper, such as obtained in large quantities upon the production of printed circuit boards, can also be used for this, provided that it does not contain further metals. This waste, consisting of the polymeric base material and the copper layers applied thereto, can be disposed of in

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traditional manner only at high expense due to the firm bond between the two materials. After the profitable dissolving of the copper of this waste in a metal-ion generator suitable for this, a sorted disposal of the base material is possible. In similar fashion, reject circuit boards can also be used.

Furthermore, filters for the removal of mechanical and/or chemical residues can also be inserted in the circulation of the plating solution. However, the need for them is less than with electrolytic cells having soluble anodes, since the anode sludge produced by the mixture of phosphorus to the anodes is not present.

For the further explanation of the invention, and further preferred embodiments, reference is had to the following diagrammatic figures.

- Fig. 1 shows the principle of an apparatus for the dip treatment;
- Fig. 2 shows the principle of an apparatus without and with diaphragm;
- Fig. 3 shows the principle of an apparatus with serial conducting of the plating solution;
- Fig. 4 shows the principle of an apparatus for the horizontal transport of the material being treated;
- Fig. 5 shows a metal-ion generator on an apparatus for dip treatment;

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Fig. 6 shows a metal-ion generator on an apparatus for the horizontal transport of the material being treated.

In Fig. 1, the process of the invention is shown on basis of a diagrammatically shown apparatus. The electrolyte space 1 is located in the container 3. The metal-ion generator 2 is so constructed and arranged with respect to the container 3 as to result in short paths for the feeding of the plating solution from the anodes 5 to the metal-ion generator and from there back again into the electrolyte space. For this reason, in the present case, the metal-ion generator is divided into two parts arranged in the vicinity of the insoluble anodes. This division in two is, however, not necessary. Thus, for instance, it can also be arranged as a single unit to the side of or below the bath container. The copper parts to be dissolved are introduced in a loose pile into the metal-ion generator in order to permit easy passage of the plating solution through the generator. On the other hand, however, a minimum loading with copper parts must be maintained therein. The pump 11 pumps the plating solution in a closed circuit through the arrangement. It is essential that the material 6 being treated, which is connected as cathode, be acted upon by the plating solution which is enriched in copper ions, as indicated by the arrows 14, via nozzle assemblies or surge nozzles, not shown here. In this way, the result is obtained that the copper layers

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are deposited on the surface of the material being treated with the necessary quality and the necessary speed. Furthermore, a further flow takes place within the electrolyte space from the space 15 present in the vicinity of the material being treated in the direction towards the space 16 present in the vicinity of the anodes. The plating solution which has been brought to the anodes passes through them, in the case of perforated anode, and arrives, with the advance of the flow, into the outlet 4 which leads to the metal-ion generator. In this way, the result is obtained that a transport of anodically formed oxidizing compounds of the redox system (ferric ions) into the cathode space 15 is minimized. This, in turn, prevents the injurious decomposition of the addition compounds, with simultaneous increase of the cathodic current efficiency.

Along the transport path from the anodes via the outlet into the metal-ion generator, the addition compounds are probably decomposed via a chemical decomposition reaction with the participation of the oxidizing compounds of the redox system. Therefore, the shortest possible connection with high velocity of the plating solution to the metal-ion generator is desirable outside the electrolyte space 1.

The minimum loading of the metal-ion generator with copper parts provides assurance that the oxidizing compounds formed are completely converted within the metal-ion

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generator and the concentration of these compounds at the outlet of the metal-ion generator is lowered to a value of about zero. This means that the copper surface which is in contact with the plating solution in the metal-ion generator leads to the complete reduction of the oxidizing compound to the reduced compounds (ferrous ions), with simultaneous electroless dissolving of copper with the formation of copper ions. The reduced compounds of the redox system do not contribute to the decomposition of the addition compounds.

By targeted flow onto the cathode surfaces, the anodes, for a given total circulation, are subjected to less electrolyte exchange. In this way, the corrosive gases possibly produced at the anodes are led away correspondingly slower, so that, on the one hand, the corrosion of the anodes increases while, on the other hand, it is limited by the following measures:

- low anodic current density
- inert base material of the anodes
- inert coating of the anodes
- surface compacting of the anodes
- liquid-pervious anode geometry.

By these measures, the result is obtained that the addition compounds which are added to the plating solution in order to control the physical-chemical properties of the layer of metal can be used also in arrangements with

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insoluble, dimensionally-stable anodes. Special mixtures of the addition compounds are not necessary for this. A high cathodic current efficiency and a long life of the insoluble anodes is obtained.

Fig. 2 shows another apparatus in accordance with the invention. It differs, on the one hand, from the arrangement shown in Fig. 1 by a difference in the guidance of the plating solution within the electrolyte space, which consists of a space 15 present in the vicinity of the material being treated, namely the cathode space, and of the spaces 16 present in the vicinity of the anodes, namely the anode spaces. These spaces are separated by the dashed lines 17 in the drawing. The plating solution, which was enriched with copper ion in the metal-ion generator 2 upon the reduction of ferric to ferrous ions, flows separately into each space and passes through nozzle assemblies or surge nozzles (not shown) as shown by the arrows 12 and 14 to the anodes 5 and the cathodic treatment material 6. Mixing of the plating solution in the anode space 16 with the solution in the cathode space 15 can take place only to a slight extent, in particular for the reason that the plating solution has its own outlets 4 from the anode space and, separately therefrom, the plating solution has an outlet 18 in the cathode space. In this embodiment, the ferric ion concentration is kept small in the cathode space, which is connected directly with

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the inlet to the metal-ion generator 2, so that a short conduction path from the anode space to the metal-ion generator results. On the other hand, the transport paths from the cathode space via the outlet 18 to the generators can be long, since there are no injurious interactions between the reduced compound which is contained in the plating solution present in the cathode space and the addition compounds. In order to avoid even a slight electrolyte mixing of the plating solutions in the cathode and anode spaces, these spaces can be separated along the lines 17 by, in each case, an ion-pervious partition wall (diaphragm) which, in its turn, is not chemically changed by the plating solution. The partition walls are pervious for the plating solution only to a very slight extent, if at all, so that they permit possibly only a slow equalization of different hydrostatic pressures in the spaces 15 and 16. Polypropylene fabrics or other membranes with a permeability for metal ions and their corresponding gegenions (for instance the Nafion of DuPont de Nemours, Inc., Wilmington, Del., USA) are, for instance, suitable. By separation of the spaces by partition walls, assurance is had that the plating solution cannot pass, for instance, by eddying from the anode space into the cathode space. This measure leads also to a further decrease in the concentration of the oxidizing compounds of the redox system in the vicinity of the cathode.

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Therefore, advantageous effects with respect to the resistance to aging of the plating solution result also from these measures.

The plating solution which is present in the anode space and which contains the ferric ions formed there is, in its turn, transferred, over the shortest path, into the metal-ion generator and enriched there again with copper, with the formation of ferrous ions. In practical operation, a condition of equilibrium between the copper solution in the metal-ion generator and the deposition of copper on the material being treated is established.

Fig. 3 shows another embodiment of the invention, having a two-part metal-ion generator. The plating solution which is enriched in copper ions in the metal-ion generator 2, is introduced only into the cathode space 15. This solution contains, furthermore, only ferrous ions and no ferric ions. The plating solution is conducted in succession from the cathode space 15 to the anode space 16. The ferrous ions formed in the metal-ion generator therefore, after passing through the cathode space, enter with the plating solution via a pump into the anode space. The feeding of the plating solution into the cathode space is effected by another pump 11. A hydrodynamic constancy and the constant transport conditions resulting therefrom are advantageous for the electrochemically active additions of the redox system.

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Furthermore, this serial conducting of the plating solution permits a dividing up of the plating solution withdrawn from the cathode space. In order to control the concentration of the copper ions in the electrolyte space 1, comprising the cathode and anode spaces, a part of the solution is conducted via the lines 43 indicated in dashed line, directly into the metal-ion generator. This partial quantity contains practically no oxidizing compounds of the redox system, so that the copper dissolving rate is reduced by admixture of this portion into the stream of solution which is introduced from the anode space into the metal-ion generator. By control and/or regulation of the partial quantities of the two streams by means of three-way valves (not shown), the copper ion concentration in the plating solution can be adjusted. In the arrangement shown in Fig. 2, these possibilities are not used, although, in that case also, two separate outlets 4 and 18 are present for the plating solutions from the cathode and anode spaces. The solutions of the two spaces are brought together there and conducted jointly into the metal-ion generators. The regenerated solutions coming from the metal-ion generators are fed to the spaces 15 and 16. The manner of procedure in accordance with Fig. 3 is advantageous when the plating solutions of the anode and cathode spaces cannot be mixed together in the electrolyte space, but a complete separation

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of the discharging solutions is not assured in the outlets 4 and 18 from the anode and cathode spaces.

In Figs. 1 to 3, the introduction of the plating solution enriched in copper ions into the container 3 is shown, by way of example, to be effected from below and the introduction into the metal-ion generator from above. In corresponding manner, the off lines from outlets 4 and 18 from the container 3 are shown at the top and those from the metal-ion generator 2 at the bottom. Circulation of the plating solution in other directions is also possible, such as, for instance, the introduction of the solution into the metal-ion generator from below.

Another embodiment of the invention, particularly for the electrolytic metallizing of plate-shaped treatment material, preferably circuit boards, in horizontal passage through the arrangement, is shown in Fig. 4. The system, part of which is shown in side view, consists of the electrolytic part 20 and a metal-ion generator 21 filled with copper, shown below it. The electrolytic part 20 consists of a plurality of individual electrolytic cells. Four of these individual cells are designed by the reference numerals 22, 40, 41, 42 in Fig. 4, with an insoluble anode 23 in each case for the top side and the bottom side of the treatment material 24. The treatment material is electrically connected to a rectifier (not shown) and is cathodically

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polarized. It is transported through the installation, in the direction of the arrow 25, by means of rollers or disks 26. The transport elements 26 are uniformly distributed along the entire installation. For reasons of simplification of the drawing, they have been shown here only at the beginning and end of the transport path. Surge nozzles or flood pipes 27, 39 are also present, uniformly distributed in the electrolytic cells. They correspond to the nozzle assemblies already mentioned above.

Plating solution coming from the metal-ion generator 24 is fed by pumps 29 to the flood pipes 27, 39 via the pipelines 28. The plating solution flows through the outlet openings of the flood pipes or surge nozzles onto the surfaces of the treatment material 24. In this connection, copper ions are reduced to metallic copper and deposited as a metallic layer on the material to be treated, and the ferrous ions, also present, are conveyed with the discharging electrolyte in the direction towards the anodes 23. In order to avoid a return flow from the anodes to the cathodes, various methods are provided the effecting of which is shown diagrammatically in Fig. 4. The plating solution which is enriched with copper is used for flow to the cathode (treatment material). From the plate-shaped treatment material, the stream of solution is then so deflected that, as indicated by arrows 30, it continues in the direction

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towards the anodes. In the case of perforated anodes, which are preferably used, the solution passes through them and then passes via suction pipes 31 and pipelines 32 back into the metal-ion generator. The anodes can consist, for instance, of expanded metal or netting. Openings 33 support the flow process. In order to avoid the formation of eddying, baffle walls 34 extending in the direction towards the material being treated can be arranged on the suction pipes. The slot 35 remaining between the baffle walls and the treatment material can amount to a few millimeters. From the standpoint of fluid mechanics, this forms practically closed electrolytic cells having favorable flow conditions. The flood pipes 27 can also be provided with baffle walls 36 in order to prevent further possible eddies.

Different flood pipes in different number are shown, by way of example, in the electrolytic cells of the arrangement shown in Fig. 4. The circulation of the plating solution is such that the level 37, which is above the suction pipes, is present in the electrolytic part of the installation. In the electrolytic cell 42 shown on the right, partition walls 38 are shown between each of the anodes 23 and the treatment material 24. In this way, the exchange of the plating solutions in the cathode and anode spaces over a direct path is minimized. By the use of ion-pervious partition walls, on the other hand, an ion-exchange between the chambers is made

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possible. The solution in the cathode space can emerge at the end side. In the anode space further flood pipes 39 are provided. The solution of this chamber passes out via the suction pipes 31. For such a cell, the serial flow path such as already described on the basis of Fig. 3 is again suitable.

The leading away of the plating solution from the anode space via the suction pipes 31 into the metal-ion generator 21 can take place over the shortest path in order to keep the life of the ferric ions as short as possible. Therefore, the metal-ion generator 21 is arranged here also as close as possible to the electrolytic part 20. In this way, short connection paths and short transport times result. The principle of construction can advantageously also be so selected that the parts 20 and 21 form a complete system. Each of several flood pipes 27 is fed by a pump 29 in the manner shown in Fig. 4. However, a single pump can also be used. This would lead to longer connecting paths between the flood pipes 27, 39 and the metal-ion generator 21. The plating solution in these connecting lines contains practically no oxidizing compounds of the redox system. Thus, the protection of the addition compounds is assured in this region also.

The electroplating installation is shown in side view in Fig. 4. The parts shown (anodes, pipes) extend in length

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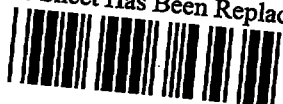
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into the depth of the drawing, and therefore transverse to the direction of transport over the material to be treated. The parts present in the electrical field between anode and cathode, such as, for instance, the flood pipes 27, consist of electrically non-conductive plastic. Their electric screening action is not disturbing here, since the material to be treated moves slowly through the installation and thus is continuously exposed to the different electrical fields.

Fig. 5 shows an arrangement in accordance with the invention having two metal-ion generators 44, an electrolyte space 1, and two additional electrolyte containers 45. This arrangement is operated in the dip process. In this case, the cell is developed symmetrically for the electroplating of the front and rear sides of the treatment material 6. The two metal-ion generators 44 shown in the figure and the electrolyte containers 45 can in each case also be provided individually and in such case arranged on both sides of the material being treated.

The metal-ion generator 44 consists of a preferably round tubular body 46 having an upper opening 47. All materials used for this are resistant to the plating solution and the additions contained in the solution. At least one pipe socket 49 extends through the bottom 48 of the metal-ion generator into the inside of the metal-ion generator. This pipe socket has lateral openings 50. They form a screen

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which, on the one hand, prevents penetration of metallic copper into the pipeline system and, on the other hand, permits the passage of the plating solution into the metal-ion generator. A small roof on top closes the top of the pipe socket. The roof at the same time holds the lateral openings 50 free of fine copper granulate which is present in this region of the metal-ion generator. Below the bottom, there is a mixing and collection chamber 51. Copper particles and impurities which were able to pass through the screen are collected in it. After opening the base plate 52, the chamber is accessible for cleaning purposes. Upon operation, the plating solution pumped out of the anode space 16, which solution is enriched in copper-dissolving ferric ions, enters. In addition, air which contains oxidizing oxygen can also be blown into the metal-ion generator via lines 56. In this case, the chamber 51 serves at the same time as mixing chamber. Through the holes 50 in the pipe socket 49, the plating solution and possibly air enter into the inside of the metal-ion generator. In the lower region of the generator there is predominantly fine copper granulate which has been formed by the dissolving of the metallic copper. It has a very large specific surface, which offers itself immediately for the dissolving of copper to the incoming plating solution which is enriched in ferric ions. The ferric ions are therefore rapidly reduced to ferrous

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ions, with the simultaneous dissolving of copper. Within the metal-ion generator, the quantity of ferric ions decreases rapidly towards the top. This has the result that the electrolytic copper which has been introduced as granulate or sections 53 is dissolved in upward direction to a continuously lesser extent. The dimensions of the granulate remain large in the upper region of the metal-ion generator. Thus, the permeability for the plating solution is also retained. Through the overflow 54, the solution discharges without pressure from the metal-ion generator into the electrolyte container 45. Within the metal-ion generator, the overflow 54 bends downward in such a manner that copper granulate 53 which slides downward from above cannot lead to the clogging of the generator. As a result of the sufficiently large dwell times, adapted to each other, of the plating solution which has entered into the generator, and which, at the same time, is sufficiently long for the dissolving of the copper surface offered, the plating solution which flows over the overflow 54 into the electrolyte container 45 contains practically no ferric ions any longer. Such an over-dimensioning of the regeneration unit thus provides assurance that the attack of the ferric ions on the addition compounds of the plating solution is complete already in the middle region of the generator.

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The filling and refilling of the metal-ion generator with metallic copper 53 is effected from above, through the opening 47 of, for instance, hopper shape. It can be closed by a cover. The region above the overflow 54, in which no plating solution is present, serves for the storing of metallic copper which is to be dissolved in the metal-ion generator. The filling and refilling can be effected manually. The arrangement is excellently suited for the automating of the filling process due to the absence of pressure at the filling opening 47 and the vertical or oblique arrangement. The filling can take place continuously or batchwise. Transport belts or vibratory conveyors (not shown here) which are known from the conveyance art transport the metallic copper into the openings 47 of the generators.

The invention has the advantage that copper parts of different geometrical shape can be dissolved in the metal-ion generator. Different shapes, however, have a different piling behavior. In order to maintain the permeability of the pile for the plating solution and to assure a sufficiently large copper surface which is accessible to the solution, additional individual measures are possible:

Downwardly inclined plates 55 within the generator prevent too great a compacting of the copper in the lower region. The plates are provided with holes the dimensions of which are adapted to the size of the metallic copper parts

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introduced. The holes are selected from plate to plate smaller from top to bottom corresponding to the dissolving of the copper. Similarly, the dimensions of the plates can increase from the top to the bottom. The angle of inclination can also be adapted to the circumstances of the pieces of copper introduced into the metal-ion generator.

The inclined position of the metal-ion generator itself can have the same result. By the blowing of air 56 into the lower region of the metal-ion generator or into the mixing and collecting chamber 51, a copper-dissolving substance, in this case oxygen, can also be introduced. In addition to this, the eddying of the copper granulate in the metal-ion generator connected therewith increases the reduction of the ferric ions and the dissolving of the copper. At the same time, the permeability for the plating solution through the copper parts is increased. With copper fillings which hook on to each other, it may be advisable to shake the metal-ion generator at times or continuously. The shaking movement can preferably be obtained from a vibrating conveyor, with which the automatic filling can at the same time be effected. All the measures described above for disturbance-free continuous operation of the metal-ion generator can also be combined with each other.

The electrolyte containers 45, 67 shown in Figs. 5 and 6 serve to reduce the dependence of the flow of the plating

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solution along the treatment material 6, 69 on the flow through the metal-ion generator 44', 66. This has the advantage that, in both circuits, the quantity of plating solution and its speed can be adjusted individually. These processes are described below with reference to Fig. 5.

The plating solution is conveyed by a pump 57 from the electrolyte container 45 into the electrolyte space 1. The solution flows through the flood pipes 58 arranged there onto the treatment material 6 and from the flow pipes 59 onto the liquid-pervious insoluble anodes 5. The division of the stream of solution over the flow pipes 58 and 59 is effected by adjustable valves, not shown in the drawing. From the cathode space 15, the plating solution flows via the outlet 8 through pipelines 60 and the outlet 61 back into the electrolyte container 45. Closely behind the anodes 5 there are suction pipes 62 through which the plating solution enriched with ferric ions is drawn off by means of the pump 63 and conveyed with high speed into the metal-ion generator. From there, the solution enriched with ferrous and cupric ions then returns again into the electrolyte container 45.

The division of the streams over the flood pipes 58 and 59 is so adjusted that an excess results in the cathode space 15. This equalizes itself with the anode space 16. If the two spaces are separated by a partition wall 17, as shown in Fig. 5, then at least one opening 64 in the partition wall

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sees to it that the equalizing of the plating solutions in the two spaces can take place in the direction indicated by the arrow. In order to avoid a mixing of the solutions in the electrolyte space 1 and a convective transport of ferric ions from the anode space to the cathode space, it therefore need merely be seen to it that a higher hydrostatic pressure is present in the plating solution in the cathode space 15 than in the anode space 16. This is assured by a corresponding adjustment of the partial streams through the flood pipe 58 and the flood pipes 59 of the circuit of the pump 57. In addition, the circuits of the pumps 57 and 63 are independent of each other.

Within the metal-ion generator, all ferric ions introduced with the feed stream are reduced to ferrous ions. Nevertheless, it cannot be excluded that a very small, scarcely measurable number of ferric ions pass through the metal-ion generator and enter into the electrolyte container 45. In order to reduce the ferric ions which have entered into said container to ferrous ions, copper parts 65 are introduced also into this container. In this case, copper scrap may also be used.

Another embodiment of the apparatus in accordance with the invention for the carrying out of the process is shown in Fig. 6. There is concerned here a horizontal circuit board electroplating installation shown in cross section. The

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figure shows the metal-ion generator 66, an electrolyte container and an electroplating cell 68. The circuit board 69 which is to be metallized is gripped in the arrangement by clamps 70 and conveyed horizontally through the installation. The contacting of the circuit board with the negative pole of a rectifier (not shown) is also effected via these clamps. In another embodiment, the contacting could also be effected by contact wheels. A pump 71 pumps the plating solution via flood pipes 72, 73 to the circuit boards and to the insoluble perforated anodes 74. Via outlets 75, the plating solution is conducted out of the cathode space back into the electrolyte container 67. From the anode space, the pump 86 conducts the plating solution which has been enriched with ferric ions through suction pipes 76 at high speed into the metal-ion generator. An outlet 77, which is developed as overflow for regulating the level, sees to it that excess plating solution passes from the upper region of the anode space also into circuit to the metal-ion generator 66 and not into the electrolyte container 67. The metal-ion generator is constructed in the manner which was described with reference to Fig. 5. Via the overflow 78, the plating solution passes back into the electrolyte container 67. In the latter, there are also contained copper parts 79 which effect a reduction to ferrous ions of stray ferric ions which are possibly present in this region. Furthermore, partition

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walls 80 are provided between the anode and cathode spaces. Openings 81 in these partition walls see, here also, to an equalization of the streams of the plating solution from the cathode space into the anode space. These directions of flow are also established if no partition walls are present.

Horizontally operating continuous installations such as shown in Figs. 4 and 6, and vertically operating electroplating installations have dimensions of several meters in length of the electrolytic cells. Therefore, in practice, preferably several metal-ion generators are arranged along the installation. This makes it possible to set them up in close spatial vicinity to the electrolytic cell or effect a partial or complete placing of electrolytic cell, electrolyte container, and metal-ion generator one within the other.

During the passage of a circuit board through the electroplating installation, the clamps 70 are also metallized in the region of their contacts 82. This layer must be removed again before the clamps are again used. This is done, in known manner, during the return of the clamps to the start of the electroplating installation. In this connection, the returning clamps 83 pass through a separate compartment 84 which is connected with the plating solution in the electrolytic cell 68. For the demetallization, the clamps 83 are connected via wiper contacts with the positive

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pole of a rectifier, not shown. The negative pole of this rectifier is connected to a cathode plate 85. During the electrolytic demetallization process, copper deposits on the insulating layers of the clamps 83 lose electric contact with the current supply before they are completely dissolved. Therefore, disturbing deposits of copper on these regions remain back. In accordance with the invention, therefore, the parameters for the demetallization, namely current and time, are so adjusted that, for instance, only 70% of the demetallization path is required for the removal of the metal layer. In the remaining path, Fe^{3+} ions are produced by the electrolysis current on the metallic contacted parts of the clamps. These ions are present precisely at the place where contact-less copper deposits are possibly still present. They dissolve this copper electroless. No noticeable increase in ferric ions in the electrolytic cell occurs as a result of this since, as compared with the metallizing of the treatment material, only very small currents and surfaces are concerned.

In order to maintain an operable deposition of metal, the copper content in the plating solution must be kept within given limits. This presupposes that the consumption rate and the rate of addition of copper ions correspond. In order to check the copper content, the absorption power of the plating solution can be measured at a wavelength of for

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instance 700 nm. The use of an ion-sensitive electrode has also proven suitable. The measured value obtained serves as actual value of a controller the control value of which is used to maintain the copper-ion concentration in the specific embodiments of the invention described.

For the analytical noting of the concentrations of the compounds of the redox system, a potential measurement can be carried out. For this purpose, a measurement cell is used which is formed of a platinum electrode and a reference electrode. By suitable calibration of the measured potential with the concentration ratio of the oxidizing and reduced compounds of the redox system for a given total concentration of the compounds, the corresponding concentration ratio can be determined. The measurement electrodes can be installed both in the anode and cathode spaces as well as in the pipelines of the arrangement.

In order to verify the anode processes, such as, for instance, the oxidation of the redox system required for the production of copper and a possible anodic decomposition of the addition compounds, a further measuring device can be provided with which the cathode potential is measured with respect to a reference electrode. For this purpose, the anode is connected via a potential measuring instrument with the corresponding reference electrode.

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The continuous or discontinuous measurement of further galvanotechnical parameters is advisable, such as, for instance the determination of the content of addition compounds by means of cyclic voltametrics. Thus, after lengthy pauses in operation, temporary changes in the concentration can occur. Knowledge of the instantaneous values can be utilized in order to avoid improper dosaging of the chemicals to be added.

The following examples serve for further explanation of the invention:

Example 1

In an arrangement in accordance with Fig. 2, using the measures in accordance with the invention (large specific surface of the copper parts in the metal-ion generator, high velocity of flow in the entire arrangement, conducting of the flow in such a manner that the oxidizing compounds of the redox compounds formed by oxidation at the anode cannot reach the cathode), a copper bath having the following composition was used:

80 g/liter copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

180 g/liter sulfuric acid, conc.

10 g/liter iron as ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)

0.08 g/liter sodium chloride

with the following brighteners:

1.5 g/liter polypropylene glycol

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0.006 g/liter 3-mercaptopropane-1-sulfonic acid, sodium
salt

0.001 g/liter N-acetylthiourea

A current efficiency of 84% was determined. The
consumption was determined over 100 amp hours/liter as:

propyleneglycol	3.3 g/kAh
3-mercaptopropane-1-sulfonic acid	
sodium salt	0.3 g/kAh
N-acetylthiourea	0.04 g/kAh

The elongation upon rupture of the deposited layers
amounted to 17% at the end of the test.

Example 2

The test of Example 1 was repeated in the arrangement
shown in Fig. 3, the plating solution being conducted
serially through the cathode and anode spaces. A current
efficiency of 92% was obtained. The consumption, again
determined over 100 amp hours/liter, was:

propyleneglycol	2.0 g/kAh
3-mercaptopropane-1-sulfonic acid	
sodium salt	0.2 g/kAh
N-acetylthiourea	0.02 g/kAh

The elongation upon rupture was improved to 20%. In
this test, the coated circuit boards passed a second
soldering shock test (10 seconds at 288°C soldering

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temperature) without cracks in the region of the holes. The deposition was uniformly shiny.

Example 3

In a horizontal installation in accordance with Fig. 4, circuit boards were copper-plated in a plating solution of the following composition:

80 g/liter copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

200 g/liter sulfuric acid, conc.

8 g/liter iron as ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$)

0.06 g/liter sodium chloride

As brighteners there were added:

1.0 g/liter polypropylene glycol

0.01 g/liter 3-(benzthiazolyl-2-thio)-

propylsulfonic acid, sodium salt

0.05 g/liter acetamide

With an electrolyte temperature 34°C , bright metal layers were obtained on a scratched copper laminate with a current density of 6 amps/dm^2 . The circuit board metallized in this manner withstood five soldering shock tests (10 seconds at a soldering temperature of 288°C). The current efficiency was 91.%. No problems arose in the handling (making up of the addition substances consumed) of the plating solution.

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Example 4 (Comparison Example)

The test described in Example 1 was carried out in an electrolysis cell. The measures in accordance with the invention were not used, in particular not the feeding of the stream to the cathodes and anode in accordance with the invention.

At a temperature of the plating solution of 30°C, bright metal layers were obtained on scratched copper laminate surface with a current density of 4 map/dm². The cathodic current efficiency was only 68%. The consumption of the addition compounds without entrainment of the plating solution by lifting the treatment material out of the bath container amounted, averaged over 100 amp hours/liter, was:

propyleneglycol	5 g/kAh
3-mercaptopropane-1-sulfonic acid	
sodium salt	1.6 g/kAh
N-acetylthiourea	0.2 g/kAh

The elongation upon rupture of the deposited layers was only 14% at the end of the test.

Example 5 (Comparison Example)

Copper layers were deposited on circuit boards in accordance with Example 1 after a substrate of copper had been previously deposited from the solution for a lengthy period of time (2000 amp hours/liter).

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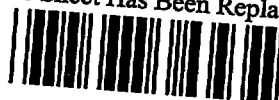
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The circuit boards no longer withstood two soldering shock tests (10 seconds at a soldering temperature of 288°C) without cracks. Furthermore, non-uniform copper layers were obtained. In Examples 1 to 3, copper layers with good to very good elongation upon rupture were, to be sure, deposited. The cathodic current efficiency and the consumption of the addition compounds which were added to the plating solution in order to control the physical-mechanical layer properties, were satisfactory. The appearance of the copper layers was excellent and withstood the use tests.

After lengthy loading of the plating solution upon the electrolytic deposition of copper, on the other hand, no suitable results were obtained any longer.

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CLAIMS

1. A process for the electrolytic deposition of uniform metal layers of given physical-mechanical properties, in particular layers of copper, with high current efficiency from a plating solution containing ions of the deposited metal, compounds of a electrochemically reversible redox system, and addition compounds for controlling the physical-mechanical properties of the metal layers, in which
 - cathodes;
 - insoluble, dimensionally stable anodes;
 - a metal-ion generator by means of which the metal ions are formed by the dissolving of suitable metal parts upon passage of the plating solution containing oxidizing compounds of the redox system formed by anodic oxidation; and
 - means by which the concentration of the oxidizing compounds in the direct vicinity of the cathode is minimized, preferably to a value of less than about 0.015 moles/literare used.
2. A process according to Claim 1, characterized by the fact that the concentration of the compounds of the redox system is held slightly below a value which is

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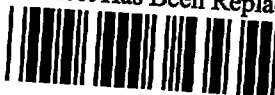
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necessary in order to maintain the metal-ion concentration.

3. A process according to any of the preceding claims, characterized by the fact that the surface of the metal parts is selected so large that the concentration of the oxidizing compounds is lowered to a value of about zero upon passage through the metal-ion generator.
4. A process according to any of the preceding claims, characterized by the fact that the plating solution passes to the anodes with a high velocity of flow and is transferred from there to the metal-ion generator with high velocity.
5. A process according to any of the preceding claims, characterized by the fact that at least one second oxidizing compound, preferably oxygen, is furthermore introduced into the metal-ion generator.
6. A process according to any of the preceding claims, characterized by the fact that a part of the solution present in the cathode space is conducted directly to the metal-ion generator without being fed to the anodes.
7. A process according to any of the preceding claims, characterized by the fact that the plating solution which is conducted through the metal-ion generator flows

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directly to the cathode and then, by deflection of the direction of flow, to the anodes.

8. An apparatus for the electrolytic deposition of uniform layers of metal of given physical-mechanical properties, in particular copper, with high current density, from a plating solution which is in contact with cathodes (6, 24, 69) and with insoluble, preferably perforated, dimensionally stable anodes (5, 23, 74), comprising an electrolyte space (1) arranged between the cathodes and the anodes, means for feeding the plating solution to the cathode and anode, a metal-ion generator (2, 21, 44, 66), a first means for transferring the plating solution fed to the anodes to the metal-ion generator, and a second means for transferring the plating solution emerging from the metal-ion generator into the electrolyte space, said means bridging over a distance of small space between the anodes and the metal-ion generator.
9. An apparatus according to Claim 8, characterized by the fact that means (31, 62, 76) are provided by which the plating solution present in the vicinity of the anodes is drawn off with high velocity or is removed via outlets (4, 61, 77) and transferred to the metal-ion generator (2, 21, 44, 66).

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10. An apparatus according to either of Claims 8 or 9, characterized by the fact that the electrolyte space (1) is divided into several compartments by ion-permeable partition walls (17, 38, 80).
11. An apparatus according to any of Claims 8 to 10, characterized by the fact that outlets (18, 75) are provided by which the plating solution present in the vicinity of the cathodes is removed from the electrolyte space (1) and brought to the metal-ion generator (2, 21, 44, 66).
12. An apparatus according to any of Claims 8 to 11, characterized by the fact that as metal-ion generator (2, 21, 44, 66) there is provided a tubular apparatus which can be filled from the top and is provided with a bottom (48) in its lower region and, for the entrance of the plating solution, with at least one pipe connection (49) having lateral openings (50), and, in its upper region, with an overflow (54, 78) which discharges into an electrolyte container (45, 67),
13. An apparatus according to any of Claims 8 to 12, characterized by oblique, preferably perforated, plates (55) within the metal-ion generator (2, 21, 44, 66).

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14. An apparatus according to any of Claims 8 to 13,
characterized by means for the blowing-in of air (56)
arranged in the lower region of the metal-ion generator
(2, 21, 44, 66).
15. An apparatus according to any of Claims 8 to 14,
characterized by means (26, 70, 82) for the horizontal
grasping, electrical contacting, and movement of the
cathodes in horizontal direction.
16. The use of the process according to any of Claims 1 to 7
for the metallizing of circuit boards.
17. A process for the electrolytic deposition of metals,
characterized by some or all of the new features or by
combinations of the features disclosed.
18. An apparatus for the electrolytic deposition of metals,
characterized by some or all of the new features or by
combinations of the features disclosed.

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PROCESS AND ARRANGEMENT FOR THE ELECTROLYTIC DEPOSITION
OF METAL LAYERS

ABSTRACT OF THE DISCLOSURE

For the electrolytic deposition of uniform layers of metal having given physical-mechanical properties, particularly of copper, soluble anodes are not used, since their geometrical shape is changed by the deposition and therefore the distribution of the lines of force in the electrolytic cell are continuously changed.

In order to solve the problems occurring in this connection, a process has been proposed in which compounds of a redox system added to the plating solution are converted during the deposition on the insoluble anodes. The compounds produced in this connection dissolve new metal ions from a reservoir which contains parts of the metal to be deposited, so as again to supplement the metal ions removed from the solution by deposition.

The present invention describes a procedure in which, differing from the prior art, the addition compounds are not destroyed.

Fig. 6

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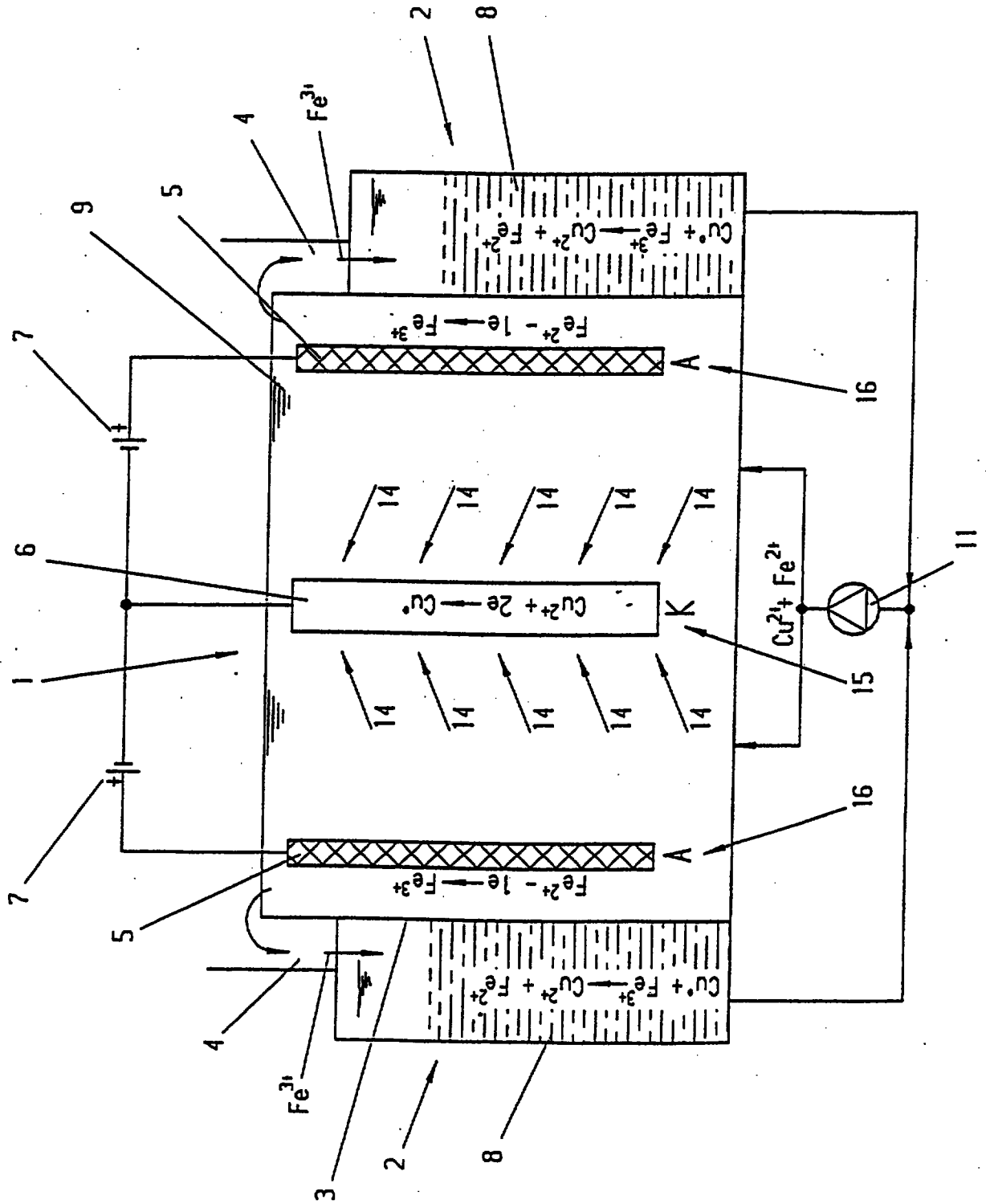


Fig. 1

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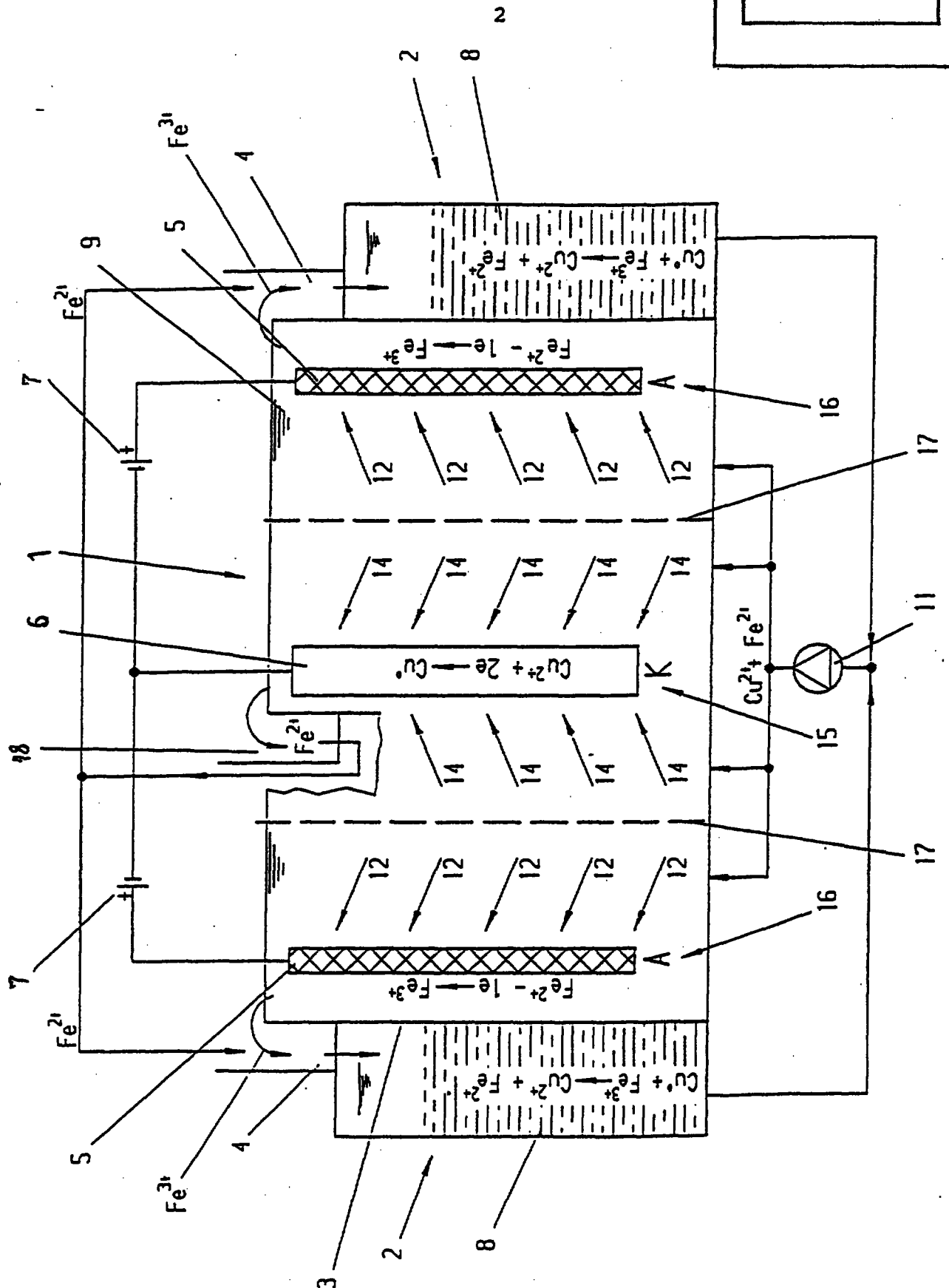


Fig. 2

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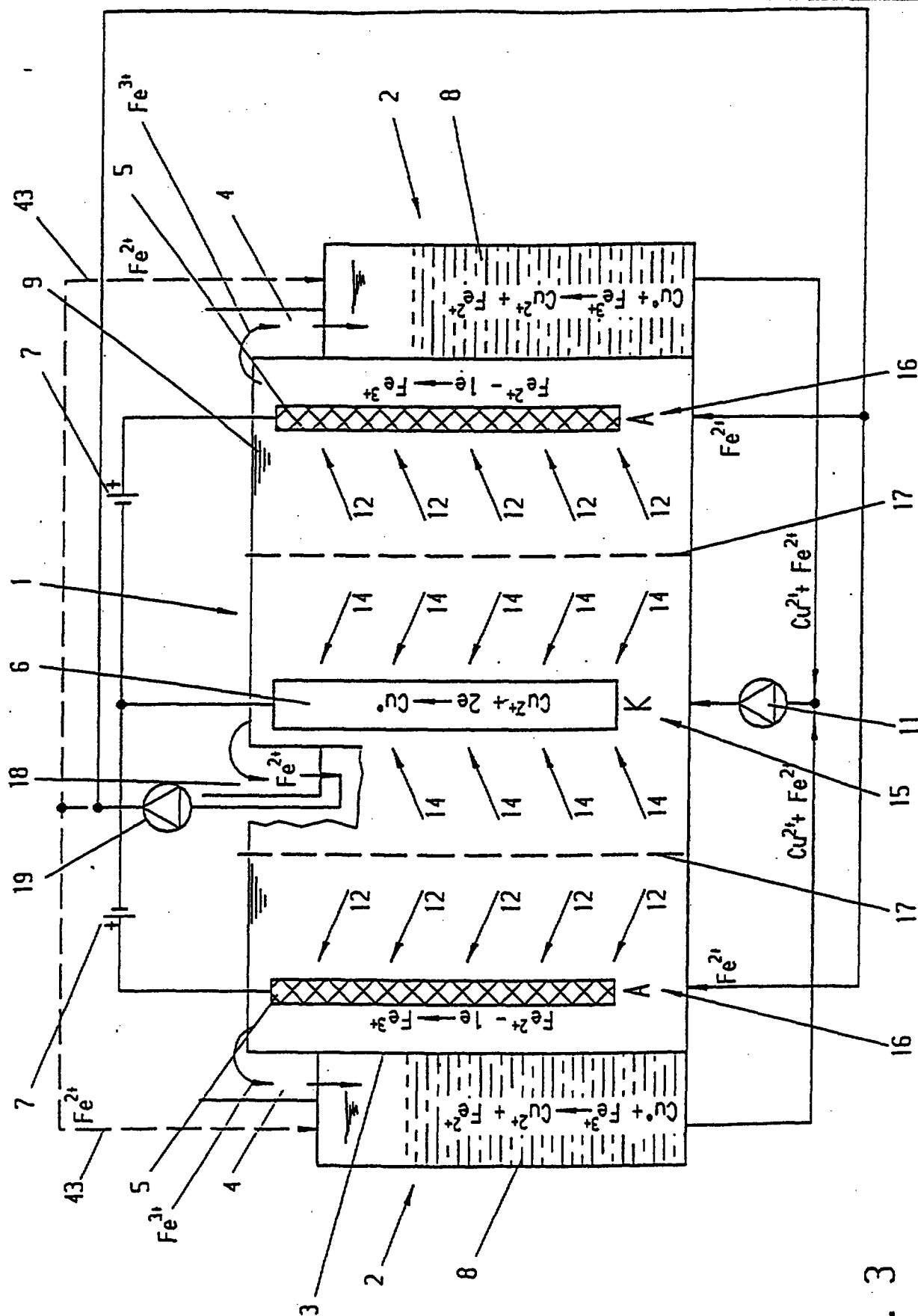


Fig. 3



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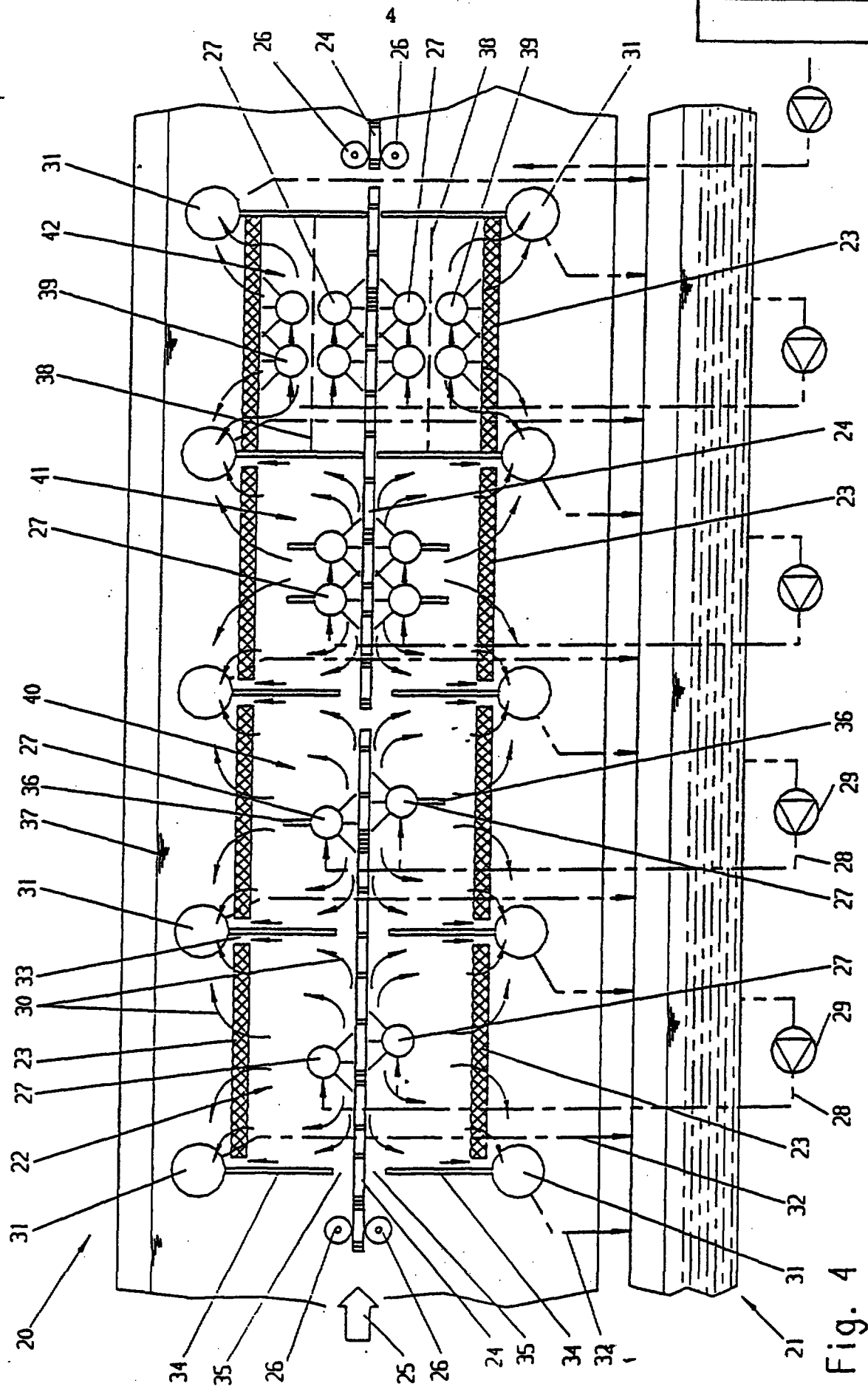


Fig. 4



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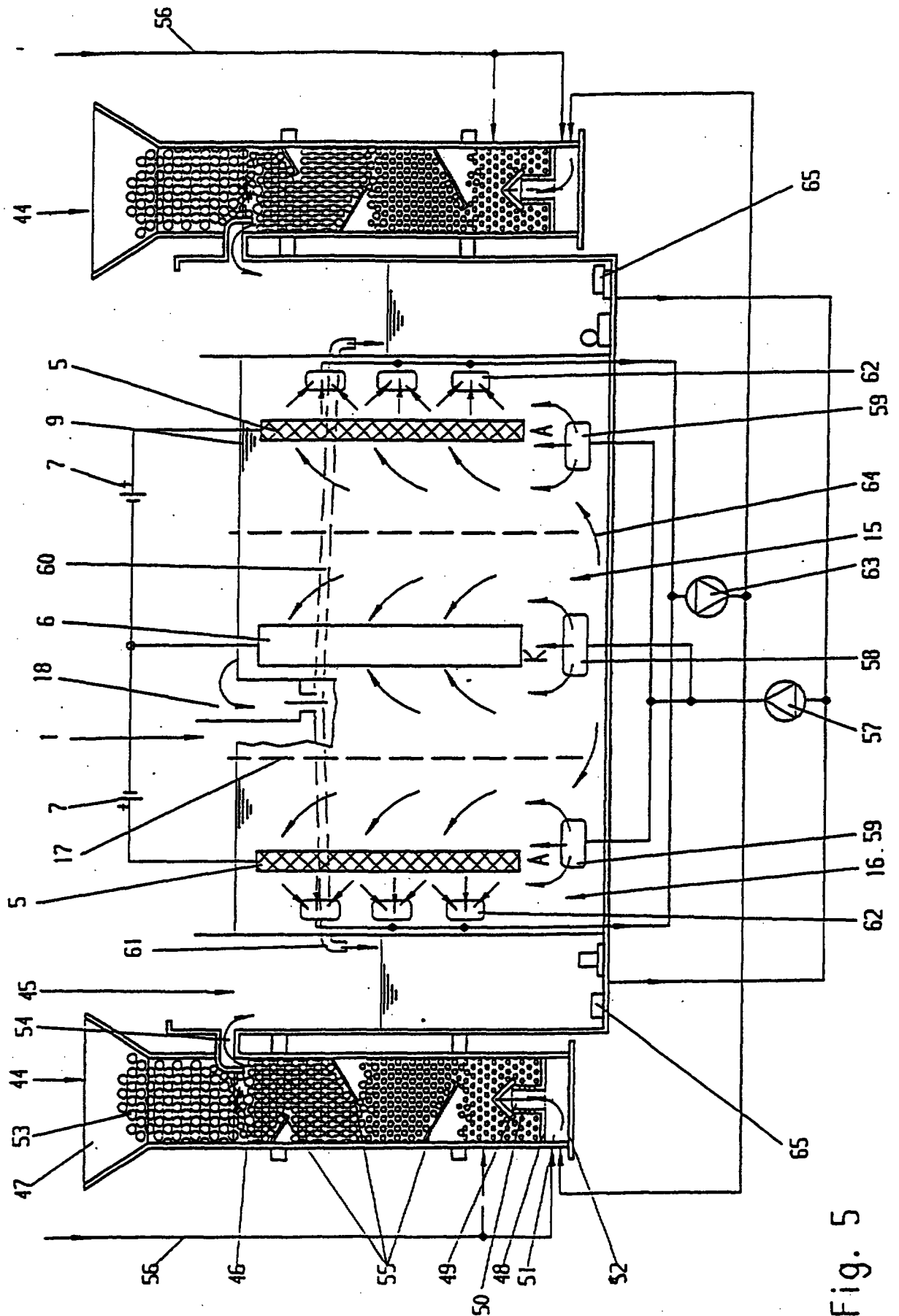


Fig. 5

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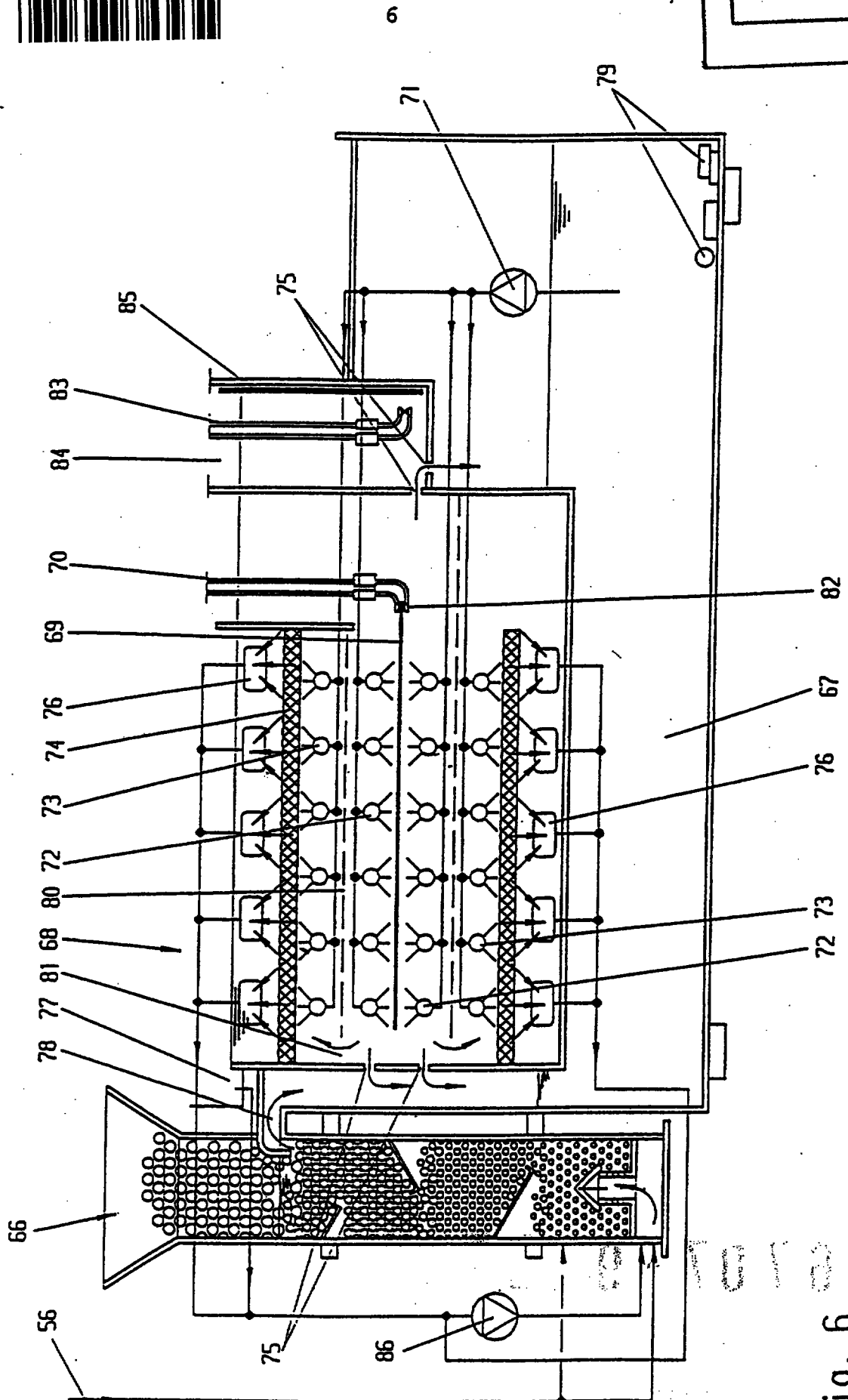


Fig. 6

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PROCESS AND DEVICE FOR ELECTROLYTIC PREPARATION OF METALLIC LAYERS

The invention relates to a method and device for the electrolytic deposition of uniformly thick metal layers, preferably made of copper, with specific physical-mechanical properties.

The electrolytic plating, for example with copper, of at least superficially electrically conductive workpieces has been known for a long time. For this purpose, the workpieces to be coated are connected as cathodes and are brought into contact together with anodes in the electrolytic deposition solution. For the deposition, an electrical current flow is produced between the anode and the cathode.

Anodes made from metal, which is deposited from the deposition solution, are normally used. In this case, the quantity of metal in the deposition solution which is deposited from the solution is supplied again to the anodes by dissolving. In the case of copper, the deposited quantity and the anodically dissolved quantity are roughly the same when the charge throughput is predetermined. This method can be carried out simply since, at least in the case of copper, only intermittent metering and adjustment of the metal ion concentrations in the deposition solution is required.

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However, disadvantages have come to light in the execution of this method while using these soluble anodes. If the thickness of the deposited metal layers on the surface of the workpiece is to be totally uniform at all points then the soluble anodes are only suited to this mentioned purpose in a limited manner since they change their shape in time by dissolving so that the field line distribution likewise changes in the electrolytic bath. The use of smaller, for example spherical metal pieces as anodes in insoluble metal baskets is also only suited in a limited manner to solving the problem since the metal parts frequently become wedged together and, as a consequence of the dissolving process, frequently form gaps when being lowered during stacking of the metal parts.

Several attempts have therefore been made to use insoluble and hence dimensionally stable anodes instead of soluble anodes. For this purpose, titanium or special steel for example may be considered. By using these anode materials, gases are formed such as for example oxygen or chlorine during electrolytic deposition since the anodic metal dissolving no longer takes place. The resultant gases attack the anode materials and dissolve these gradually.

In the German Patent publication DD 215 589 B5 a method for electrolytic metal deposition is described where

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insoluble metal anodes are used and in which reversible electrochemically replaceable materials are added to the deposition solution as a supplement, which are transported by intensive forced convection with the deposition solution to the anodes of a deposition device, are replaced electrochemically there by the electrolytic current, are directed after their replacement by means of intensive forced convection from the anodes into a regenerating chamber, are returned electrochemically to their initial condition in the regenerating chamber on regenerating metal located in said chamber with simultaneous external electroless metal dissolving of the regenerating metal and, in this initial condition, are conducted back to the deposition device with intensive forced convection. By using this method, the disadvantages presented when using insoluble anodes are avoided. Instead of using corrosive gases, the materials added to the deposition solution are oxidised on the anode so that the anodes are not attacked.

The dissolving of the metal in the regenerating chamber is hereby independent of the process for metal deposition on the item to be treated. The concentration of the metal ions to be deposited is therefore regulated by the effective metal surface in the regeneration chamber and by the flow velocity during circulation. If there is a shortage of metal ions the effective metal surface and/or

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the flow velocity from the deposition chamber to the regeneration chamber is increased, or if there is a surplus of metal ions, correspondingly reduced. This procedure assumes therefore that a high concentration of the reversible electrochemically replaceable material is contained in the deposition solution. This leads to the oxidised compounds of the supplemented materials (redox system) being reduced again on the cathode so that the current efficiency is decreased.

In the German published Patent application DE 31 10 320 A1 a method for cation reduction by anode supported electrolysis of cations in the cathode chamber of a cell is described, the anode chamber containing iron (II)-ions as reduction means and the anodes being moved relative to the anolytes surrounding the anodes.

In the German published Patent application DE 31 00 635 A1, a method and device for regenerating an electroplating solution with a metal to be deposited in an electroplating device is described, the metal to be electrolytically deposited being provided in an electroplating solution contained in an electroplating container and a supply of the metal to be deposited being provided within a sealed chamber, the gases produced in the electroplating container during progress of the electroplating process being conducted together with the electroplating solution

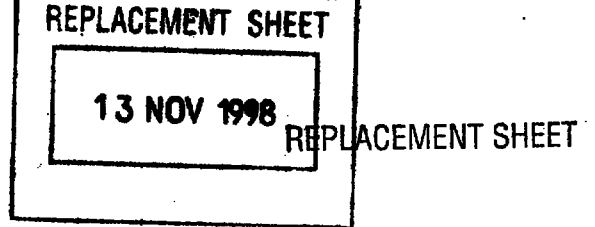
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into the sealed chamber and being applied there to the metal supply to dissolve it and subsequently the dissolved metal supply being added again to the electroplating solution in the electroplating container. The device required for the execution of this method is however very demanding since, amongst other things, this must be carried out in sealed conditions.

The mentioned methods have the advantage that the deposition solutions to be regenerated contain no additive compounds which are normally required however for controlling the physical-mechanical properties of the metal layers to be deposited. As far as these materials are concerned, organic materials are predominantly used.

The required physical-mechanical layer properties are only achieved by means of these additive compounds, properties such as for example, adequate sheen, high fracture elongation and resistance of the layer to tears during soldering shock tests. Without supplement of these compounds the layers are dark, matt and rough.

In the publication DD 261 613 A1, a method is described for electrolytic copper deposition from acidic electrolytes with a dimensionally stable anode while using specific additives to produce copper layers with defined physical-mechanical properties, the deposition electrolyte



also containing the already mentioned electrochemically, reversibly replaceable supplement materials.

It has emerged that the quality of the metal layers which are deposited from depositing solutions of this type firstly indeed correspond to requirements, namely with respect to the physical-mechanical properties, however, after a fairly long deposition time, layers with reduced quality are obtained even when the materials in the deposition solution, the concentration of which has been reduced during deposition by usage, are regenerated. Only slightly ductile copper layers are obtained from ageing deposition solutions so that layers of this type on the circuit boards tear in the region of the bores, if these are subjected to a soldering shock test. In addition, the metal layer surface changes disadvantageously by becoming matt and rough.

Therefore the problem underlying the present invention is to avoid the disadvantages of the methods and arrangements according to the state of the art and to find an economical method and device suited to that purpose for the electrolytic deposition of metal layers, especially those made of copper; the metal layers deposited according to the method and by means of the device having the prescribed physical-mechanical properties, by adding additive compounds to the deposition solution to control

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the metal layer properties and not changing the metal layer properties disadvantageously even after a fairly long deposition time. In addition, the metal layer thicknesses should be almost identical at all points on the surface of the item to be treated and deposition should be possible with a high current efficiency.

The problem is resolved by the characteristics of Claims 1 and 8. Preferred embodiments of the invention are given in the sub-Claims.

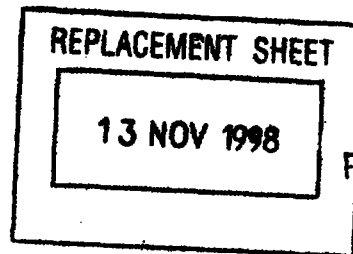
In order to achieve adequately uniform layer thicknesses on the surface of the item to be treated, insoluble, dimensionally stable anodes are used. For regeneration of the metal ions, which have been depleted by deposition and which in a preferred application are copper ions, a metal ion generator is used in which parts of the metal to be deposited are contained. The deposition solution contains, in addition to the metal ions, compounds of an electrochemically reversible redox system. For regeneration of the deposition solution, which has been depleted of metal ions by usage, said deposition solution is passed over the anodes, oxidising compounds of the redox system being formed. Subsequently, the solution is directed through the metal ion generator, the oxidising compounds reacting with the metal parts by forming metal ions. At the same time, the oxidising compounds of the

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redox system are transformed into the reduced form. By means of forming metal ions, the overall concentration of the metal ion concentration contained in the deposition solution is kept constant. From the metal ion generator, the deposition solution proceeds back again into the electrolytic chamber which is in contact with the cathodes and anodes.

The solution also contains additive compounds for controlling the physical-mechanical layer properties. In order to maintain the layer properties even after a fairly long period of deposition from the deposition solution means are provided, according to the invention, with which the concentration of oxidising compounds of the redox system can be minimised in the immediate vicinity of the cathode, preferably to a value beneath approx. 0.015 mol/litre.

Obviously, the additive compounds can be replaced by the oxidising compounds of the redox system. As a result, the concentration of additive compounds would for one thing be reduced in an uncontrolled manner. Since the concentration regulation of these compounds in general is very costly, but as the content of compounds has a great effect on the physical-mechanical properties of the layers, inevitably only layers with variable characteristics could be deposited since an analysis



technique which is adequately fast-working and precise is not available for demands of this type.

This problem would also be made worse in that reaction products are formed during replacement of the additive compounds, said reaction products changing the layer properties disadvantageously so that, after electrolysis has taken place over a fairly long time, layers can only be deposited with properties which would not meet the set requirements, even while maintaining the content of additive compounds by reconstituting the damaging reaction products.

The means according to the invention by which the concentration of the oxidising compounds can be minimised in the vicinity of the cathode, preferably to a value beneath approx. 0.015 mol/litre, are shown in the following.

The entire quantity of the compounds of the redox system added to the deposition solution is calculated in such a way that practically the entire amount of the oxidising compounds of the redox system which are supplied to the metal ion generator with the deposition solution is required for the dissolving there of the metal parts during formation of the metal ions.

The quantity of metal ions which is delivered subsequently by dissolving must exactly regenerate the portion of deposition solution which is lost during deposition. In order to maintain the metal ion concentration and to reduce in total the amount of the oxidising compounds which have been introduced into the metal ion generator, a minimum size is required therefore for the surface area of the metal part in the metal ion generator. This surface area can, if desired, be enlarged upwards, in particular however it does not need to be variable. Hence, the subsequent supply of the metal parts into the metal ion generator can be achieved in any quantities above the mentioned minimum quantity in a technically simple manner.

The spatial distance between the anodes and the metal ion generator must be small, and the connections for conveying the deposition solution which has flowed against the anodes to the metal ion generator and from the metal ion generator back into the electrolytic chamber must be short. It is achieved thus that the dwell time of the oxidising compounds in the electrolytic solution is short. By means of fast conveyance of the deposition solution containing the oxidising compounds into the metal ion generator, these compounds have only a short life span also until they are transformed in the compounds of the redox system.

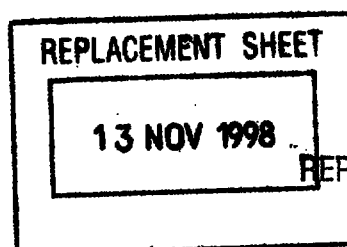
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In addition, the flow velocity of the deposition solution must be as large as possible especially during transference from the anodes to the metal ion generator.

In order to keep the concentration of oxidising compounds as small as possible, the possibility further exists of introducing a further oxidation means directly into the metal ion generator. The oxygen contained in the air is particularly suited to this purpose. During the reaction of oxygen with the metal parts, water alone is produced, which has no effect on the deposition process.

In order to introduce air into the metal ion generator, means are provided in the lower region of the generator for injecting oxygen from the air.

Another possibility for replenishing the metal ions which are removed from the deposition solution by deposition resides basically in adding the metal ions to the deposition solution in the form of their compounds or salts. However, it cannot be prevented in this case that the concentration of anionic parts of the compounds or salts, which are necessarily added with the metal ions, increases in a sustained manner by means of the continual supplement of the compounds, with the result that the solution must be discarded after a certain time. If in the present case only a small portion of the metal ions to



be regenerated is regenerated by adding the corresponding compounds or salts, then the length of time until the solution is discarded can be fairly long. By combining the regenerating of the metal ions through adding salts with regeneration of the solution in the metal ion generator, the addition of the compounds or salts can be reduced to a small percentage of the regeneration requirement.

It is advantageous in this case that the possibility exists of influencing the metal ion concentration in the deposition solution in a simple and fast manner with respect to control technique.

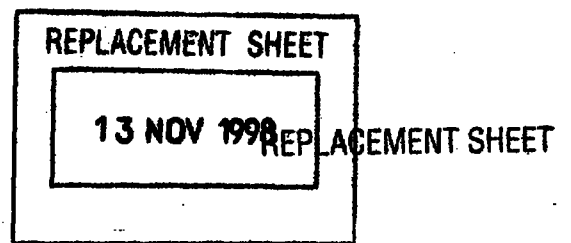
By means of reducing the life span of the oxidising compounds of the redox system formed on the anode, which is achieved by means of the previously mentioned measures, and by minimising the concentration of compounds, a possible decomposition of the compounds is avoided or at least considerably reduced.

The concentration of metal ions in the electrolytic chamber can also be affected by a special circulation control of the deposition solution. In the cathode chamber there are located the reduced compounds of the redox system which are transferred on the anodes by the electrolytic current in an electrochemical manner back to

oxidising compounds. The quantity of oxidising compounds and hence the concentration of metal ions can be reduced if only a part of the deposition solution from the area located in the vicinity of the cathode is directed onto the anodes and from there into the metal ion generator. The other part of this solution not containing the oxidising compounds is conducted on the other hand directly into the metal ion generator. For this purpose, there are provided separate outlets for the deposition solution which are located in the vicinity of the cathode. The solution branching off via the outlets proceeds through suitable ducts into the metal ion generator.

The surface area of the metal to be removed is once again amply dimensioned so that all the oxidising compounds introduced into the metal ion generator can be converted electrochemically.

By using this measure, simple control of the metal ion concentration in the deposition solution and hence automation of the control system, which can be realised in a technically simple manner, is made possible. By regulating the volume flows of deposition solution from the cathode via the anode into the metal ion generator on the one hand and from the cathode directly into the metal ion generator on the other, the concentration of metal ions can be adjusted in a simple manner.



For controlling purposes, the flow velocity of the deposition solution during circulation and the voltage between the cathode and the anode can furthermore also be adjusted.

The flow conditions in the electrolytic chamber can be arranged in such a way that, on one hand, a flow of deposition solution is directed from the cathode to the anode and, on the other hand, the cathode is however firstly directly flowed against by the deposition solution. The latter is required for producing uniform layers with adequately high current densities and with the prescribed physical-mechanical properties in an economical manner. These flows are brought about by flooding the cathodes with jet connections or surge jets and by subsequent deflection of this flow onto the anodes.

The preferred arrangement for carrying out the method according to the invention comprises in addition to the cathodes, insoluble, preferably perforated, dimensionally stable anodes, devices for flooding the cathodes and anodes with the deposition solution (jet connections, surge jets), means for deflecting the flow to the anodes and connection pipes for transferring the deposition solution flowing against the anode to the metal ion generator and for transferring the deposition solution

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emerging from the metal ion generator back to the electrolytic chamber. In a preferred embodiment, in order to increase the flow velocity during the transference of the deposition solution from the anodes to the metal ion generator, there can also be means provided for extracting the deposition solution.

In order to avoid mixing of parts of the deposition solution which are located in the vicinity of the cathode or the anode, the electrolytic chamber can also be subdivided into several compartments by ion-permeable separating walls (ion exchangers, diaphragms).

The metal ion generator is preferably a tube-shaped device which can be filled from the top and which is provided in the lower region with a base and, for admission of the electrolytes, with at least one connection pipe with lateral openings, and in the upper region, with an overflow opening into an electrolyte container. In a particularly favourable embodiment, inclined, preferably perforated plates are inserted in the interior of the metal ion generator.

The method is suited preferably to the plating of circuit boards. In this case, copper particularly is deposited on their surfaces and the sleeve surfaces of the bores.

Normal plunging arrangements in which the circuit boards are submerged in the deposition solution from above may be used or also horizontal units in which the circuit boards are gripped horizontally and transported through the unit in a horizontal direction using appropriate means.

As well as copper, which can be deposited preferably in a similarly used arrangement using the method according to the invention, other metals also can be used basically for deposition, such as for example nickel, in the manner according to the invention.

The basic composition of a copper bath can vary within relatively large boundaries when the method according to the invention is used. In general, an aqueous solution of the following composition is used:

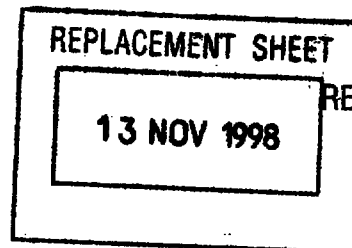
copper sulphate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$)	20 - 250 g/litre
preferably	80 - 140 g/litre or
	180 - 220 g/litre
sulphuric acid, conc.	50 - 350 g/litre
preferably	180 - 280 g/litre or
	50 - 90 g/litre
iron (II) sulphate	
($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$)	0.1 - 50 g/litre
preferably	5 - 15 g/litre
chloride ions (added for	
example as NaCl)	0.01 - 0.18 g/litre
preferably	0.03 - 0.1 g/litre.

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Instead of copper sulphate, other copper salts can be used at least in part. Even the sulphuric acid can be partly or wholly replaced by fluoroboric acid, methanosulphonic acid or other acids. The chloride ions are added as alkali chlorides, for example sodium chloride or in the form of salt acids. The addition of sodium chloride can be dispensed with wholly or partly if halogen ions are already contained in the supplements.

The effective $\text{Fe}^{2+}/\text{Fe}^{3+}$ Redox system is formed from iron (II) sulphate heptahydrate. It is exceptionally suited to regenerating copper ions in aqueous, acidic copper baths. However, other water soluble iron salts, particularly iron (III) sulphate nonahydrate, can also be used as long as the salts contain no biologically non-degradable (hard) complexing agents in the compound since the latter present problems during waste disposal (e.g. iron ammonium alum).

Besides iron salts, compounds of the elements titanium, cerium, vanadium, manganese, chromium and others are likewise suitable as further redox systems. Compounds which may be used are in particular titanium sulphuric acid, cerium (IV) sulphate, sodium metavanadate, manganese (II) sulphate and sodium chromate. Combinations of the previously mentioned redox systems may also be used for special applications.



With the method according to the invention, the elements which are actually known and trusted in electrolytic metal deposition can be retained. Thus, for example normal brighteners, levelling and wetting agents can be added to the deposition solution. In order to obtain copper deposits with the prescribed physical-mechanical properties, at least one water soluble sulphur compound and one oxygen-containing compound of high molecular weight are added. Additive compounds, such as nitrogen containing sulphur compounds, polymer nitrogen compounds and/or polymer phenazonium compounds may also be used.

The additive compounds are contained in the deposition solution within the following ranges:

normal oxygen containing		
compounds of high molecular		
weight	0.005 - 20 g/litre	
preferably	0.01 - 5 g/litre	
normal water soluble,		
organic sulphur compounds	0.0005 - 0.4 g/litre	preferably
	0.001 - 0.15 g/litre	

Thiocarbamide derivatives and/or polymer phenazonium compounds and/or polymer nitrogen compounds are used as additive compounds in the following concentrations:

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	0.0001 - 0.50 g/litre,
preferably	0.0005 - 0.04 g/litre

In order to prepare the deposition solution, the additive compounds are added to the presently given basic composition. The conditions during the copper deposition are given in the following:

pH value:	< 1
temperature:	15° C - 50° C
preferably	25° C - 40° C
cathodic current density:	0.5 - 12 A/dm ²
preferably	3 - 7 A/dm ²

In the following Table 1, a few oxidised compounds of high molecular content are shown:

Table 1 (oxygen-containing compounds of high molecular weight)

carboxymethylcellulose

nonylphenol-polyglycolether

octandiol-bis-(polyalkyleneglycolether)

octanolpolyalkyleneglycolether

oleic acid-polyglycolester

polyethylene-propyleneglycol + polyethyleneglycol

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polyethyleneglycol-dimethylether

polyoxypropyleneglycol

polypropyleneglycol

polyvinylalcohol

stearic acid polyglycolester

stearylalcohol-polyglycolether

β -naphthol-polyglycolether

Table 2 (sulphur compounds)

3-(benzthiazolyl-2-thio)-propylsulphonic acid, sodium salt

3-mercaptopropane-1-sulphonic acid, sodium salt

ethylenedithiodipropylsulphonic acid, sodium salt

bis-(p-sulphophenyl)-disulphide, bisodium salt

bis-(ω -sulphobutyl)-disulphide, bisodium salt

bis-(ω -sulphohydroxypropyl)-disulphide, bisodium salt

bis-(ω -sulphopropyl)-disulphide, bisodium salt

bis-(ω -sulphopropyl)-sulphide, bisodium salt

methyl-(ω -sulphopropyl)-disulphide, bisodium salt

methyl-(ω -sulphopropyl)-trisulphide, bisodium salt

O-ethyl-dithiocarbonic acid-S-(ω -sulphopropyl)-ester,

potassium salt

thioglycol acid

thiophosphorus acid-O-ethyl-bis-(ω -sulphopropyl)-ester,

bisodium salt

thiophosphorus acid-tris-(ω -sulphopropyl)-ester, trisodium

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salt

In the previous Table 2 some sulphur compounds with suitable functional groups for producing water solubility are displayed.

The deposition solution is moved by injecting air into the electrolyte chamber. By additional streaming of air against the anode or the cathode, the convection is increased in the region of the respective surfaces. As a result, the transportation of material in the vicinity of the cathode or anode is optimised so that greater current densities can be achieved. If necessary, aggressive oxidation agents occurring in small amounts, such as for example oxygen and chlorine are removed hence from the anodes. Movement of the anodes and cathodes also causes improved transportation of the material to the respective surfaces. Consequently, constant diffusion controlled deposition is achieved. The movements can take place horizontally, vertically, in a uniformly lateral movement and/or by vibration. A combination with blowing with air is particularly effective.

Inert material is used for the anodes. Anodic workpieces which are chemically and electrochemically stable relative to the deposition solution and the redox system used, for example titanium, iridium, ruthenium or their oxides or

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mixed oxide systems are suitable. Titanium anodes with an iridium oxide surface, which was blasted with spherical-shaped bodies and consequently sealed non-porously, were adequately stable and had thus a long life span. By means of the anodic current density or the anode potential regulated via the voltage between the cathode and the anode, the quantity of aggressive reaction products occurring on the anode is determined. Therefore, so as not to exceed this value, large, effective anode surfaces are sought after. Thus with limited spatial dimensions, preferably perforated anodes, for example anode networks or expanded metal are used with a corresponding coating. Consequently, the advantage of the large, effective surface is combined with the possibility at the same time of intensively flooding the anodes with the deposition solution so that possibly occurring aggressive reaction products can be removed. Anodic networks and/or expanded metal may be used additionally in several places. Consequently, the effective surface is correspondingly increased so that the anodic current density in a preset electroplating current is reduced.

Metal is regenerated in a separate container, namely the metal ion generator through which deposition solution flows. In the metal ion generator there are located in the case of copper deposition, metallic copper parts, for example in the form of pieces, balls or pellets. The

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metallic copper used for regeneration does not need to contain phosphorus; however, if present, phosphorus does not cause a problem. In the conventional use of soluble copper anodes, the composition of the anode material on the other hand is very relevant. In this case, the copper anodes must contain approximately 0.05% phosphorus. Workpieces of this type are expensive and the supplement of phosphorus occasions residues in the electrolytic cell which have to be removed by additional filtering.

Since according to the method according to the invention metallic copper parts which contain no supplements may be used, electrolyte copper, including copper scrap, is used as a rule. An interesting variant consists of the circuit board waste which is coated with copper, as occurs in large quantities in the production of circuit boards, having the capacity to be used likewise for this purpose, as long as said waste contains no further metals. This waste consisting of the polymer base material and the deposited copper layers, because of the adhesive bond between the two materials, can only be disposed of in a traditional manner at high cost. After the profitable removal of the copper from this waste in a metal ion generator suited to this purpose, disposal of the base material according to type is possible. In a similar manner, reject circuit boards can also be used.

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In the circulation procedure of the ~~deposition solution~~, filters can be introduced furthermore for separating the residues mechanically or chemically. However, the requirement for these is smaller in comparison to electrolytic cells with soluble anodes because the anode slime which is caused by the addition of phosphorus to the anodes does not occur.

The subsequent schematic Figures serve further to explain the invention and the further preferred embodiments.

Figure 1 - basis of a device for immersion treatment,

Figure 2 - basis of a device with and without a diaphragm,

Figure 3 - basis of a device with series control of the deposition solution,

Figure 4 - basis of a device with horizontal transportation of the item to be treated,

Figure 5 - metal ion generator on a device for immersion treatment,

Figure 6 - metal ion generator on a device for the transportation of the item to be treated.

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In Figure 1, the method according to the invention is shown with reference to a schematic device. The electrolyte chamber 1 is located in the container 3. The metal ion generator 2 is constructed and arranged with reference to the container 3 in such a way that short routes occur in directing the deposition solution from the anodes 5 to the metal ion generator and from there back into the electrolyte chamber. For this reason, the metal ion generator in the present case is shown in two parts and arranged respectively in the vicinity of the insoluble anodes. This two-piece construction is however not mandatory. It can therefore also be arranged for example as a one-piece unit at the side or beneath the bath container. The copper parts 8 to be dissolved are inserted loosely piled into the metal ion generator to enable the deposition solution to be directed easily through the generator. In the latter however, a minimum charge of copper parts must not be exceeded on the other hand. The pump 11 conveys the deposition solution during circulation through the arrangement. It is essential that the item to be treated 6 which is configured as a cathode, as is indicated with arrows 14, is flooded with deposition solution which has been enriched with copper ions via jet connections or surge jets which are not shown here. Consequently, it is achieved that the copper layers are deposited on the surfaces of the item to be treated with

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the required quality and speed. Furthermore, a further flow occurs within the electrolyte chamber from the chamber 15 which is located near the item to be treated in the direction of the chambers 16 which are located near the anodes. The deposition solution flowing against the anodes penetrates through the latter if the anodes are perforated and proceeds with the continuing flow into the outlet 4 which leads into the metal ion generator. It is achieved thus that transportation of anodically formed, oxidising compounds of the redox system (iron (III) ions) into the cathode chamber 15 is minimised. This reduces once again the damaging dissolving of the additive compounds with simultaneous increasing of the cathodic current efficiency.

Along the transportation route from the anodes, via the outlet into the metal ion generator, the additive compounds are dissolved probably by a chemical separation reaction involving the oxidising compounds of the redox system. For this reason, outwith the electrolyte chamber 1 as short a connection as possible is striven for with high flow velocity of the deposition solution to the metal ion generator.

The minimal charging of the metal ion generator with copper parts guarantees that the formed oxidising compounds within the metal ion generator are entirely

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transformed and the concentration of these compounds at the exit of the metal ion generator is dropped to a value of approximately zero. This implies that the copper surface which is contact with the deposition solution in the metal ion generator leads to complete reduction of the oxidising compounds to the reduced compounds (iron (II) ions) with simultaneous externally electroless dissolving of copper during formation of copper ions. The reduced compounds of the redox system do not contribute to the dissolving of the additive compounds.

By means of specific streaming of the cathode surfaces, the anodes are subjected during a prescribed entire circulation cycle to a smaller exchange of electrolytes. Consequently, the aggressive gases occurring by chance on the anodes are removed correspondingly more slowly so that the corrosion of the anodes increases on the one hand but on the other is limited by the following measures:

- low anodic current density
- inert anode basic material
- inert anode coating
- anode surface sealing
- liquid permeable anode geometry.

By means of these measures it is achieved that the additive compounds, which are added to the deposition

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solution for controlling the physical-mechanical properties of the metal layers, can also be used in arrangements with insoluble, dimensionally stable anodes. Special mixtures of the additive compounds are not required for this purpose. High cathodic current efficiency and a long serviceable life of the insoluble anodes are achieved.

A further device according to the invention is shown in Figure 2. For one thing, said device differs from the arrangement according to Figure 1 in that the operation of the deposition solution within the electrolyte chamber is different, said chamber consisting of a chamber 15, which is located near the item to be treated, namely the cathode chamber, and the chambers 16, the anode chambers, which are located near the anodes. These chambers are separated in the pictorial representation by the broken lines 17. The deposition solution, which has been enriched in the metal ion generator 2 with copper ions during reduction from Fe (III)- to Fe (II) ions, flows into each chamber separately and proceeds, corresponding to the arrows 12 and 14, through jet connections or surge jets (not shown) onto the anodes 5 or onto the cathodic item to be treated 6. Mixing of the deposition solution in the anodic chamber 16 with that in the cathode chamber 15 can only occur on a small scale in particular for the reason that the deposition solution can flow out of the anode chamber

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via its own outlets 4 and, separate therefrom, the deposition solution in the cathode chamber has its own outlet 18. In this embodiment, the Fe (III) ion concentration in the cathode chamber, which is directly connected to the inlet to the metal ion generator 2, is kept small so that there is a short travelling route from the anodic chamber to the metal ion generator 2. In contrast, the transportation routes from the cathode chamber via the outlet 18 to the generators can be long since no damaging interaction occurs between the reduced compound, which is contained in the deposition solution located in the cathode chamber, and the additive compounds. In order also to avoid a slight mixing of the electrolytes in the deposition solutions in the cathode and anode chambers, these chambers can be separated along the lines 17 by one ion-permeable separating wall respectively (diaphragm) which for its part is not changed chemically by the deposition solution. The separating walls are only very slightly or not at all permeable to the deposition solution so that, if necessary, they only permit a slow equalisation of varying hydrostatic pressures in the chambers 15 and 16. Polypropylene material for example or other membranes with permeability for metal ions and their corresponding counterions (for example, Nafion from the firm DuPont de Nemours, Inc., Wilmington, Del., USA) are suitable. By virtue of separating the chambers with dividing walls, it is

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guaranteed that the deposition solution cannot proceed, for example because of turbulence, from the anode chamber to the cathode chamber. This measure leads likewise to a further lowering of the concentration of oxidising compounds in the redox system in the vicinity of the cathode. Thus, by virtue of these measures advantageous effects also occur with respect to the resistance to ageing of the deposition solution.

The deposition solution which is located in the anode chamber and contains the Fe (III) ions formed there is once again transferred to the metal ion generator by the shortest route and is enriched there with copper again upon formation of the Fe (II) ions. In the practical process, a state of equilibrium is set between the copper dissolving in the metal ion generator and the copper deposition on the item to be treated.

A further embodiment of the invention with a two-part metal ion generator is shown in Figure 3. The deposition solution which has been enriched with copper ions in the metal ion generator 2 is conducted only into the cathode chamber 15. This deposition solution contains furthermore only Fe (II) ions and no Fe (III) ions. The deposition solution is directed in series from the cathode chamber 15 to the anode chamber 16. Thus, the Fe (II) ions formed in the metal ion generator proceed into the anode chamber via

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a pump 19, after going through the cathode chamber with the deposition solution. The supply of the deposition solution into the cathode chamber is brought about by a further pump 11. Hydrodynamic constancy is advantageous and also the constant transportation conditions resulting therefrom for the electrochemically active supplements of the redox system.

Furthermore, this operation of the deposition solution in series permits division of the deposition solution drawn from the cathode chamber. In order to regulate the concentration of copper ions in the electrolyte chamber 1, comprising the cathode and anode chambers, a part of the solution is conducted directly into the metal ion generator via the pipelines 43 which are shown in broken lines. This partial quantity contains almost no oxidising compounds of the redox system so that by mixing in this portion into the stream of solution, which comes from the anode chamber and is directed into the metal ion generator, the speed of the copper dissolving is decreased. By controlling and/or regulating the partial quantities of both streams by means of three-way valves (not shown), the copper ion concentration in the deposition solution can hence be adjusted. In the arrangement shown in Figure 2, these options are not used although, there also, two separate outlets 4 and 18 for the deposition solutions from the cathode and the anode

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chamber are present. There, the solutions from both chambers are directed together and conducted together into the metal ion generators. The regenerated solutions emerging from the metal ion generators are supplied to the chambers 15 and 16. The procedural method according to Figure 3 is then advantageous if the deposition solutions from the anode and cathode chambers cannot be mixed in the electrolyte chamber but complete separation of the draining solutions in the outlets 4 and 18 from the anode and the cathode chambers cannot be guaranteed.

In Figures 1 to 3, the introduction of the deposition solution, which is enriched with copper ions, into the container 3 is shown for example from below and into the metal ion generator from above. Correspondingly, the outgoing streams through outlets 4 and 18 out of the container 3 are shown above and out of the metal ion generator 2 below. Circulations of the deposition solution in other directions are likewise possible, such as for example the introduction of the solution into the metal ion generator from below.

A further embodiment of the invention, especially for the electrolytic plating of a plate-shaped item for treatment, preferably circuit boards, in a horizontal course through the arrangement is shown in Figure 4. The unit which is shown in side-view as a section consists of the

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electrolytic part 20 and a metal ion generator 21, shown thereunder, filled with copper. The electrolytic part 20 consists of several electrolytic single cells. Four of these single cells are shown in Figure 4 with the reference numbers 22, 40, 41, 42, and indeed with one insoluble anode 23 respectively for the upper side and for the under side of the item for treatment 24. The item to be treated is electrically connected to a not shown rectifier and is given cathodic polarity. It is transported through the unit in the direction of the arrows 25, guided by rollers or discs. The transportation elements 26 are located along the entire unit, uniformly distributed. For reasons of simplification of the representation, the latter are reproduced here only at the beginning and at the end of the transportation route. In the electrolytic cells, surge jets or flooding pipes 27, 39 are located, likewise uniformly distributed. The latter correspond to the already presently mentioned jet connections.

Deposition solution coming from the metal ion generator 21 is supplied, conveyed via pumps 29, to the flooding pipes 27, 39 via the pipelines 28. By means of the exit openings of the flooding pipes or surge jets, the deposition solution flows against the surfaces of the item to be treated 24. Copper ions are thereby reduced to metallic copper and deposited onto the item to be treated

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as a metal layer and the likewise present iron (II) ions are conveyed with the electrolytes, which are flowing away in the direction of the anodes 23. In order to avoid reverse flow from the anodes to the cathodes, various measures are provided, the realisation of which is shown in Figure 4 schematically. The deposition solution which has been enriched with copper is used for flooding the cathode (item for treatment). The solution stream is subsequently diverted from the plate-shaped item to be treated in such a manner that it is displaced in the direction of the anodes, as indicated by the arrows 30. In the case of the preferably used perforated anodes, the solution penetrates through the latter and proceeds subsequently back into the metal ion generator via suction pipes 31 and pipelines 32. The anodes may consist for example of expanded metal or networks. Passages 33 support the streaming through process. In order to avoid turbulence, baffles 34 which extend in the direction of the item to be treated can be installed in the suction pipes. The gap 35 remaining between the baffles and the item to be treated may be a few millimetres. This forms, from the point of view of fluid technology, almost sealed electrolytic cells with favourable flow conditions. The flooding pipes 27 can also be provided with baffles 36 in order to stop any further possible turbulence.

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In the electrolytic cells of the arrangement in Figure 4, various flooding pipes, for example, are shown in varying numbers. The circulation of the deposition solution is directed in such a way that, in the electrolytic part of the unit, the level 37 lying above the suction pipes is adjusted. In the electrolytic cell 42 which is shown on the right, there are separating walls 38 depicted respectively between the anodes 23 and the item to be treated 24. Consequently, the direct exchange of deposition solution in the cathode and anode chambers is minimised. By using ion-permeable separating walls on the other hand, ion exchange between the chambers is made possible. The solution in the cathode chamber can emerge on the front side. Further flooding pipes 39 are provided in the anode chamber. The solution of this chamber emerges via the suction pipes 31. Once again, the flow operation in series is suited to a cell of this type, as was described already with reference to Figure 3.

The draining of the deposition solution out of the anode chamber into the metal ion generator 21 via the suction pipes 31 can take place by the shortest route in order to keep the life span of the iron (III) ions as short as possible. Therefore, the metal ion generator 21 is also arranged here as closely as possible to the electrolytic part 20. Consequently, short connection routes and small transportation times result. The construction principle

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can also be chosen advantageously such that the parts 20 and 21 form a total system. Several flooding pipes 27 are supplied respectively by one pump 29 and, in fact, in the manner shown in Figure 4. However, one single pump may also be used. This would lead to fairly long connecting routes between the flooding pipes 27, 39 and the metal ion generator 21. The deposition solution in these connection pipes contains practically no oxidising compounds of the redox system. Hence, protection of the additive compounds is also guaranteed in this area.

The electroplating unit is shown in Figure 4 in side view. The parts shown (anodes, pipes) extend in longitudinal extension into the depth of the drawing i.e. transversely to the direction of transportation above the item to be treated. The parts located in the electrical field between the anode and the cathode, such for example as the flooding pipes 27, are made of electrically non-conductive plastic material. Their electrical screening effect does not interfere here because the item to be treated moves slowly through the unit and is hence exposed continuously to the various electrical fields.

In Figure 5, a creative arrangement with two metal ion generators 44, an electrolytic chamber 1 and two further electrolyte containers 45 is shown. This arrangement is operated in the submerging procedure. In this case, the

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cell is constructed symmetrically for electroplating the front and the rear side of the item to be treated 6. Both metal ion generators 44 which are shown in the Figure and the electrolyte containers 45 respectively can also be provided singly and in this case be assigned to both sides of the item to be treated.

The metal ion generator 44 consists of a preferably round pipe body 46 with an upper opening 47. All the materials used here are resistant to the deposition solution and the supplements contained in the solution. Through the base 48 of the metal ion generator there projects at least one connecting pipe 49 into the interior of the metal ion generator. This connecting pipe has lateral openings 50. These form a filter which on the one hand prevents penetration of the metallic copper into the pipeline system and on the other allows penetration of the deposition solution into the metal ion generator. A small overhanging lid seals the pipe support at the top. At the same time, the lid keeps the lateral openings 50 free of fine copper granulate which is situated in this region of the metal ion generator. Beneath the base, a mixing and collecting chamber 51 is situated. Copper particles and impurities which were able to pass through the filter are collected in said chamber. After opening the base plate 52, the chamber is accessible for cleaning purposes. During operation, the deposition solution, which is pumped

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out of the anode chamber 16 and which is enriched with copper dissolving Fe (III) ions, flows in. In addition, air containing oxidising oxygen can also be injected into the metal ion generator via pipelines 56. In this case, the chamber 51 serves at the same time as a mixing chamber. By means of the holes 50 of the connecting pipe 49, the deposition solution and, if necessary, air proceeds into the interior of the metal ion generator.

In the lower region of the generator there are found predominantly fine copper granulates which have arisen from dissolving the metallic copper. They have a very large specific surface area which is presented immediately to the inflowing deposition solution enriched with Fe (III) ions in order to dissolve the copper. The Fe (III) ions are therefore reduced as quickly as possible to Fe (II) ions with simultaneous dissolving of the copper. In the interior of the metal ion generator, the quantity of Fe (III) ions is reduced quickly in an upward direction. This has the effect that the electrolyte copper which is inserted as granulates or sections 53 is dissolved up the way on a smaller and smaller scale. The dimensions of the granulates remain large in the upper region of the metal ion generator. Hence, the permeability to the deposition solution is also maintained. By means of the overflow 54, the solution is drained without pressure out of the metal ion generator into the electrolyte container. In the

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interior of the metal ion generator, the overflow bends downwards in such a way that copper granulates 53 dropping from above cannot lead to a blockage in the metal ion generator. As a consequence of the synchronised length of dwell time for the deposition solution flowing into the generator and the length of time for the simultaneous dissolving of the presented copper surface, the deposition solution flowing into the electrolyte chamber 45 via the overflow 54 contains virtually no Fe (III) ions any longer. This type of oversizing of the regenerating unit ensures thus that the attack of the Fe (III) ions on the additive compounds of the deposition solution is already ended in the central area of the generator.

The filling and refilling of the metal ion generator with metallic copper 53 takes place from above through, for example, the funnel-shaped opening 47. This can be sealed with a lid. The area above the overflow 54 in which there is no deposition solution serves for storing the metallic copper which is to be dissolved in the metal ion generator. The filling and refilling can be done manually. The arrangement is exceptionally suited to automation of the filling procedure as a consequence of the lack of pressure at the filling opening 47 and the perpendicular or inclined assembly. This can take place continuously or intermittently. Conveyor belts or oscillating conveyors, which are known from conveyance

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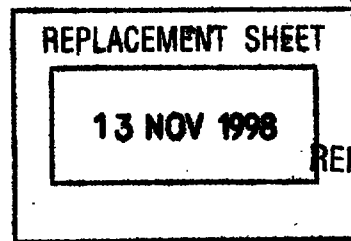
technology but not shown here, transport the metallic copper into the openings 47 of the generators.

It is advantageous in the invention that, in the metal ion generator, copper parts of various geometric shapes can be dissolved. However, different shapes have a different stacking behaviour. In order to maintain the permeability of the stack for the deposition solution and to ensure a sufficiently large copper surface which is accessible to the solution, individual measures are also available.

Plates 55 which are inclined downwards in the interior of the generator prevent too much compacting of the copper in the lower region.

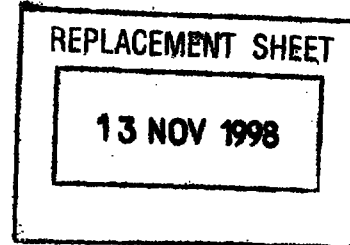
The plates are provided with openings, the dimensions of which accommodate the size of the poured-in metallic parts. The openings are made differently from plate to plate corresponding to the dissolving of the copper, becoming smaller from top to bottom. Similarly, the dimensions of the plates can increase from top to bottom. The angles of the inclinations may likewise accommodate the conditions of the copper pieces poured into the metal ion generator.

The inclined position of the metal ion generator itself can have the same effect. By means of injecting air 56



into the lower region of the metal ion generator or into the mixing or collecting chamber 51, a copper dissolving material, in this case oxygen, is also inserted. Furthermore, the associated turbulence of the copper granulates in the metal ion generator increases the reduction of the Fe (III) ions and increases the dissolving of the copper. At the same time, the permeability to the deposition solution is increased by the copper parts. With mutually interlocking copper fillings it can be useful to vibrate the metal ion generator intermittently or constantly. The vibration motion can be performed preferably by an oscillating conveyor with which the automatic filling is taken care of at the same time. All the presently described measures for a trouble-free continuous operation of the metal ion generator can also be combined together.

The electrolyte containers 45, 67 which are shown in Figures 5 and 6 serve to reduce the dependency of the flow of deposition solution to the item to be treated 6, 69 from the flow through the metal ion generator. This has the advantage that, in both circulations, the quantity of deposition solution and its velocity can be adjusted individually. These procedures are described subsequently with reference to Figure 5.



The deposition solution is conveyed by a pump 57 from the electrolyte container 45 into the electrolyte chamber 1. By means of the flooding pipes 58 arranged there, the solution flows against the item to be treated 6 and out of the flooding pipes 59 onto the liquid-permeable insoluble anodes 5. The dividing of the stream of solution into the flooding pipes 58 and 59 is achieved by adjustable valves, not shown here. From the cathode chamber 15, the deposition solution flows back via the outlet 18 through pipelines 60 and the outlet 61 into the electrolyte container 45 once again. Right behind the anodes 5, there are located suction pipes 62 through which the deposition solution enriched with Fe (III) ions is suctioned off by the pump 63 and conveyed to the metal ion generator at great speed. From there, the solution which is enriched with Fe (II)- and Cu (II) ions then proceeds back again into the electrolyte container 45.

The division of the flows into the flooding pipes 58 and 59 is adjusted in such a manner that a surplus occurs in the cathode chamber 15. Said surplus is evened out towards the anode chamber 16. If the two walls are separated by a dividing wall 17, as is shown in Figure 5, at least one opening 64 in the dividing wall ensures that the equalisation of the deposition solutions in both chambers can take place in the direction of the arrows. In order to avoid the solutions being mixed in the

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electrolyte chamber 1 and to avoid convective transportation of the Fe (III) ions from the anode to the cathode chamber, it must only be ensured accordingly that higher hydrostatic pressure exists in the deposition solution in the cathode chamber 15 relative to that in the anode chamber 16. This is ensured by a corresponding adjustment of the partial streams through the flooding pipe 58 and the flooding pipes 59 in the circulation of the pump 57. In addition, the circulations of the pumps 57 and 63 are independent of one another.

In the metal ion generator, all the Fe (III) ions, which are introduced by the conveyance stream, are reduced to Fe (II) ions. It cannot be ruled out however that a very small, barely detectable number of Fe (III) ions passes through the metal ion generator and proceeds into the electrolyte container 45. In order to reduce the Fe (III) ions, which have proceeded into this container 45, into Fe (II) ions, copper parts 65 are also added to the container. For this purpose, copper scrap may also be used.

A further embodiment of the device according to the invention for carrying out the method is shown in Figure 6. This concerns here a horizontal electroplating unit for circuit boards which is shown in cross-section. In the Figure, the metal ion generator 66, an electrolyte

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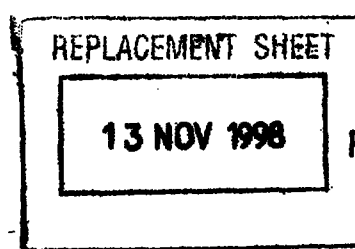
container and an electroplating cell 68 are shown. The circuit board 69 to be plated is gripped by clamps 70 and conveyed horizontally through the unit. The connecting of the circuit board with the negative terminal of a rectifier (not shown) is likewise achieved via these clamps. In another embodiment, connecting could also be achieved via contact wheels. A pump 71 conveys the deposition solution via flooding pipes 72, 73 to the circuit boards and to the insoluble perforated anodes 74. The deposition solution is directed back from the cathode chamber into the electrolyte chamber 67 via outlets 75. From the anode chamber, the pump 86 conveys the deposition solution, which is enriched with Fe (III) ions, through suction pipes 76 into the metal ion generator at great speed. An outlet 77, which is designed as an overflow for regulating the level, ensures that excess deposition solution from the upper region of the anode chamber also proceeds into the circulation to the metal ion generator 66 and not into the electrolyte container 67. The metal ion generator is designed in the manner which was described with reference to Figure 5. The deposition solution proceeds back once again into the electrolyte container 67 via the overflow 78. Copper parts 79 are also situated in the latter, said copper parts causing reduction from Fe (III) ions, which have possibly strayed into this area, to Fe (II) ions. Furthermore, dividing walls 80 are also provided between the anode and the

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cathode chambers. Openings 81 in these dividing walls also ensure here equalisation of the flows of deposition solution from the cathode chamber into the anode chamber. These flow directions are also set when there are no dividing walls.

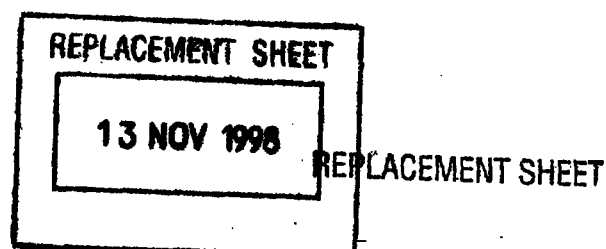
Horizontally operating through-put units, as shown in the Figures 4 and 6 and vertically operating electroplating units have longitudinal dimensions of several metres for the electrolytic cells. For that reason, preferably several metal ion generators are arranged in practice along the unit. This permits them to be assembled spatially near to the electrolytic cell or for the electrolytic cell, the electrolytic container and the metal ion generator to be fitted together in part or in total.

During the course of a circuit board through the electroplating unit, the clamps 70 are also plated in the region of their contacts 82. This layer must be removed again before reusing the clamps. This occurs in a known manner during the return journey of the clamps to the start of the electroplating unit. The returning clamps 83 proceed thereby through a separate compartment 84 which is connected to the deposition solution in the electrolytic cell 68. In order to be deplated, the clamps 83 are connected to the positive terminal of a rectifier (not



shown) via sliding contacts. The negative terminal of this rectifier is connected to a cathode blank 85. During the electrolytic deplating procedure, copper deposits on the insulated layers of the clamps 83 lose electrical contact with the current supply before being totally dissolved. Consequently, interfering copper deposits remain behind in these regions. According to the invention, the parameters of current and time for deplating are set in such a way therefore that for example only 70 % of the deplating route is required for removing the metal layer. In the then remaining stretch, Fe^{3+} ions are produced by the electrolysis stream on the metallic and contacting parts of the clamps. Said ions are situated exactly where possibly still contactless copper deposits are present. They dissolve this copper without external current. A detectable increase of Fe (III) ions in the electrolytic cell does not occur consequently as, in comparison to the plating of the item to be treated, only very small currents and surfaces are involved.

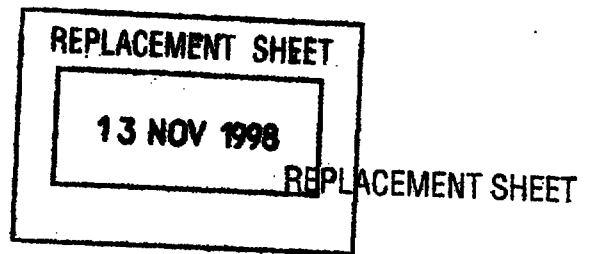
In order to maintain an operational metal deposition, the copper content in the deposition solution must be kept within specific boundaries. This presupposes that the consumption rate and the rate of resupply of the copper ions correspond. In order to control the copper content, the absorption capacity of the deposition solution can be measured using a wavelength of about 700nm. The use of an



ion-sensitive electrode has also proved its worth. The obtained measurement serves as an actual value of a control system, the regulated quantity of which is referred to for maintaining the copper ion concentration in the respective, described embodiments of the invention.

For the analytical tracking of the concentrations of the compounds of the redox system, a potential measurement can be performed. For this purpose, a measuring cell is used which is constructed from a platinum electrode and a reference electrode. By means of a corresponding calibration of the measured potential situation with the concentration ratio of the oxidising and the reduced compounds of the redox system for a given total concentration of the compounds, the respective concentration ratio can be determined. The meter electrodes can be installed both in the anode and cathode chambers as well as in the pipelines of the arrangement.

In order to control the anode processes, such as for example the oxidation of the redox system necessary for copper production and a possible anodic dissolving of the additive compounds, a further measuring device can be provided in which the anode potential is measured relative to a reference electrode. For this purpose, the anode is connected to the corresponding reference electrode via a potential measuring device.



The continuous or intermittent measuring technique for determining further electroplating parameters is useful, such for example, as for calculating the quantity of additive compounds by means of cyclical voltametry. Thus, after fairly long operational breaks temporary adjustments of the concentrations can occur. The knowledge of momentary measurements can be used to avoid wrong doses of the chemicals to be regenerated.

The following examples serve further to explain the invention:

Example 1

In an arrangement according to Figure 2 and using the measures according to the invention (large specific surface area of the copper parts in the metal ion generator, high flow velocity in the total arrangement, conducting of the flow so that the oxidising compounds of the redox system, formed on the anode by oxidation, cannot proceed back to the cathode), a copper bath was used with the following composition:

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80 g/litre copper sulphate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$)
180 g/litre concentrated sulphuric acid
10 g/litre iron as iron (II) sulphate ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$)
0.08 g/litre sodium chloride

with the following brighteners:

1.5 g/litre polypropylene glycol
0.006 g/litre 3-mercaptopropane-1-sulphonic acid, sodium
salt 0.001 g/litre N-acetylthiocarbamide

A current efficiency of 84% was detected. The consumption
was detected at over 100 Ah/litre with:

polypropylene glycol	3.3 g/kAh
3-mercaptopropane-1-sulphonic acid, sodium salt	0.3 g/kAh
N-acetylthiocarbamide	0.04 g/kAh

The fracture elongation of the deposited layers was 17% at
the end of the experiment.

Example 2

The experiment of Example 1 was repeated in the
arrangement shown in Figure 3, the deposition solution

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being conducted in series through the cathode and the anode chamber. A current efficiency of 92% was achieved. The consumption, again detected at over 100 Ah/litre, was:

polypropylene glycol	2.0 g/kAh
3-mercaptopropane-1-sulphonic acid, sodium salt	0.2 g/kAh
N-acetylthiocarbamide	0.02 g/kAh

The fracture elongation improved to 20%. In this experiment, the coated circuit boards withstood a two-fold soldering shock test (10 seconds at 288° C soldering temperature) without tears in the region of the bores. The deposition was uniformly glossy.

Example 3

In a horizontal unit according to Figure 4, circuit boards were copper-plated in a deposition solution of the following composition:

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80 g/litre copper sulphate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$)

200 g/litre concentrated sulphuric acid

8 g/litre iron as iron (II) sulphate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$)

0.06 g/litre sodium chloride

The following were added as brighteners:

1.0 g/litre polyethylene glycol

0.01 g/litre 3-(benzothiazolyl-2-thio)-propylsulphonic
acid, sodium salt

0.05 g/litre acetamide

At an electrolyte temperature of 34%, glossy metal layers were obtained on a scratched copper laminate surface at a current density of 6 A/dm². The circuit board, plated in such a manner, withstood a five-fold soldering shock test (10 seconds at 288° C soldering temperature). The current efficiency was 91%. In the controlling (subsequent adding of the consumed added materials) of the deposition solution no problems arose.

Example 4 (comparative example)

In an electrolysis cell, the experiment described in Example 1 was performed. The measures according to the invention were not applied, in particular there was no

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flooding of the anodes and cathodes according to the invention.

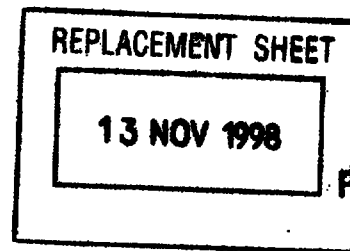
With a temperature of 30° C in the deposition solution, glossy metal layers were produced on a scratched copper laminate surface at a current density of 4 A/dm². The cathodic current density was only 68%. The consumption of additive compounds, without entrainment of the deposition solution by virtue of lifting the item to be treated out of the bath container, was averaged to over 100 Ah/litre.

polypropylene glycol	5 g/kAh
3-mercaptopropane-1-sulphonic acid, sodium salt	1.6 g/kAh
N-acetylthiocarbamide	0.2 g/kAh

The fracture elongation of the deposited layers was only 14% at the end of the experiment.

Example 5 (comparative example)

According to Example 1, copper layers were deposited on circuit boards after copper from the solution had been deposited onto a substrate previously over a fairly long time span (2000 Ah/litre).



The circuit boards no longer withstood a two-fold soldering shock test (10 seconds at 288° C soldering temperature) without tears. In addition, non-uniform copper layers were obtained. In the Examples 1 to 3, copper layers with good to very good fracture elongation were in fact deposited. The cathodic current efficiency and the consumption of additive compounds, which were added to the deposition solution to control the physical-mechanical layer properties, were satisfactory. The appearance of the copper layers was perfect and withstood the tests for application of the technique.

After fairly long use of the deposition solution during the electrolytic deposition of copper, no more perfect results were obtained on the other hand.

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Claims

1. Method for the electrolytic deposition of uniformly thick metal layers of specific physical-mechanical properties, more especially copper layers, having a high electrolytic efficiency, from a deposition solution, containing ions of the deposited metal, compounds of an electrochemically reversible redox system and additive compounds for controlling the physical-mechanical properties of the metal layers, wherein the following are used:

- cathodes;
- insoluble, dimensionally stable anodes;
- a metal ion generator, by means of which the metal ions are formed by dissolving appropriate metal parts whilst the deposition solution, formed by anodic oxidation and containing oxidising compounds of the redox system, are conducted through said generator;
- means, whereby the concentration of the oxidising compounds in the immediate vicinity of the cathode is minimised, preferably to a value below substantially 0.01 S mol/litre; and



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- means, which bridge a short spacing, for transferring the deposition solution, which flows against the anodes, to the metal ion generator.
2. Method according to claim 1, characterised in that the concentration of the compounds of the redox system is kept slightly below a value which is required to maintain the metal ion concentration.
 3. Method according to one of the preceding claims, characterised in that the surface of the metal parts is selected to be so large that the concentration of the oxidising compounds is reduced to a value of substantially zero as they are conducted through the metal ion generator.
 4. Method according to one of the preceding claims, characterised in that the deposition solution flows against the anodes at a high velocity of flow and from there is transferred at a high velocity to the metal ion generator.
 5. Method according to one of the preceding claims, characterised in that at least a second oxidising compound, preferably oxygen, is additionally introduced to the metal ion generator.



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6. Method according to one of the preceding claims, characterised in that a portion of the solution situated in the cathode chamber is transferred directly to the metal ion generator without flowing against the anodes
7. Method according to one of the preceding claims, characterised in that the deposition solution, conducted through the metal ion generator, flows directly against the cathode and subsequently against the anodes as a result of a deflection of the direction of flow.
8. Apparatus for the electrolytic deposition of uniformly thick metal layers of specific physical-mechanical properties, more especially copper layers, having a high electrolytic efficiency, from a deposition solution which is in contact with cathodes (6, 24: 69) and insoluble, preferably perforated, dimensionally stable anodes (5, 23, 74), comprising
- an electrolyte chamber (1) disposed between the cathodes and anodes;
 - devices for causing the deposition solution to flow against the cathodes and anodes;
 - a metal ion generator (2, 21; 44, 66);



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- a first means for transferring the deposition solution, which flows against the anodes, to the metal ion generator;
 - this means bridging a small spatial distance between the anodes and the metal ion generator;
 - a second means for transferring the deposition solution, emerging from the metal ion generator to the electrolyte chamber; and
 - additional means, whereby the concentration of oxidising compounds, contained in the deposition solution, is minimised in the immediate vicinity of the cathode.
9. Apparatus according to claim 8, characterised in that means (31, 62, 76) are provided, whereby the deposition solution, situated in the vicinity of the anodes, is evacuated at high velocity or removed via outlets (4, 61, 77) and transferred to the metal ion generator (2, 21, 44, 66).
10. Apparatus according to one of claims 8 or 9, characterised in that the electrolyte chamber (1) is divided into a plurality of compartments by ion-permeable dividing walls (17, 38, 80).
11. Apparatus according to one of claims 8 to 10, characterised in that outlets (18, 75) are provided,



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whereby the deposition solution, situated in the vicinity of the cathodes, is removed from the electrolyte chamber (1) and transferred to the metal ion generator (2, 21, 44, 66).

12. Apparatus according to one of claims 8 to 11, characterised in that a tubular device, fillable from above, is provided as the metal ion generator (2, 21, 44, 66), said tubular device being provided, in the lower region, with a base (48) and with at least one connection pipe (49) with lateral apertures (50) for the induction of the deposition solution and, in the upper region, with an overflow (54, 78) extending into an electrolyte container (45, 67).
13. Apparatus according to one of claims 8 to 12, characterised by inclined, preferably perforated plates (55) in the interior of the metal ion generator (2, 21, 44, 66).
14. Apparatus according to one of claims 8 to 13, characterised by means for the injection of air (56) disposed in the lower region of the metal ion generator (2, 21, 44, 66).
15. Apparatus according to one of claims 8 to 14, characterised by means (26, 70, 82) for the horizontal



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picking-up, electrical contacting and displacing of
the cathodes in the horizontal direction.

16. Method according to one of claims 1 to 7 for
metallising printed circuit boards.

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PROCESS AND DEVICE FOR ELECTROLYTIC PREPARATION OF METALLIC LAYERS

ABSTRACT OF THE DISCLOSURE

For the electrolytic deposition of uniform layers of metal having given physical-mechanical properties, particularly of copper, soluble anodes are not used, since their geometrical shape is changed by the deposition and therefore the distribution of the lines of force in the electrolytic cell are continuously changed.

In order to solve the problems occurring in this connection, a process has been proposed in which compounds of a redox system added to the plating solution are converted during the deposition on the insoluble anodes. The compounds produced in this connection dissolve new metal ions from a reservoir which contains parts of the metal to be deposited, so as again to supplement the metal ions removed from the solution by deposition.

The present invention describes a procedure in which, differing from the prior art, the addition compounds are not destroyed.

Fig. 6

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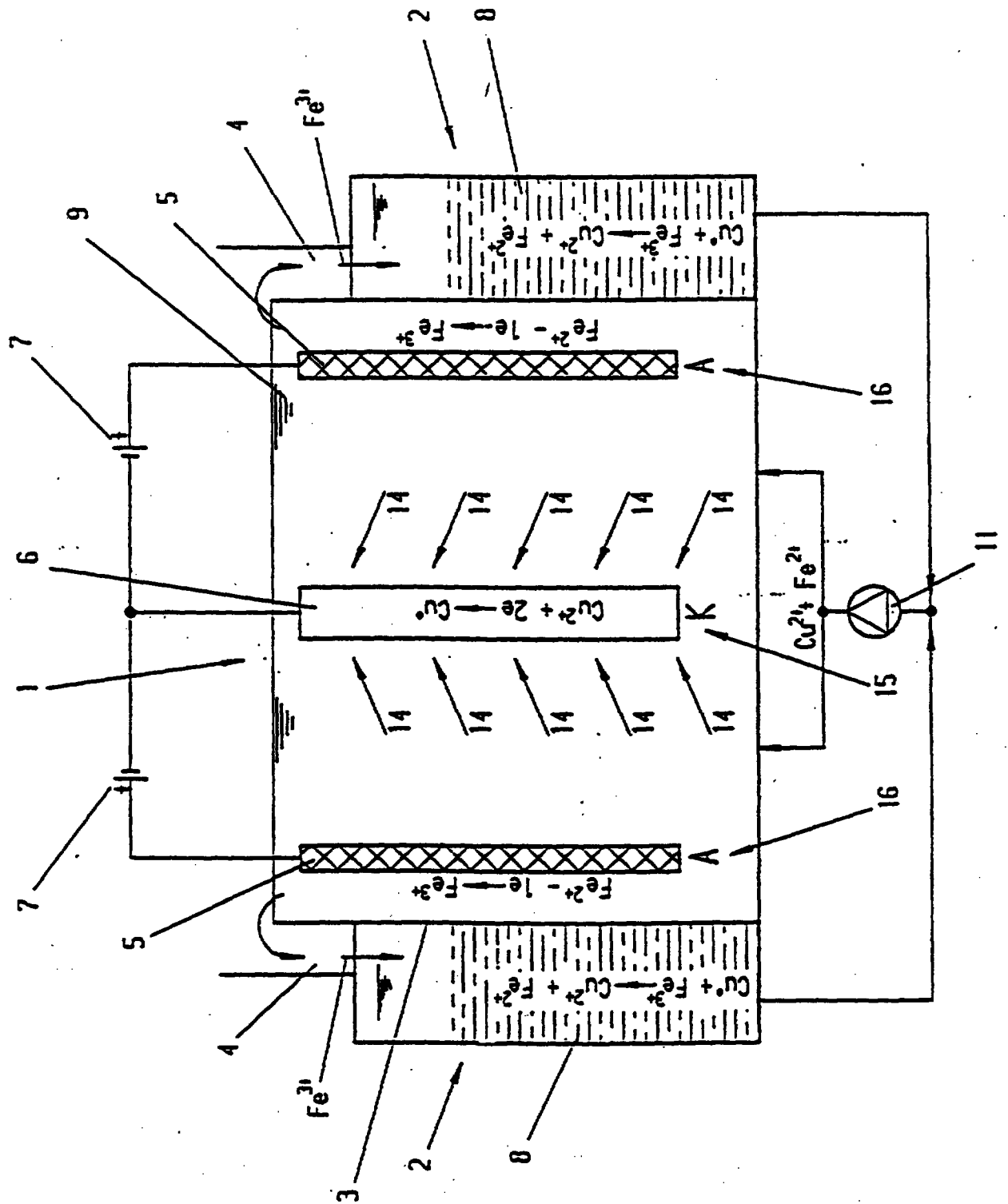


Fig. 1

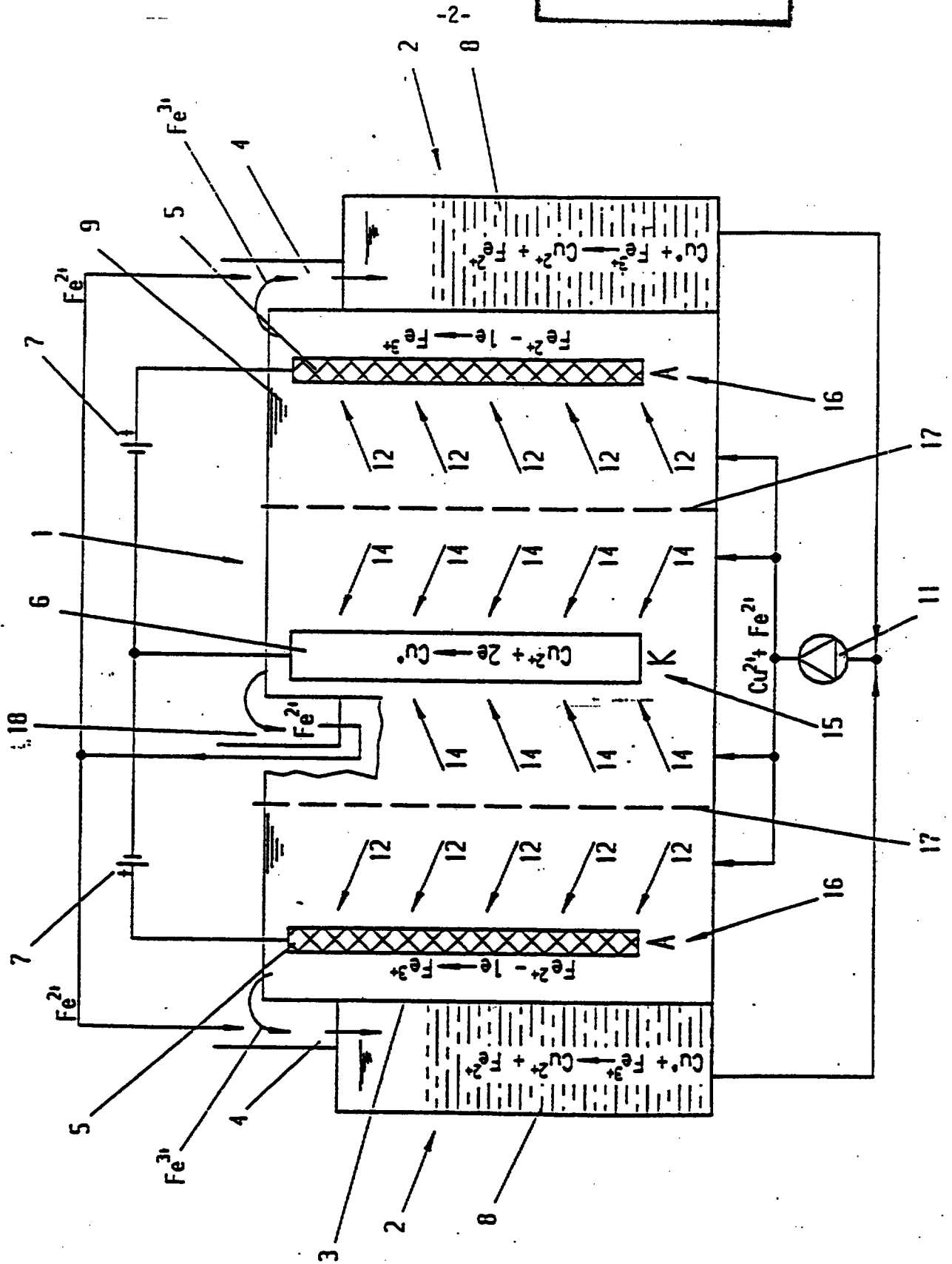


Fig. 2

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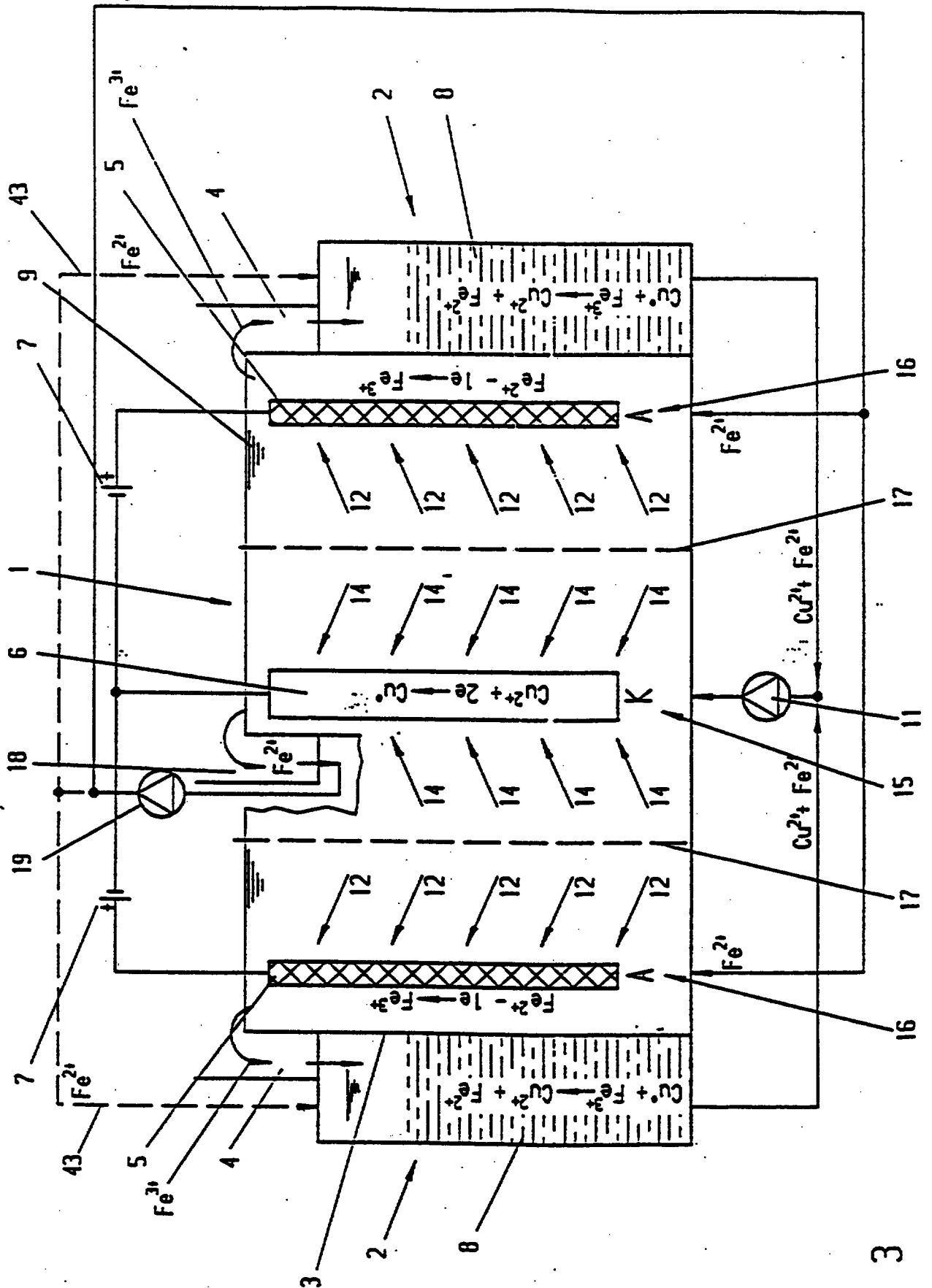


Fig. 3

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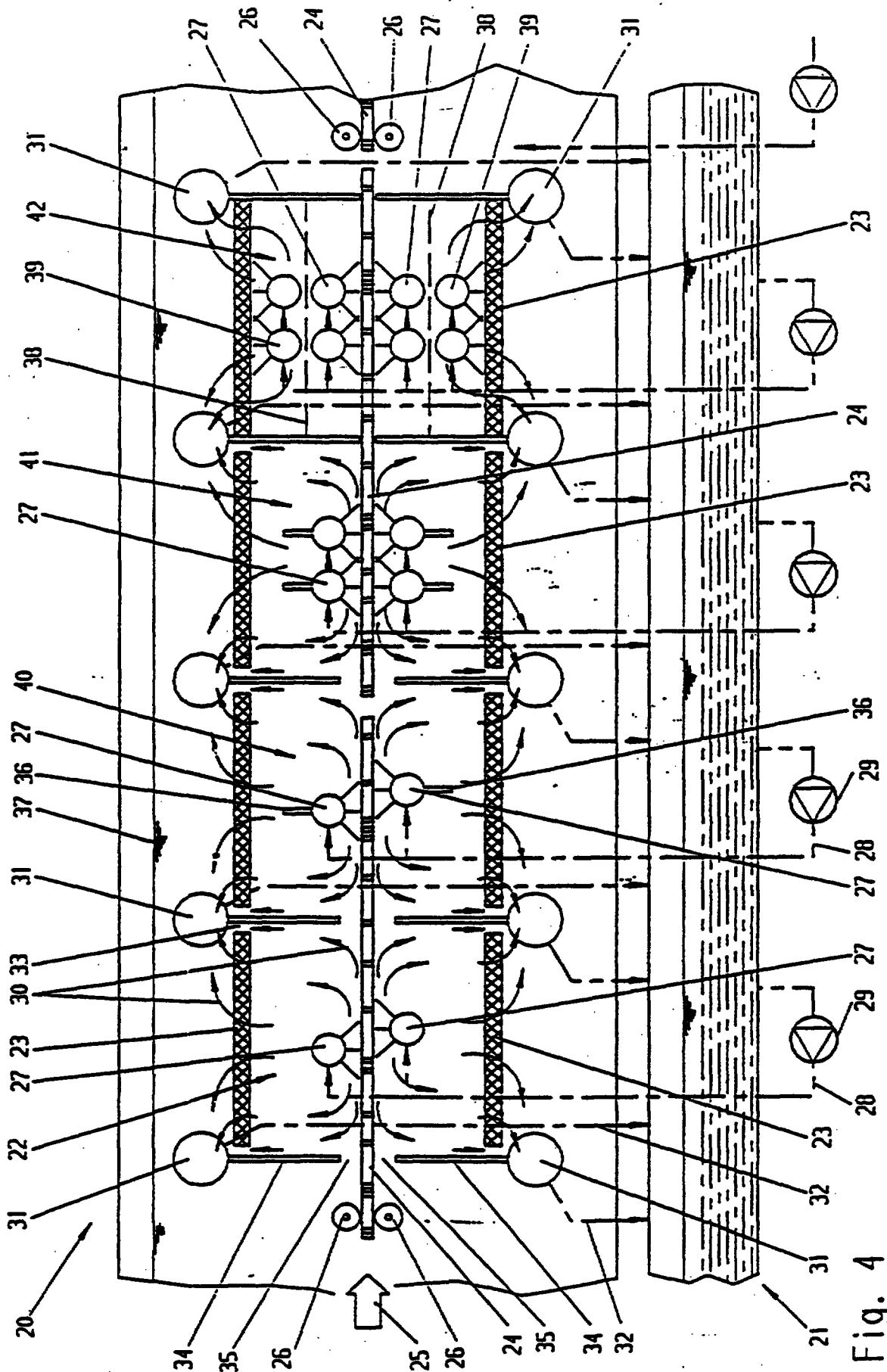


Fig. 4

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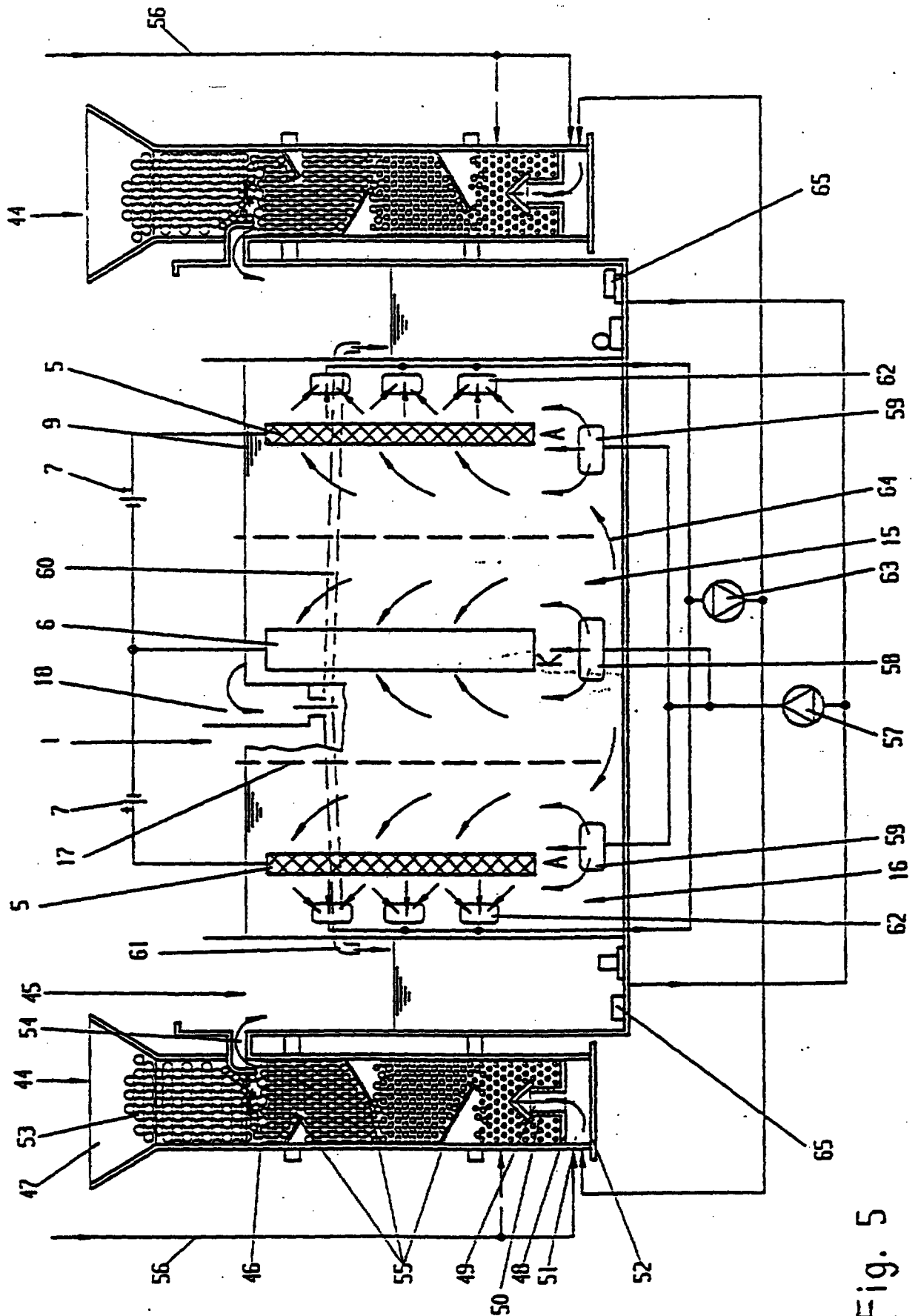


Fig. 5

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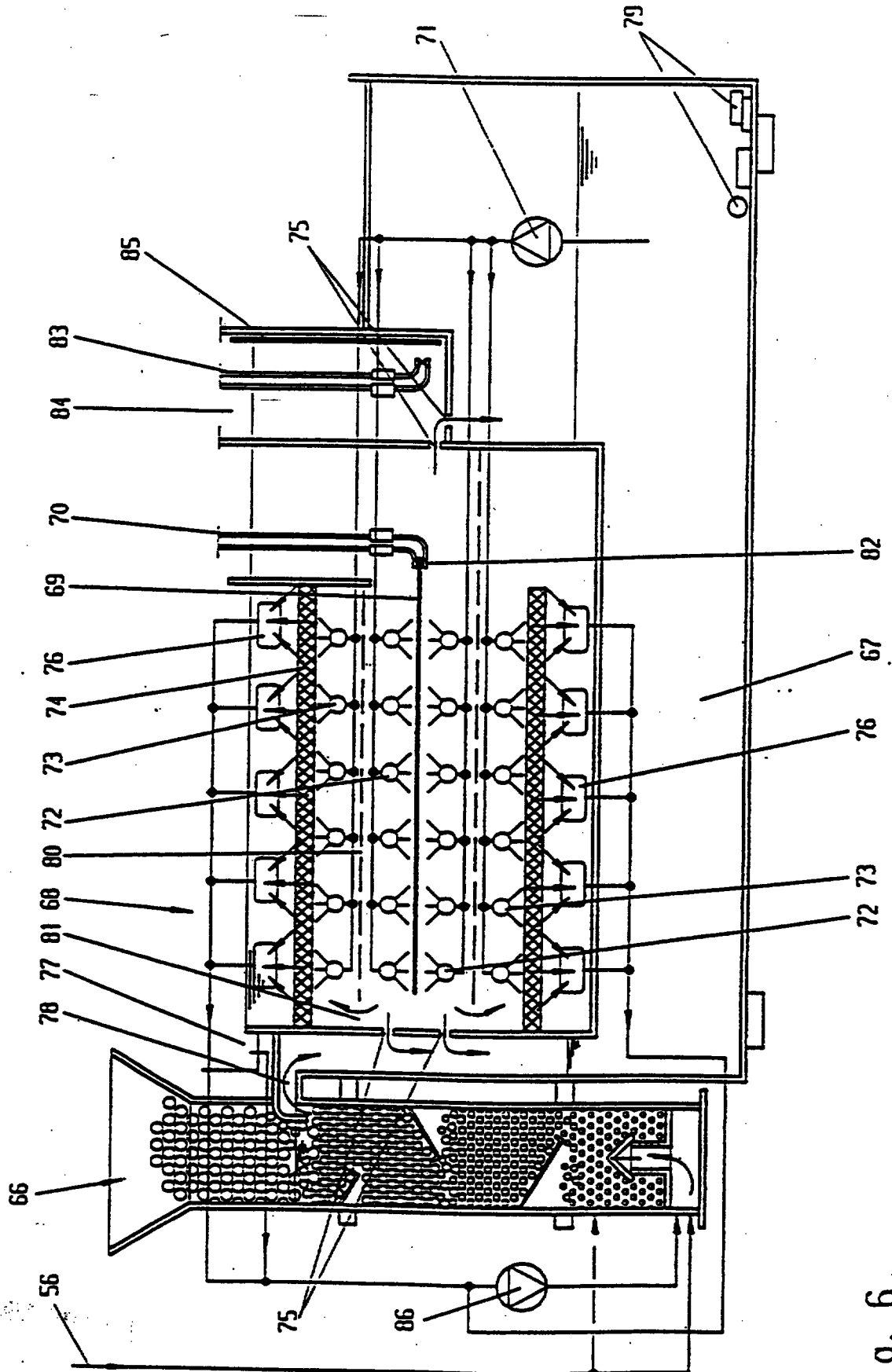


Fig. 6