

**METHOD FOR ELECTROLYTIC SEPARATION OF METALS
FROM ELECTROLYTES WITH PROCESS ORGANICS**

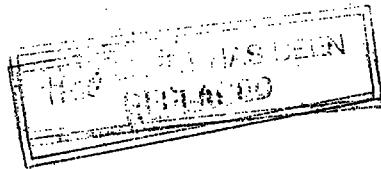
Description:

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The invention relates to a method of electrolytic separation of metals, using soluble or insoluble anodes.

10 The physical properties of the separated metal may be varied within wide limits by the addition of materials to the electrolytes. For this purpose organic additive materials, also called process organics or additive compounds, have become widely used. For example they
15 determine properties of the separated coatings such as brightness, expansion and hardness. This process organic material is known in the technology of printed circuit boards as a brightener and leveller.

20 During electrolysis, the process organic material is continuously consumed in small amounts. This occurs in all areas of the electroplating system, i.e. at the cathode, at the anode and in the entire volume of electrolyte. The consumed amount of process organic
25 material must be replaced, this as a rule being effected discontinuously. However, due to this, increased amounts of decomposition products and

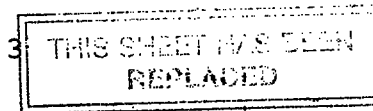


deposits occur, in effect because of the consumption due to separation of the process organics and also due to the excess amount of organic material located at least intermittently in the electrolyte.

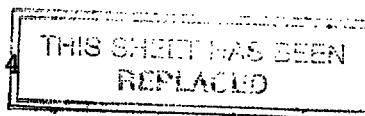
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Because of the extremely complex method of determining process organics in the electrolyte, there are used for subsequent dosing indirect magnitudes such for example as the converted ampere-hours of the electrolytic process. Erroneous dosages cannot be excluded. The resultant quality shortfalls in the separated coating often become apparent extremely late, i.e. great damage can be caused. An example of this is the appearance of errors due to process organics in printed circuit boards, such as splitting at the edge of perforations, which makes its appearance felt only during subsequent soldering of components or even later.

The decomposition products of process organics are distributed in an uncontrolled manner in the entire amount of electrolyte in the electrolytic system. This distribution is supported by electrolyte movements due to the process and air insufflations in the electrolytic cell as well as by the generally widely-distributed circulation of electrolyte through accessory sections and particle filters. These filters are not capable of separating the decomposition



products. The presence of the decomposition products can only be indicated analytically with a high outlay. Due to the multiplicity of materials involved and to the differing concentrations, their effect on the material for treatment in the electrolytic cell cannot be foreseen. The necessarily continuous supplementation of the consumed process organics means that the concentration of decomposition products in the electrolyte also increases. Attempts to counteract this damaging concentration by filtration have met with only limited success. Due to the extensive distribution of the process organics and of their decomposition products in the entire electrolytic system, the material for treatment cannot be protected from exposure to irregular concentrations. Thus in the region of the material for treatment, the concentration of process organics conditional upon dosing and the amount of decomposition products fluctuates. Consequently, the quality of the metal coating deposited on the material for treatment is subject to uncontrolled fluctuations. For example, when electroplating printed circuit boards, the sporadic formation of so-called pimples is observed, which form at the point of deposition of the decomposition products. Treated material with these dot-shaped increases in coating thickness is generally scrap. Likewise, formation of grit on the deposited coating,



which is occasionally observed, leads to scrapping. In addition, the ultimate elongation of copper coatings on printed circuit boards decreases as the residence time in an electrolytic bath continues, although the

5 concentration of process organics, which may be determined by analysis, lies within prescribed limits. In order to avoid an unacceptable accumulation of impurities in the electrolyte, the latter is continuously circulated through filters. Cartridge

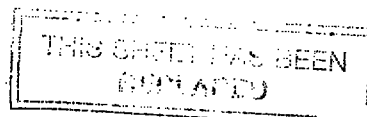
10 filters, which can separate particles at less than 0.2 μm , are widely used. As a rule, the organic decomposition products pass unhindered through such filters. The same applies also to the unconsumed process organics. The return of circulated filtrate

15 into the cathode space is used in order to cause the electrolyte to flow over the material for treatment.

If the acceptable minimum limits of physical properties of the separated coatings are not achieved, although

20 the concentration of the process organics is sufficiently high, the electrolyte must be cleaned. In a new electrolysis system, with a newly-used electrolyte, this point in time can be reached after about 3 months, independently of the current density,

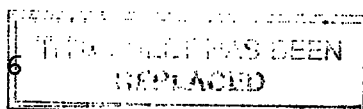
25 especially if standards of quality of the electrolytic layer are high. This is for example the case in the technology of printed circuit boards. Further cleaning



of the electrolyte and of the electrolytic system thereafter become necessary at shorter intervals. This is caused by the fact that it is not possible entirely to remove the decomposition products from the process
5 organics which are not only present in the electrolyte but also on all the walls, tubes, anodes and further in bath inclusions, units and apparatus.

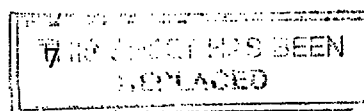
Cleaning of the electrolyte of organic decomposition
10 products is effected by an activated carbon treatment and by flushing of all containers and surfaces which come into contact with the electrolyte. For this purpose, toxic solvents are to some extent necessary. In addition to the disadvantage of incomplete cleaning,
15 there is the fact that electrolytic operation must be interrupted for about one day. Further, a part of the electrolyte, together with the activated carbon, must be disposed of in a cost-intensive manner.

20 When insoluble anodes are used, the metal content in the electrolytic cell must be continuously supplemented to correspond with the separation of metal. Suitable for this purpose are metallic salts which are added to the electrolyte. This may be more advantageously
25 effected with a redox agent as an additive to the electrolyte. This involves a material which is reversibly electrochemically convertible. Such a



method is described by Patent DD 215 589 A1. The additive material oxidises at the anodes of an electrolytic cell. In a regenerating chamber, this oxidised stage of the redox agent dissolves the metal to be electrolytically deposited in an externally currentless manner. Thus the additive is again reduced to its initial condition. The oxidised stage attacks process organics present in the electrolyte extremely intensively, but not the reduced stage. Furthermore, the presence of the oxidised stage of the redox agent at the cathode reduces the cathodic current yield to uneconomic levels.

This method thus only operates satisfactorily in electrolytic processes which operate without process organics. This for example is the case in dull copper plating. If however the deposited metallic coatings must have specific physical properties which may only be achieved by the addition of process organics to the electrolyte, then the method described before is unsuitable. This is caused by the presence of the oxidised stage of the redox agent, destroying the process organics, in the entire electrolytic system. Similarly, in this electrolytic method, the process organics are distributed in the electrolyte in the entire electrolytic system. The result is an extremely rapid decomposition of the process organics by the



oxidised stage of the redox agent, causing a rapid enrichment in decomposition product.

The object of the invention is therefore to find a
5 method and a device for metal deposition from electrolytes which contain organic additives, and which enables continuous operation with uniform quality of the deposited coating under conditions which are environmentally friendly and cost-effective. The
10 method is intended to enable the use of soluble and insoluble anodes.

This object is achieved by claims 1 and 12. Preferred embodiments of the invention are indicated in the sub-
15 claims.

The solution to this problem encompasses a method and a device for electrolytic deposition of metals with specific physical properties on the surfaces of
20 material for treatment.

The method is characterised by the following features:

- a treatment solution containing additive compounds
25 (process organics) serving to control the physical properties of the metals, set in motion and circulated

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by fluid flow, is brought into contact with the material for treatment and anode,

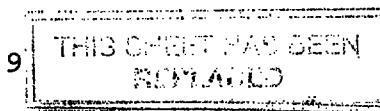
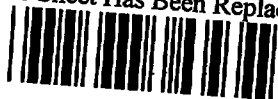
- the additive compounds are added to the treatment
5 solution at a point in the system where they can pass rapidly on to the material for treatment by means of fluid flow, i.e. at a point where they are relevant to the process,

10 - the treatment solution is guided fluidically in the deposition chamber in such a way that it does not mix with solutions from the region of the anodes, and/or

- the solution present in the vicinity of the anodes
15 (anode chamber), and the solution present in the vicinity of the material for treatment (cathode chamber) are separated from one another by ion-permeable means in such a way that these solutions do not mix, and

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- consequent decomposition products and unconsumed additive compounds in the solution are removed by means of filters from the treatment solution present in the anode chamber and/or flowing away from the anode
25 chamber and/or from the cathode chamber.

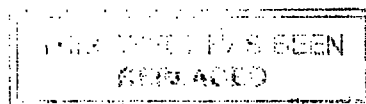


Treatment solution is substantially understood to be the solution continuously circulated, if necessary charged with additive residues and decomposition products, which serves for treatment of the material.

- 5 Otherwise the term solution is substantially only used in order to identify a solution which has a composition different from that of the treatment solution.

It is also possible according to the invention to add
10 to the solution intended for the anode chambers additives which have an effect on the anode action, its solubility behaviour and gas formation at the anode, in order to counteract negative operational conditions. These in part superfluous additives and on occasion
15 further decomposition products, anode sludge and similar, are again filtered out of the solution by correspondingly selected and equipped filters in the circuit.

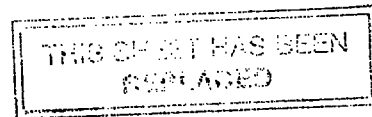
- 20 A further development of the invention consists in removing the additive compounds from the treatment solution present in a cathode flow circuit connected with the cathode chamber and from the anode flow circuit connected with the anode chamber and separate
25 from the cathode flow circuit, by means of filters associated with the individual circuits.



The concentration of the additive compounds in the treatment solution may be maintained by continuous addition of the compounds in the amount corresponding at least to the continuous consumption of said additive compounds. If the additive compounds in the treatment solution conveyed to the material for treatment are entirely removed by filters, the supplementary amount for maintaining the prescribed concentration of the additive compounds in the cathode chamber may easily be determined by calculation. As a result of an imminent lack of additive compounds in the treatment solution at the point where the compounds are added to the solution, the amount of additive compounds to be subsequently dosed is substantially derived from the volume of circulated treatment solution, and need not be determined from the results of analysis.

In a further embodiment, the solutions are passed and filtered out of the cathode or anode chamber via separate circuits. For example, the solutions may be passed separately through filters and thereafter returned in common into the individual chambers.

In a further embodiment, the treatment solution is circulated in a serial circuit from the material via filter and anode and from that point back again to the material for treatment.



Filters such for example as wound cartridge filters, rotary disc filters, pre-coated filters, gravitational separators, activated carbon filters, osmotic filters, molecular screens and ion exchangers are used as
5 filters.

The additive compounds may also be removed by additional filtering by means of activated carbon in an additional electrolyte container serving to receive the
10 filtered treatment solutions. In order to prevent the activated carbon from being flushed into the solution, it is housed in suitable vessels, bags or sacks, through which the solution flows.

15 If insoluble anodes are used for electrolytic deposition, the loss of metal ions caused by deposition in the treatment solution may be compensated for by chemical dissolution of metal particles by means of compounds of electro-chemically reversible redox
20 systems added to the treatment solution.

In this case it is extraordinarily advantageous if the metal particles present in a separate regenerating chamber have an effective surface which is so large
25 that practically all the metal-dissolving compounds of the redox system circulated to the regenerating chamber

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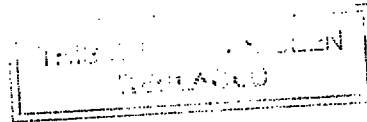
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are chemically reduced with simultaneous dissolution of the metal particles.

The method according to the invention is carried out by
5 means of a device comprising:

- a deposition chamber, anodes, supply of current for polarising the material for treatment with respect to the anodes, and pumps and lines for conveying the
10 treatment agent in the device,
- means of supplying current to the treatment solution and/or ion-permeable means for avoiding mixture of the solution present in the vicinity of the anodes and the
15 solution present in the vicinity of the material for treatment,
- means of dosing the additive compounds, these being so placed in the system that the additive compounds to
20 be dosed can rapidly pass fluidically into the vicinity of the material for treatment,
- filters for removing consequent decomposition products and superfluous additive compounds from the
25 circulated treatment solution.



The method according to the invention will be explained in the following with reference to a drawing, which shows specifically:

5 Figure 1: diagram of an electrolytic system;

Figure 2: diagram of an electrolytic system without electrolyte container;

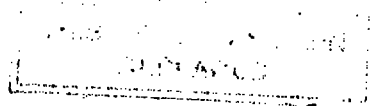
10 Figure 3: diagram of an electrolytic system with insoluble anodes;

Figure 4: diagram of an electrolytic system with insoluble anodes for plate-shaped material
15 for treatment.

The schematic view of an electrolytic system in Figure 1 shows a bath container 1 with the anodes 2 for the front and rear sides of the cathodic material for
20 treatment 3.

The bath is supplied with current by means of the current sources 4. The bath container 1 is subdivided in a fluid-tight yet ion-permeable manner by diaphragms
25 S into a cathode chamber 6 and to anode chambers 7.

The treatment fluid/the electrolyte 8 in the cathode chamber 6 can flow through an outlet 9 here indicated



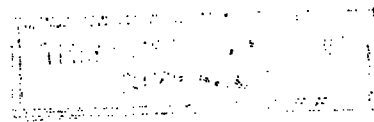
as an overflow. The electrolytes in the anode chambers 7 have the outlets 10. Conveyed by the pump 11, the electrolyte in the cathode chamber 6 passes into the particle filter 12 and into the activated carbon filter 13, and thereafter into the electrolyte container 14. Similarly, the electrolyte from the anode chambers 7, conveyed by the pump 15, passes through the particle filter 16 into the electrolyte container 14. A further pump 17 conveys the electrolyte back into the cathode chamber 6 and into the anode chambers 7 through multi-way valves not shown. The process organics are added in a metered fashion to the electrolyte flow in the cathode chamber 6. These process organics are conveyed by means of a metering pump 18 from the storage container 19. The electrolyte flow in the cathode chamber 6 is distributed by the pipe 20.

Figure 2 shows diagrammatically an electrolytic system similar to Figure 1, yet without an electrolyte container. In this case the electrolyte is circulated, serially from the cathode chamber 6, through the filters 12 and 13 into the anode chambers 7, and from that point back through the filter 16 into the cathode chamber 6. Otherwise the electrolytic system in Figure 2 corresponds to that in Figure 1.



Figure 3 shows schematically utilisation of the method according to the invention using insoluble anodes 21 in a third embodiment of the electrolytic system, whose electrolyte is enriched in a separate regenerating
5 chamber 22 with the metal to be electrolytically deposited. The regenerating chamber 22 is filled with metal particles 23. This metal for dissolution is stored so as to be permeable by electrolyte. Circulation of the electrolyte corresponds to the
10 procedures as described with reference to Figure 2.

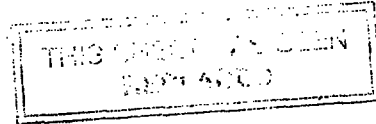
Figure 4 shows the theoretical procedures of the method according to the invention in an electrolytic system for plate-shaped material 24, using insoluble anodes
15 25. The material 24 is transported horizontally through the electrolytic system. Electrolyte flows over it in the cathode chamber 26 by means of flood tubes 27. This electrolyte is again separated in a fluid-tight but ion-permeable manner by diaphragms 28
20 from the electrolyte in the anode chamber 29. The circulated electrolyte, conveyed by the pump 13, passes from the cathode chamber 26 into a particle filter 31 and an activated carbon filter 32, and from this point into the electrolyte container 33. The pump 35 conveys
25 the electrolyte from this container into the flood tubes 27, to the cathode, and into the flood tubes 36 to the insoluble anodes 25. The electrolyte, conveyed



by the pump 39, passes through suction tubes 37 and through the outlet 38 into the regenerating chamber 40, which is filled with the metal which is to be dissolved. The electrolyte, enriched with metal ions, is again passed through the following particle filter 41 to the electrolyte container 33. In this container 34 there may be located replaceable bags or sacks for holding activated carbon 42 for receiving any process organics still present in the electrolyte. The process organics in the storage container 43, conveyed by the metering pump 44, is mixed with the electrolyte, which is introduced into the cathode chamber 26. The electrolytic system shown schematically in Figure 4 may also be operated with soluble anodes. In this case the regenerating chamber 40 is omitted.

The particular features of the method according to the invention usable in all the electrolytic systems illustrated, will be further explained in the following:

The region of the electrolyte relevant to the process for the process organics, is kept spatially small by one or a plurality of diaphragms. During electrolysis, this region is as a rule only the cathode chamber. At this point the process organics are present at a concentration not greater than that necessary to



achieve qualitatively perfect metallic coatings. At least one diaphragm 5 divides the electrolytic cell in Figure 1 into two electrolytic regions, i.e. into the anode chamber 7 and the cathode chamber 6.

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The electrolyte in the cathode chamber 6 is circulated by a pump 11. Directly after the electrolytic cell there are located, as an example in Figures 1 to 4, a particle filter 12 and an activated carbon filter 13 for removing the organic components of the electrolyte. The activated carbon filter is of such large dimensions that practically all the process organics still present in the electrolyte and their decomposition products are continuously removed.

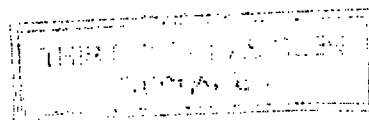
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When there is a high loading of impurities on the material for treatment, an additional electrolyte circuit for the cathode chamber may be passed through a further particle filter. Similarly, in the case for example of a heavy occurrence of anode sludge, an additional filter circuit with separate filter may be set up for the anode chamber. This has the advantage that the amount of circulated electrolyte in the circuit through the particle filter 12 and through the activated carbon filter 13 may be adapted to the consumption of process organics of the electrolytic cell in a more precise way.

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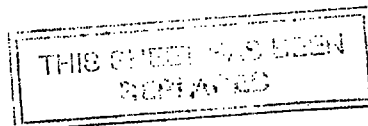
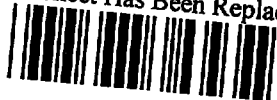
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For the filters 12, 13, 16, 31, 32, all known means and methods known in practice can be used, such for example as wound-cartridge filters, rotary disc filters, pre-coated filters, gravitational separators, molecular
5 screens, activated carbon treatment, osmotic filters, ion exchangers and other physically or chemically operating separating arrangements. It is further possible to use electrical potentials in order to generate electrical and magnetic fields in filters.

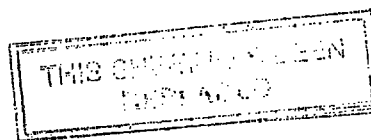
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After the filters, the electrolyte in an electrolytic system according to Figure 1 passes into an electrolyte container 14 and only from this point back into the electrolytic cell. The electrolyte in the electrolyte
15 container 14 is, according to the invention, extensively free of process organics. Thus decomposition products of organic origin cannot form here. Thus none of the disruptive organic deposits already described can occur here. A further pump 17
20 conveys the electrolyte free of process organics back into the electrolytic cell. Generally only the electrolyte fed to the cathode chamber need be enriched with new organics by continuous metering. This is appropriately effected before the electrolyte passes
25 into the cathode chamber 6. In exceptional cases, a specific organic material may be metered also into the electrolyte which is introduced into the anode chamber.



The residual amount is again filtered out in the electrolyte circuit after the electrolytic cell. For this purpose individual filters designed for the organic material may be used. This situation is not
5 shown in the Figures. It is of advantage in the invention that these metered amounts can always originate from an equal concentration of the process organics in the electrolyte, i.e. from concentration zero. That is to say that this corresponds practically
10 to a new use of the electrolyte. For this purpose the metered amounts of process organics per component and per unit of electrolyte volume are known and thus may be extremely precisely supplemented without great technical outlay. Permanent subsequent metering is
15 therefore not based on analysis of the process organics, a factor which is technically extremely complex, such for example as cyclic voltametry. Intermittent monitoring procedures are restricted only to the indication of process organics in regions which
20 according to the invention should be free of organics.

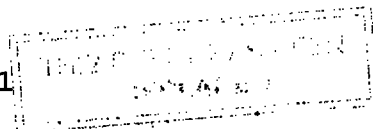
The subsequent metering of process organics is effected continuously, or so to speak continuously, in such a way that precisely the required concentration is re-
25 established in the electrolytic cell and there only in the chamber relevant to the process. A suitable metering point is an injection point in the pipeline



system for the electrolyte circuit in the vicinity of the electrolytic cell. The consumption of process organics is also small in volumetric terms. Because the metering of larger volumes is technically simpler, 5 the process organics may be pre-diluted as far as the removal of the electrolyte from the electrolytic cell by the material for treatment will permit. Suitable liquids, or the electrolyte itself, are used for dilution. Continuous metering of these process 10 organics into the injection point and their mixture in the pipeline ensures their uniform distribution in the space in the electrolytic cell relevant to the process.

In a further electrolytic system according to Figure 2, 15 the electrolyte is removed from the cathode space 6 and, after filtration, is passed into the anode chamber 7, free of process organics. From this point it is then pumped back into the cathode chamber by pump 15, this electrolyte, as described, being enriched with 20 process organics by metering.

The use of diaphragms in order to avoid admixture of the electrolytes in the anode chambers with the electrolyte in the cathode chamber may also be omitted. 25 In this case the current supply of the electrolyte returned to the electrolytic cell should be so selected that no admixture takes place. This may be achieved

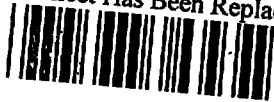


with the aid of flood tubes aligned in a controlled manner in the theoretical separation of the chambers. In an electrolytic system according to Figure 4, the anodes 25 are flooded with electrolyte in a controlled manner by the flood tubes 36, and the cathode by the flood tubes 27. When there is a sufficient circulating quantity of electrolyte and thus a corresponding flow speed, the diaphragm 28 may be omitted.

When insoluble anodes are used, the metal content in the electrolyte may be supplemented with the aid of a suitable redox agent. Care must however be taken that the process organics required in the cathode are not mixed with the oxidised stage of the redox agent. This requirement is precisely fulfilled by the method according to the invention. The process organics are located, separated by diaphragms 5, 28, only in the cathode chamber 6, 26, which is free of the aggressive oxidised stage of the redox agent. Thus the organics are protected at this point. The anode chamber 7, 29 and the connecting regeneration chamber 22, 40 is free of process organics, but contains the oxidised stage of the redox agent, necessary to dissolve the metal in the regenerating chamber 22, 40.

25

When in addition, through the availability of a sufficiently large effective surface of the metal to be



dissolved in the regenerating chamber 22, 40 all the ions here present in the electrolyte of the oxidised stage of the redox agent are reduced, the electrolyte to be conveyed from the regenerating chamber into the cathode chamber is free of aggressive materials which could attack the process organics at that point. Thus the invention enables enrichment of the electrolyte in metal, with the aid of a redox agent.

10 The method according to the invention ensures a permanent high-quality deposition of metallic coatings from electrolytes which contain additives of process organics. In this respect the use of soluble and insoluble anodes is possible. The method further ensures that the metered addition of the process organics which are decisive for quality, takes place under conditions which are to be ascribed to simple initial conditions of the concentrations of the process organics. The result is a technically very simple and reproducible process procedure. Complex analytical determination of the actual value of the process organics in the electrolyte is not necessary. This includes the fact that any optional process organics may be used in any optional, particularly minimum concentration, without the necessity of frequently and in a complex manner analysing the electrolyte.

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Patent Claims:

10 1. Method for electrolytically depositing metals of
specific physical properties on the surfaces of
material for treatment by means of a treatment solution
set in motion by fluidic flow and guided in a circuit,
to which are added additive compounds serving to
15 control the physical properties of the metal, in which

- the additive compounds are added to the treatment
solution at a point in the system from which they may
rapidly pass by flow on to the material for treatment,

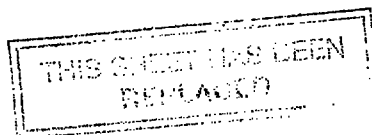
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- the solution is brought into contact with the
material for treatment and anodes,

- the treatment solution is passed into a deposition
25 chamber, and/or the solution present in the vicinity
of the anodes (anode chamber), and the solution present
in the vicinity of the material for treatment (cathode



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chamber), are separated from one another by ion-permeable means in such a way that the solutions do not mix,

- 5 - consequent decomposition products and unconsumed additive compounds are removed from the solution present in the anode chamber and/or flowing away from the anode chamber and/or cathode chamber.
- 10 2. Method according to claim 1, characterised in that there are added to the treatment solution passed to the anode chamber special additives, whose residues, inclusive of decomposition products occurring in the anode chamber, are filtered out of the return solution
- 15 in circuit by means of filters specially designed for the components to be filtered out.
3. Method according to claim 1 or 2, characterised in that the additive compounds are removed from the
- 20 treatment solution present in a cathode flow circuit connected to the cathode space, and from the treatment solution present in an anode flow circuit connected to the anode chamber and separate from the cathode flow circuit, by means of filters associated with the
- 25 individual circuits.





4. Method according to one of the preceding claims,
characterised in that the amount of additive compounds
corresponding to the concentration to be set in the
treatment solution is continuously added to the
5 treatment solution containing no additive compounds and
flowing to the cathode chamber.

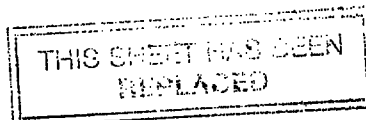
5. Method according to one of the preceding claims,
characterised in that the quantity of additive
10 compounds to be subsequently metered as a result of a
potential lack of additive compounds in the treatment
solution at a point where the compounds are added to
the solution, is substantially derived from the volume
of the circulated treatment solution.

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6. Method according to one of the preceding claims,
characterised in that filters selected from a group
containing wound cartridge-filters, rotary disc
filters, pre-coated filters, gravitational separators,
20 activated carbon filters, osmotic filters, molecular
screens and ion exchangers are used.

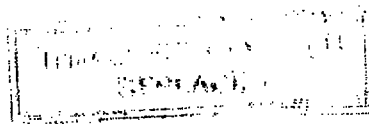
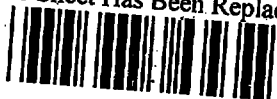
7. Method according to one of the preceding claims,
characterised in that the solution is firstly filtered
25 in a first particle filter and thereafter by means of
activated carbon.





8. Method according to one of the preceding claims, characterised in that the treatment solution is circulated from the material for treatment through filters to the anode and from this point back in a
5 circuit to the material for treatment.
9. Method according to one of claims 1 to 7, characterised in that the solutions in the anode chamber and in the cathode chamber are conveyed and
10 filtered in separate circuits.
10. Method according to one of the preceding claims, characterised in that when insoluble anodes are used, a loss of metal ions caused by electrolytic deposition is
15 compensated for by chemical dissolution of metal particles by means of compounds of electrochemically reversible redox systems added to the treatment solution.
- 20 11. Method according to claim 10, characterised in that the metal particles present in a separate regenerating chamber (10) have an effective surface of such a size that practically all the metal-dissolving compounds of the redox system circulated to the regenerating chamber
25 are chemically reduced, with simultaneous dissolution of the metal particles.





12. Device for electrolytic deposition of metals of specific physical properties on the surfaces of material for treatment (3, 24) (cathode) by means of a circulated treatment solution set in motion by fluid
5 flow, additive compounds serving to control the physical properties of the metal being capable of addition, comprising

- a deposition chamber (6, 26; 7, 29) for treatment
10 material, anodes (2, 25) a current supply (4) for polarising the material for treatment with respect to the anodes, and pumps (11, 15, 17, 30, 35) and pipes for conveying the treatment solution in the device,
15 - means for flow guidance of the treatment solution to the material for treatment and/or ion-permeable means (5, 28) in order to avoid mixture of the solution present in the vicinity of the anodes (anode chamber 7, 29) and the solution present in the vicinity of the
20 material for treatment (cathode chamber 6, 26),

- means (18, 19, 43, 44) for metered addition of the additive compounds to the treatment solution, located at a point in the circuit from which the metered
25 additive compounds are conveyed directly to the material for treatment,





- filters (12, 13, 16, 31, 32) for removing consequent decomposition products and superfluous additive compounds from the circulated treatment solution.

5 13. Device according to claim 12, characterised by filters (12, 13, 16, 31, 32) for physical and/or chemical separative cleaning, selected from a group comprising wound-cartridge filters, rotary disc filters, pre-coated filters, gravitational separators,
10 activated carbon filters, osmotic filters, molecular screens and ion exchangers and/or a combination of these filters, designed to correspond to the type of additives and decomposition products to be filtered out.

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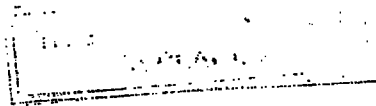
14. Device according to claims 12 or 13, characterised by an additional electrolyte container (14, 33) for receiving the filter treatment solution.

20 15. Method for electrolytic deposition of metals of specific physical properties on the surfaces of material for treatment, characterised by individual features or all new features or combinations of the disclosed features.

25

16. Device for electrolytic deposition of metals of specific physical properties on the surfaces of





material for treatment, characterised by individual features or all new features of combinations of the disclosed features.

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**METHOD FOR ELECTROLYTIC DEPOSITION OF METALS
FROM ELECTROLYTES WITH PROCESS ORGANICS**

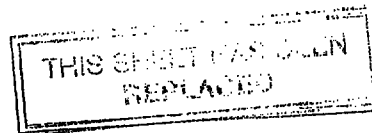
15 ABSTRACT:

The invention relates to a method of electrolytic deposition of metals from electrolytes, which contain additives or process organics in order to achieve
20 specific physical properties. Such additives are subject to continuous consumption during electrolysis, decomposition products forming from these additives, which deposit in the entire electrolytic system and thus also on the material for treatment.

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Thus the object underlying the invention is to avoid quality shortfalls in the deposited coatings caused by





material for treatment, characterised by individual features or all new features of combinations of the disclosed features.

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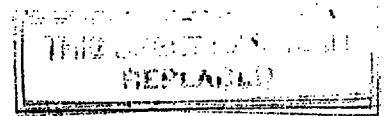
**METHOD FOR ELECTROLYTIC DEPOSITION OF METALS
FROM ELECTROLYTES WITH PROCESS ORGANICS**

15 ABSTRACT:

The invention relates to a method of electrolytic deposition of metals from electrolytes, which contain additives or process organics in order to achieve
20 specific physical properties. Such additives are subject to continuous consumption during electrolysis, decomposition products forming from these additives, which deposit in the entire electrolytic system and thus also on the material for treatment.

25

Thus the object underlying the invention is to avoid quality shortfalls in the deposited coatings caused by



organic residues, and in this way to achieve a continuous metal deposition with uniform quality of the metal coatings. This object is achieved by spatial limitation of the concentration of the process organics
5 to the electrolyte region in the electrolytic system in which it is relevant to the process. The circulated electrolyte is kept free of process organics by filters. Renewed metered addition of process organics is effected in dependence on consumption directly
10 before the region relevant to the process.

(Figure 1)

0-811-1-1
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METHOD FOR ELECTROLYTIC SEPARATION OF METALS
FROM ELECTROLYTES WITH PROCESS ORGANICS

Description:

5

The invention relates to a method of electrolytic deposition of metals, using soluble or insoluble anodes.

10 The physical properties of the deposited metal may be varied within wide limits by the addition of materials to the electrolytes. For this purpose organic additive materials, also called process organics or additive compounds, have become widely used. For example they
15 determine properties of the deposited coatings such as brightness, elongation and hardness. This process organic material is known in the technology of printed circuit boards as a brightener and leveller.

20 During electrolysis, the process organic material is continuously consumed in small amounts. This occurs in all areas of the electroplating system, i.e. at the cathode, at the anode and in the entire volume of electrolyte. The consumed amount of process organic
25 material must be replaced, this as a rule being effected discontinuously. However, due to this, increased amounts of decomposition products and

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deposits occur, in effect because of the consumption due to deposition of the process organics and also due to the excess amount of organic material located at least intermittently in the electrolyte.

5

Because of the extremely complex method of determining process organics in the electrolyte, there are used for subsequent dosing indirect magnitudes such for example as the converted ampere-hours of the electrolytic process. Erroneous dosages cannot be excluded. The resultant quality shortfalls in the deposited coating often become apparent extremely late, i.e. great damage can be caused. An example of this is the appearance of errors due to process organics in printed circuit boards, such as cracks at the edge of perforations, which makes its appearance felt only during subsequent soldering of components or even later.

The decomposition products of process organics are distributed in an uncontrolled manner in the entire amount of electrolyte in the electrolytic system. This distribution is supported by electrolyte movements due to the process and air insufflations in the electrolytic cell as well as by the generally widely-distributed circulation of electrolyte through accessory sections and particle filters. These filters are not capable of separating the decomposition

products. The presence of the decomposition products can only be indicated analytically with a high outlay. Due to the multiplicity of materials involved and to the differing concentrations, their effect on the material for treatment in the electrolytic cell cannot be foreseen. The necessarily continuous supplementation of the consumed process organics means that the concentration of decomposition products in the electrolyte also increases. Attempts to counteract this damaging concentration by filtration have met with only limited success. Due to the extensive distribution of the process organics and of their decomposition products in the entire electrolytic system, the material for treatment cannot be protected from exposure to irregular concentrations. Thus in the region of the material for treatment, the concentration of process organics conditional upon dosing and the amount of decomposition products fluctuates. Consequently, the quality of the metal coating deposited on the material for treatment is subject to uncontrolled fluctuations. For example, when electroplating printed circuit boards, the sporadic formation of so-called pimples is observed, which form at the point of deposition of the decomposition products. Treated material with these dot-shaped increases in coating thickness is generally scrap. Likewise, formation of grit on the deposited coating,

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which is occasionally observed, leads to scrapping. In addition, the ultimate elongation of copper coatings on printed circuit boards decreases as the residence time of an electrolytic bath continues, although the

5 concentration of process organics, which may be determined by analysis, lies within prescribed limits. In order to avoid an unacceptable accumulation of impurities in the electrolyte, the latter is continuously circulated through filters. Cartridge

10 filters, which can separate particles at less than 0.2 um, are widely used. As a rule, the organic decomposition products pass unhindered through such filters. The same applies also to the unconsumed process organics. The return of circulated filtrate

15 into the cathode space is used in order to cause the electrolyte to flow over the material for treatment.

If the acceptable minimum limits of physical properties of the deposited coatings are not achieved, although

20 the concentration of the process organics is sufficiently high, the electrolyte must be cleaned. In a new electrolysis system, with a newly-used electrolyte, this point in time can be reached after about 3 months, dependent on the current density,

25 especially if standards of quality of the electrolytic layer are high. This is for example the case in the technology of printed circuit boards. Further cleaning

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of the electrolyte and of the electrolytic system. thereafter become necessary at shorter intervals. This is caused by the fact that it is not possible entirely to remove the decomposition products of the process
5 organics which are not only present in the electrolyte but also on all the walls, tubes, anodes and further in bath inclusions, units and apparatus.

Cleaning of the electrolyte of organic decomposition
10 products is effected by an activated carbon treatment and by flushing of all containers and surfaces which come into contact with the electrolyte. For this purpose, toxic solvents are to some extent necessary. In addition to the disadvantage of incomplete cleaning,
15 there is the fact that electrolytic operation must be interrupted for about one day. Further, a part of the electrolyte, together with the activated carbon, must be disposed of in a cost-intensive manner.

20 When insoluble anodes are used, the metal content in the electrolytic cell must be continuously supplemented to correspond with the deposition of metal. Suitable for this purpose are metallic salts which are added to the electrolyte. This may be more advantageously
25 effected with a redox agent as an additive to the electrolyte. This involves a material which is reversibly electrochemically convertible. Such a

method is described by Patent DD 215 589 A1. The additive material oxidises at the anodes of an electrolytic cell. In a regenerating chamber, this oxidised stage of the redox agent dissolves the metal to be electrolytically deposited in an externally electroless manner. Thus the additive is again reduced to its initial condition. The oxidised stage attacks process organics present in the electrolyte extremely intensively, but not the reduced stage. Furthermore, the presence of the oxidised stage of the redox agent at the cathode reduces the cathodic current yield to uneconomic levels.

This method thus only operates satisfactorily in electrolytic processes which operate without process organics. This for example is the case in dull copper plating. If however the deposited metallic coatings must have specific physical properties which may only be achieved by the addition of process organics to the electrolyte, then the method described before is unsuitable. This is caused by the presence of the oxidised stage of the redox agent, destroying the process organics, in the entire electrolytic system. Similarly, in this electrolytic method, the process organics are distributed in the electrolyte in the entire electrolytic system. The result is an extremely rapid decomposition of the process organics by the

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oxidised stage of the redox agent, causing a rapid enrichment in decomposition product.

The object of the invention is therefore to find a
5 method and a device for metal deposition from electrolytes which contain organic additives, and which enables continuous operation with uniform quality of the deposited coating under conditions which are environmentally friendly and cost-effective. The
10 method is intended to enable the use of soluble and insoluble anodes.

This object is achieved by claims 1 and 12. Preferred embodiments of the invention are indicated in the sub-
15 claims.

The solution to this problem encompasses a method and a device for electrolytic deposition of metals with specific physical properties on the surfaces of
20 material for treatment.

The method is characterised by the following features:

- a treatment solution containing additive compounds
25 (process organics) serving to control the physical properties of the metals, set in motion and circulated

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by fluid flow, is brought into contact with the material for treatment and anodes,

- the additive compounds are added to the treatment solution at a point in the system where they can pass rapidly on to the material for treatment by means of fluid flow, i.e. at a point where they are relevant to the process,
- 10 - the treatment solution is guided fluidically in the deposition chamber in such a way that it does not mix with solutions from the region of the anodes, and/or
- the solution present in the vicinity of the anodes
15 (anode chamber), and the solution present in the vicinity of the material for treatment (cathode chamber) are separated from one another by ion-permeable means in such a way that these solutions do not mix, and
- 20 - consequent decomposition products and unconsumed additive compounds in the solution are removed by means of filters from the treatment solution present in the anode chamber and/or flowing away from the anode
25 chamber and/or from the cathode chamber.

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Treatment solution is substantially understood to be the solution continuously circulated, if necessary charged with additive residues and decomposition products, which serves for treatment of the material.

- 5 Otherwise the term solution is substantially only used in order to identify a solution which has a composition different from that of the treatment solution.

- It is also possible according to the invention to add
10 to the solution intended for the anode chambers additives which have an effect on the anode action, its solubility behaviour and gas formation at the anode, in order to counteract negative operational conditions. These in part superfluous additives and on occasion
15 further decomposition products, anode sludge and similar, are again filtered out of the solution by correspondingly selected and equipped filters in the circuit.

- 20 A further development of the invention consists in removing the additive compounds from the treatment solution present in a cathode flow circuit connected with the cathode chamber and from the anode flow circuit connected with the anode chamber and separated
25 from the cathode flow circuit, by means of filters associated with the individual circuits.

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The concentration of the additive compounds in the treatment solution may be maintained by continuous addition of the compounds in the amount corresponding at least to the continuous consumption of said additive compounds. If the additive compounds in the treatment solution conveyed to the material for treatment are entirely removed by filters, the supplementary amount for maintaining the prescribed concentration of the additive compounds in the cathode chamber may easily be determined by calculation. As a result of an imminent lack of additive compounds in the treatment solution at the point where the compounds are added to the solution, the amount of additive compounds to be subsequently dosed is substantially derived from the volume of circulated treatment solution, and need not be determined from the results of analysis.

In a further embodiment, the solutions are passed and filtered out of the cathode or anode chamber via separate circuits. For example, the solutions may be passed separately through filters and thereafter returned in common into the individual chambers.

In a further embodiment, the treatment solution is circulated in a serial circuit from the material via filter and anode and from that point back again to the material for treatment.

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Filters such for example as wound cartridge filters, rotary disc filters, pre-coated filters, gravitational separators, activated carbon filters, osmotic filters, molecular sieves and ion exchangers are used as
5 filters.

The additive compounds may also be removed by additional filtering by means of activated carbon in an additional electrolyte container serving to receive the
10 filtered treatment solutions. In order to prevent the activated carbon from being flushed into the solution, it is housed in suitable vessels, bags or sacks, through which the solution flows.

15 If insoluble anodes are used for electrolytic deposition, the loss of metal ions caused by deposition in the treatment solution may be compensated for by chemical dissolution of metal particles by means of compounds of electro-chemically reversible redox
20 systems added to the treatment solution.

In this case it is extraordinarily advantageous if the metal particles present in a separate regenerating chamber have an effective surface which is so large
25 that practically all the metal-dissolving compounds of the redox system circulated to the regenerating chamber

are chemically reduced with simultaneous dissolution of the metal particles.

The method according to the invention is carried out by
5 means of a device comprising:

- a deposition chamber, anodes, supply of current for polarising the material for treatment with respect to the anodes, and pumps and lines for conveying the
10 treatment agent in the device,
- means of supplying a flow of the treatment solution and/or ion-permeable means for avoiding mixture of the solution present in the vicinity of the anodes and the
15 solution present in the vicinity of the material for treatment,
- means of dosing the additive compounds, these being so placed in the system that the additive compounds to
20 be dosed can rapidly pass fluidically into the vicinity of the material for treatment,
- filters for removing consequent decomposition products and superfluous additive compounds from the
25 circulated treatment solution.

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The method according to the invention will be explained in the following with reference to a drawing, which shows specifically:

5 Figure 1: diagram of an electrolytic system;

Figure 2: diagram of an electrolytic system without electrolyte container;

10 Figure 3: diagram of an electrolytic system with insoluble anodes;

Figure 4: diagram of an electrolytic system with insoluble anodes for plate-shaped material for treatment.
15

The schematic view of an electrolytic system in Figure 1 shows a bath container 1 with the anodes 2 for the front and rear sides of the cathodic material for
20 treatment 3.

The bath is supplied with current by means of the current sources 4. The bath container 1 is subdivided in a fluid-tight yet ion-permeable manner by diaphragms
25 S into a cathode chamber 6 and two anode chambers 7. The treatment fluid/the electrolyte 8 in the cathode chamber 6 can flow through an outlet 9 here indicated

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as an overflow. The electrolytes in the anode chambers 7 have the outlets 10. Conveyed by the pump 11, the electrolyte in the cathode chamber 6 passes into the particle filter 12 and into the activated carbon filter 13, and thereafter into the electrolyte container 14. Similarly, the electrolyte from the anode chambers 7, conveyed by the pump 15, passes through the particle filter 16 into the electrolyte container 14. A further pump 17 conveys the electrolyte back into the cathode chamber 6 and into the anode chambers 7 through multi-way valves not shown. The process organics are added in a metered fashion to the electrolyte flow in the cathode chamber 6. These process organics are conveyed by means of a metering pump 18 from the storage container 19. The electrolyte flow in the cathode chamber 6 is distributed by the pipe 20.

Figure 2 shows diagrammatically an electrolytic system similar to Figure 1, yet without an electrolyte container. In this case the electrolyte is circulated, serially from the cathode chamber 6, through the filters 12 and 13 into the anode chambers 7, and from that point back through the filter 16 into the cathode chamber 6. Otherwise the electrolytic system in Figure 2 corresponds to that in Figure 1.

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Figure 3 shows schematically utilisation of the method according to the invention using insoluble anodes 21 in a third embodiment of the electrolytic system, whose electrolyte is enriched in a separate regenerating
5 chamber 22 with the metal to be electrolytically deposited. The regenerating chamber 22 is filled with metal particles 23. This metal for dissolution is stored so as to be permeable by electrolyte. Circulation of the electrolyte corresponds to the
10 procedures as described with reference to Figure 2.

Figure 4 shows the theoretical procedures of the method according to the invention in an electrolytic system for plate-shaped material 24, using insoluble anodes
15 25. The material 24 is transported horizontally through the electrolytic system. Electrolyte flows over it in the cathode chamber 26 by means of flood tubes 27. This electrolyte is again separated in a fluid-tight but ion-permeable manner by diaphragms 28
20 from the electrolyte in the anode chamber 29. The circulated electrolyte, conveyed by the pump 30, passes from the cathode chamber 26 into a particle filter 31 and an activated carbon filter 32, and from this point into the electrolyte container 33. The pump 35 conveys
25 the electrolyte from this container into the flood tubes 27, to the cathode, and into the flood tubes 36 to the insoluble anodes 25. The electrolyte, conveyed

by the pump 39, passes through suction tubes 37 and through the outlet 38 into the regenerating chamber 40, which is filled with the metal which is to be dissolved. The electrolyte, enriched with metal ions, is again passed through the following particle filter 41 to the electrolyte container 33. In this container 33 there may be located replaceable bags or sacks for holding activated carbon 42 for receiving any process organics still present in the electrolyte. The process organics in the storage container 43, conveyed by the metering pump 44, is mixed with the electrolyte, which is introduced into the cathode chamber 26. The electrolytic system shown schematically in Figure 4 may also be operated with soluble anodes. In this case the regenerating chamber 40 is omitted.

The particular features of the method according to the invention usable in all the electrolytic systems illustrated, will be further explained in the following:

The region of the electrolyte relevant to the process for the process organics, is kept spatially small by one or a plurality of diaphragms. During electrolysis, this region is as a rule only the cathode chamber. At this point the process organics are present at a concentration not greater than that necessary to

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achieve qualitatively perfect metallic coatings. At least one diaphragm 8 divides the electrolytic cell in Figure 1 into two electrolytic regions, i.e. into the anode chamber 7 and the cathode chamber 6.

5

The electrolyte in the cathode chamber 6 is circulated by a pump 11. Directly after the electrolytic cell there are located, as an example in Figures 1 to 4, a particle filter 12 and an activated carbon filter 13

10 for removing the organic components of the electrolyte. The activated carbon filter is of such large dimensions that practically all the process organics still present in the electrolyte and their decomposition products are continuously removed.

15

When there is a high loading of impurities on the material for treatment, an additional electrolyte circuit for the cathode chamber may be passed through a further particle filter. Similarly, in the case for

20 example of a heavy occurrence of anode sludge, an additional filter circuit with separate filter may be set up for the anode chamber. This has the advantage that the amount of circulated electrolyte in the circuit through the particle filter 12 and through the
25 activated carbon filter 13 may be adapted to the consumption of process organics of the electrolytic cell in a more precise way.

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For the filters 12, 13, 16, 31, 32, all known means and methods known in practice can be used, such for example as wound-cartridge filters, rotary disc filters, pre-coated filters, gravitational separators, molecular
5 sieves, activated carbon treatment, osmotic filters, ion exchangers and other physically or chemically operating separating arrangements. It is further possible to use electrical potentials in order to generate electrical and magnetic fields in filters.

10

After the filters, the electrolyte in an electrolytic system according to Figure 1 passes into an electrolyte container 14 and only from this point back into the electrolytic cell. The electrolyte in the electrolyte
15 container 14 is, according to the invention, extensively free of process organics. Thus decomposition products of organic origin cannot form here. Thus none of the disruptive organic deposits already described can occur here. A further pump 17
20 conveys the electrolyte free of process organics back into the electrolytic cell. Generally only the electrolyte fed to the cathode chamber need be enriched with new organics by continuous metering. This is appropriately effected before the electrolyte passes
25 into the cathode chamber 6. In exceptional cases, a specific organic material may be metered also into the electrolyte which is introduced into the anode chamber.

The residual amount is again filtered out in the electrolyte circuit after the electrolytic cell. For this purpose individual filters designed for the organic material may be used. This situation is not shown in the Figures. It is of advantage in the invention that these metered amounts can always originate from an equal concentration of the process organics in the electrolyte, i.e. from concentration zero. That is to say that this corresponds practically to a new make-up of the electrolyte. For this purpose the metered amounts of process organics per component and per unit of electrolyte volume are known and thus may be extremely precisely supplemented without great technical outlay. Permanent subsequent metering is therefore not based on analysis of the process organics, a factor which is technically extremely complex, such for example as cyclic voltametry. Intermittent monitoring procedures are restricted only to the indication of process organics in regions which according to the invention should be free of organics.

The subsequent metering of process organics is effected continuously, or so to speak continuously, in such a way that precisely the required concentration is re-established in the electrolytic cell and there only in the chamber relevant to the process. A suitable metering point is an injection point in the pipeline

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system for the electrolyte circuit in the vicinity of the electrolytic cell. The consumption of process organics is also small in volumetric terms. Because the metering of larger volumes is technically simpler, 5 the process organics may be pre-diluted as far as the removal of the electrolyte from the electrolytic cell by the material for treatment will permit. Suitable liquids, or the electrolyte itself, are used for dilution. Continuous metering of these process 10 organics into the injection point and their mixture in the pipeline ensures their uniform distribution in the space in the electrolytic cell relevant to the process.

In a further electrolytic system according to Figure 2, 15 the electrolyte is removed from the cathode space 6 and, after filtration, is passed into the anode chamber 7, free of process organics. From this point it is then pumped back into the cathode chamber by pump 15, this electrolyte, as described, being enriched with 20 process organics by metering.

The use of diaphragms in order to avoid admixture of the electrolytes in the anode chambers with the electrolyte in the cathode chamber may also be omitted. 25 In this case the fluid supply of the electrolyte returned to the electrolytic cell should be so selected that no admixture takes place. This may be achieved

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with the aid of flood tubes aligned in a controlled manner in the theoretical separation of the chambers. In an electrolytic system according to Figure 4, the anodes 25 are flooded with electrolyte in a controlled manner by the flood tubes 36, and the cathode by the flood tubes 27. When there is a sufficient circulating quantity of electrolyte and thus a corresponding flow speed, the diaphragm 28 may be omitted.

When insoluble anodes are used, the metal content in the electrolyte may be supplemented with the aid of a suitable redox agent. Care must however be taken that the process organics required at the cathode are not mixed with the oxidised stage of the redox agent. This requirement is precisely fulfilled by the method according to the invention. The process organics are located, separated by diaphragms 5, 28, only in the cathode chamber 6, 26, which is free of the aggressive oxidised stage of the redox agent. Thus the organics are protected at this point. The anode chamber 7, 29 and the connecting regeneration chamber 22, 40 is free of process organics, but contains the oxidised stage of the redox agent, necessary to dissolve the metal in the regenerating chamber 22, 40.

25

When in addition, through the availability of a sufficiently large effective surface of the metal to be

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dissolved in the regenerating chamber 22, 40 all the ions here present in the electrolyte of the oxidised stage of the redox agent are reduced, the electrolyte to be conveyed from the regenerating chamber into the cathode chamber is free of aggressive materials which could attack the process organics at that point. Thus the invention enables enrichment of the electrolyte in metal, with the aid of a redox agent.

- 10 The method according to the invention ensures a permanent high-quality deposition of metallic coatings from electrolytes which contain additives of process organics. In this respect the use of soluble and insoluble anodes is possible. The method further
- 15 ensures that the metered addition of the process organics which are decisive for quality, takes place under conditions which are to be ascribed to simple initial conditions of the concentrations of the process organics. The result is a technically very simple and
- 20 reproducible process procedure. Complex analytical determination of the actual value of the process organics in the electrolyte is not necessary. This includes the fact that any optional process organics may be used in any optional, particularly minimum
- 25 concentration, without the necessity of frequently and in a complex manner analysing the electrolyte.

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Patent Claims:

10 1. Method for electrolytically depositing metals of
specific physical properties on the surfaces of
material for treatment by means of a treatment solution
set in motion by fluidic flow and guided in a circuit,
to which are added additive compounds serving to
15 control the physical properties of the metal, in which

- the additive compounds are added to the treatment
solution at a point in the system from which they may
rapidly pass by flow on to the material for treatment,

20

- the solution is brought into contact with the
material for treatment and anodes,

- the treatment solution is passed into a deposition
25 chamber, and/or the solution present in the vicinity
of the anodes (anode chamber), and the solution present
in the vicinity of the material for treatment (cathode



chamber); are separated from one another by ion-permeable means in such a way that the solutions do not mix,

- 5 - consequent decomposition products and unconsumed additive compounds are removed from the solution present in the anode chamber and/or flowing away from the anode chamber and/or cathode chamber.
- 10 2. Method according to claim 1, characterised in that there are added to the treatment solution passed to the anode chamber special additives, whose residues, inclusive of decomposition products occurring in the anode chamber, are filtered out of the return solution
- 15 in circuit by means of filters specially designed for the components to be filtered out.
3. Method according to claim 1 or 2, characterised in that the additive compounds are removed from the
- 20 treatment solution present in a cathode flow circuit connected to the cathode space, and from the treatment solution present in an anode flow circuit connected to the anode chamber and separate from the cathode flow circuit, by means of filters associated with the
- 25 individual circuits.

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4. Method according to one of the preceding claims, characterised in that the amount of additive compounds corresponding to the concentration to be set in the treatment solution is continuously added to the treatment solution containing no additive compounds and flowing to the cathode chamber.

5. Method according to one of the preceding claims, characterised in that the quantity of additive compounds to be subsequently metered as a result of a potential lack of additive compounds in the treatment solution at a point where the compounds are added to the solution, is substantially derived from the volume of the circulated treatment solution.

15

6. Method according to one of the preceding claims, characterised in that filters selected from a group containing wound cartridge-filters, rotary disc filters, pre-coated filters, gravitational separators, activated carbon filters, osmotic filters, molecular sieves and ion exchangers are used.

7. Method according to one of the preceding claims, characterised in that the solution is firstly filtered in a first particle filter and thereafter by means of activated carbon.



8. Method according to one of the preceding claims, characterised in that the treatment solution is circulated from the material for treatment through filters to the anode and from this point back in a
5 circuit to the material for treatment.

9. Method according to one of claims 1 to 7, characterised in that the solutions in the anode chamber and in the cathode chamber are conveyed and
10 filtered in separate circuits.

10. Method according to one of the preceding claims, characterised in that when insoluble anodes are used, a loss of metal ions caused by electrolytic deposition is
15 compensated for by chemical dissolution of metal particles by means of compounds of electrochemically reversible redox systems added to the treatment solution.

20 11. Method according to claim 10, characterised in that the metal particles present in a separate regenerating chamber (10) have an effective surface of such a size that practically all the metal-dissolving compounds of the redox system circulated to the regenerating chamber
25 are chemically reduced, with simultaneous dissolution of the metal particles.



12. Device for electrolytic deposition of metals of specific physical properties on the surfaces of material for treatment (3, 24) (cathode) by means of a circulated treatment solution set in motion by fluid
5 flow, additive compounds serving to control the physical properties of the metal being capable of addition, comprising

- a deposition chamber (6, 26; 7, 29) for treatment
10 material, anodes (2, 25) a current supply (4) for polarising the material for treatment with respect to the anodes, and pumps (11, 15, 17, 30, 35) and pipes for conveying the treatment solution in the device,
15 - means for flow guidance of the treatment solution to the material for treatment and/or ion-permeable means (5, 28) in order to avoid mixture of the solution present in the vicinity of the anodes (anode chamber 7, 29) and the solution present in the vicinity of the
20 material for treatment (cathode chamber 6, 26),

- means (18, 19, 43, 44) for metered addition of the additive compounds to the treatment solution, located at a point in the circuit from which the metered
25 additive compounds are conveyed directly to the material for treatment,



- filters (12, 13, 16, 31, 32) for removing consequent decomposition products and superfluous additive compounds from the circulated treatment solution.

5 13. Device according to claim 12, characterised by filters (12, 13, 16, 31, 32) for physical and/or chemical separative cleaning, selected from a group comprising wound-cartridge filters, rotary disc filters, pre-coated filters, gravitational separators,
10 sieves and ion exchangers and/or a combination of these filters, designed to correspond to the type of additives and decomposition products to be filtered out.

15

14. Device according to claims 12 or 13, characterised by an additional electrolyte container (14, 33) for receiving the filter treatment solution.

20 15. Method for electrolytic deposition of metals of specific physical properties on the surfaces of material for treatment, characterised by individual features or all new features or combinations of the disclosed features.

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16. Device for electrolytic deposition of metals of specific physical properties on the surfaces of



material for treatment, characterised by individual features or all new features of combinations of the disclosed features.

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**METHOD FOR ELECTROLYTIC DEPOSITION OF METALS
FROM ELECTROLYTES WITH PROCESS ORGANICS**

15 **ABSTRACT:**

The invention relates to a method of electrolytic deposition of metals from electrolytes, which contain additives or process organics in order to achieve specific physical properties. Such additives are subject to continuous consumption during electrolysis, decomposition products forming from these additives, which deposit in the entire electrolytic system and thus also on the material for treatment.

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Thus the object underlying the invention is to avoid quality shortfalls in the deposited coatings caused by

material for treatment, characterised by individual features or all new features of combinations of the disclosed features.

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METHOD FOR ELECTROLYTIC DEPOSITION OF METALS
FROM ELECTROLYTES WITH PROCESS ORGANICS

15 ABSTRACT:

The invention relates to a method of electrolytic deposition of metals from electrolytes, which contain additives or process organics in order to achieve
20 specific physical properties. Such additives are subject to continuous consumption during electrolysis, decomposition products forming from these additives, which deposit in the entire electrolytic system and thus also on the material for treatment.

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Thus the object underlying the invention is to avoid quality shortfalls in the deposited coatings caused by

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organic residues, and in this way to achieve a continuous metal deposition with uniform quality of the metal coatings. This object is achieved by spatial limitation of the concentration of the process organics to the electrolyte region in the electrolytic system in which it is relevant to the process. The circulated electrolyte is kept free of process organics by filters. Renewed metered addition of process organics is effected in dependence on consumption directly before the region relevant to the process.

(Figure 1)