

Method and device for the purification of process solutions

The present invention relates to a method as well as a device for the purification of a process solution that can be used in the surface treatment, in particular an electrolyte for the galvanic or autocatalytic deposition of a metal or metal alloy layer on a substrate, which are adapted for at least partially removing organic or inorganic contraries from the process solution and thus increasing the service life of the process solution.

Process baths in the surface treatment are subject to modifications due to the intended mass conversion, the dragging-in of water and impurities, the dragging-out of electrolyte and due to other influences such as evaporation, anodic or cathodic secondary reaction, the capture of components from the air and false dosages. This is the reason why the used process solutions have to be regenerated continuously or in certain intervals, if a new preparation and the dump of the old process solution related therewith shall be avoided. Very different methods for removing individual contraries from process solutions, in particular from electrolytes, are known from the state of the art. Herein, in particular filtration, oxidation, extraction as well as dialysis methods have to be mentioned.

The mentioned methods can be respectively subdivided in different sub-methods. Thus, it is known to filter the process solutions for removing particles such as metal flakes, dust particles, colloids, microorganisms, anode sludge etc. Herein, the process solutions are filtered by means of suitable filters, if necessary, using filter aids such as celite or active carbon, in order to remove the contraries from the process solution. It is a drawback of this method that a filter cake is formed on the filter in the course of the filtration, which filter cake can lead to an increased flow resistance in front of the filter and finally to a clogging-up of the filter. It is possible to maintain the flow resistance of the filter device on a constant value by means of extensive industrial instrumentation, for example by using band filters.

The contraries that can be removed by means of filtration depend on the design of the filter with respect to the size of the pores and the selection of corresponding filter aids. One embodiment of the filtration relates to the micro- or ultra-filtration using suitable membrane filters. The membrane filters used herein have very small pore sizes with a

high retaining power, but disadvantageously lead to a high flow resistance. The micro- or ultra-filtration is mainly used for degreasing baths or acid or alkaline pickling baths.

It is a common aspect of the filtration methods that parasitic substances that are completely dissolved in the process solutions cannot be removed from the process solutions by this technique.

However, many process solutions used in the surface treatment comprise organic components that are decomposed in the course of the treatment process and finally form decomposition products which interfere with the process chemistry. These interfering decomposition products are often completely soluble in the process solution and cannot be captured by means of filtration methods.

A method for removing these organic decomposition products is the oxidation of the decomposition products by means of for example UV-H₂O₂ oxidation.

Herein, at least partial volumes of a process bath, for example of a bright nickel electrolyte, are treated with UV/H₂O₂. The organic components of the electrolyte are discontinuously oxidized outside the bath. All organic compounds, decomposition products and also the acting brighteners and wetting agents are oxidized. In the case of a bright nickel electrolyte the end product of such a treatment is a Watts-type base preparation which can be again admixed to the process bath. The acting additives such as brighteners and wetting agents, which have also been oxidized during the UV/H₂O₂ oxidation, have to be correspondingly dosed again. Besides this drawback, the UV/H₂O₂ oxidation is not able to remove inorganic contraries, such as for example foreign ions, from the process solutions.

Another possibility of the process solution purification is the liquid-liquid extraction with suitable liquid extraction agents. Herein, impurities are removed from the carrier liquid, for example a galvanic electrolyte to be purified, by means of a liquid extraction agent. The transport of substance from one fluid into the other that takes place herein results from the different solubilities of the substance in the fluids and the prevailing concentration gradient.

Herein, the extraction agent and the carrier liquid should be as insoluble with respect to each other as possible in order to assure a good separation and simultaneously carry over as less solvent as possible. In practice, one of the two phases is aqueous and the other one is an organic solvent or a solution of extraction agents in an organic solvent.

Since the extraction is a distribution between two non-mixable phases, the exchange and the establishment of equilibrium are realized via the interphase. A great interphase accelerates the establishment of equilibrium. Therefore, extractions on big technical scale are realized according to the mixer-settler principle. Herein, extraction agent and charged carrier liquid (electrolyte) are mixed with each other (mixer) in a first chamber. The mixture gets into the so called settler, the sedimentation chamber, via a gate of a dam. Here, the phases can separate again. The separated phases are then separately removed from the chamber. If the extraction result does not yet meet the requirements, several mixer-settler units can be placed subsequently.

The condition for a successful use of the liquid-liquid extraction is that a solvent is found which selectively dissolves the impurity to be removed and which can be easily separated again, and that the small residual quantities remaining in the electrolyte do not perturb the application aim of the process solution.

One embodiment of the liquid-liquid extraction is the membrane-supported extraction by means of hollow fibre modules. Herein, the organic extraction agent and the carrier liquid (electrolyte) are separated from each other by a porous membrane. In case of a microporous hydrophobic membrane, the organic phase will spontaneously wet the membrane and try to get through the pores to the other side of the membrane. This breaking-through can be avoided by a low overpressure on the side of the carrier liquid. The intersection between aqueous and organic phase can thus be immobilised in the pore mouth. The driving force of the substance exchange is here also the concentration gradient. The liquids are passed along both sides of the membrane. Herein, the flow rate of both phases can be varied in a wide range. Advantageously, also systems having the tendency to form emulsions can be treated with the hollow fibre supported membrane liquid-liquid extraction. Furthermore, a corresponding device for the hollow fibre module supported liquid-liquid extraction clearly requires less mobile parts in comparison to the extraction according to the mixer-settler principle.

A common aspect of the liquid-liquid extraction methods is that they are limited to corresponding non-mixable extraction/carrier liquid systems and usually no inorganic contraries, such as for example foreign ions, can be removed from the process solutions by means of the liquid-liquid extraction.

Other methods for the purification of process solutions, which are known from the state of the art, are the dialysis methods such as diffusion dialysis or electrodialysis. As in the extraction, in the ion-selective dialysis a concentration gradient is used for the substance transport between the phases, but here hydraulically impervious ion exchange membranes are used.

The centre of such a device is composed of membranes which are held together like a filter press. The anion-selective membranes theoretically retain all cations except the hydrogen ions, which migrate through the membrane due to their small size and their high mobility. The anions and the hydronium ions diffuse simultaneously. Therefore, only strongly dissociating acids offer good conditions for a use.

The process solution to be purified and the dialysis solution to be used, for example water, usually flow through the membrane stack according to the countercurrent principle. The two liquids are separated from each other by membranes and frames that enable the distribution in an alternating manner.

Besides anion-selective membranes, also cation-selective membranes or combinations of anion- and cation-selective membranes can be used.

One embodiment of the dialysis is the electrodialysis which is an electrochemical process, in which ionic components are removed from a solution or exchanged and, if necessary, concentrated by means of ion exchange membranes and the driving force of an electric field.

Herein, the created electric field can reinforce or also reverse the substance transport in the direction of the concentration gradient.

Electrodialysis units are able to also selectively separate ions that are dissolved in the process solutions. Disadvantageously, the used membranes are sensitive and, in particular in case of the electrodialysis, the method is related with a high energy demand.

Besides the already described methods, it is known from DE 43 28 876 A1 as well as from DE 43 18 793 A1 to use an adsorbent polymer for the elimination of organic contraries. Herein, the organic contraries are at least partially adsorbed on the surface of adsorbent polymers and thus removed from the process solution. Advantageously, such a method can be carried out continuously and the used adsorbent polymer can be regenerated by means of suitable solutions, for example a hydrogen peroxide bearing oxidation solution.

However, a drawback of this method is that the adsorbent polymer has to be adapted to the respective organic contraries to be removed and only removes this one very selectively. Furthermore, inorganic contraries such as for example foreign ions cannot be removed by means of this technique.

It is thus the object of the present invention to provide a method as well as a device which are able to remove a multitude of contraries from the process solution to be purified in a simple and cost-effective way while overcoming the drawbacks known from the state of the art.

With respect to the method, this aim is achieved by a method for the purification of a process solution that can be used in the surface treatment, in particular an electrolyte for the galvanic or autocatalytic deposition of a metal layer on a substrate, by means of a polymer resin which is able to receive impurities from the process solution and thus to at least partially remove the impurities from the process solution, characterized in that the process solution is successively brought into contact with at least two polymer resins or partial flows of the process solution are in parallel brought into contact with at least two polymer resins, wherein the polymer resins differ from each other with respect to their physical-chemical properties. Herein, the use of the adsorbent polymers is not limited to a bath. They can also be connected to the stand rinsing unit or the most concentrated rinsing unit of a rinsing cascade and the purified rinsing water can be

returned, if necessary, after having been concentrated again. The term process solution thus comprises a bath or a rinsing unit.

Herein, polymer resins in the sense of the invention are adsorbent resins and/or ion exchanger resins which are able to at least partially remove organic and/or inorganic impurities from the process solution. They comprise organic adsorbent resins with and without functional groups and/or inorganic adsorbent resins such as silicates, aluminosilicates, boron nitrides and also zeolites. Organic adsorbent polymers can be cross-linked polyacrylates, polystyrene, polyacrylamide and divinylbenzene/styrene copolymerisates.

Physical-chemical properties of the polymer resins in the sense of the invention in particular comprise the adsorption capacity thereof, the ion exchange capacity, the grain size or the pore size.

According to the invention, the process solution is brought into contact with the polymer resins in individual accommodating units of the polymer resins that are separated from each other. The individual accommodating units of the polymer resins are advantageously in fluidic communication with each other, such that the process solution to be purified can be successively passed through the receiving units or partial flows of the process solution can be respectively passed in parallel through the receiving units.

According to the invention, the polymer resins can be regenerated by means of suitable regeneration solutions. For this, the polymer resins are regenerated in the accommodating units by contacting the polymer resins with the regeneration solution. Advantageously, the polymer resins can be regenerated independently from each other by means of different regeneration solutions. In one embodiment of the method according to the invention, the polymer resins are at least partially regenerated by means of the same regeneration solution.

In another embodiment of the method according to the invention, the process solution is at least partially transferred from a process bath into an adsorption device, wherein the adsorption device at least comprises three accommodating units for accommodating at least two different polymer resins, such that the process solution is successively brought

into contact with the polymer resins in the accommodating units, wherein the two first accommodating units accommodate polymer resins that are able to at least partially adsorb organic impurities from the process solution and the last accommodating unit receives a ion exchanger resin that is able to at least partially remove inorganic impurities from the process solution.

In such an embodiment of the method according to the invention, at least the ion exchanger resin can be charged with a substance contained in the process solution advantageously before being contacted with the process solution, which substance is decomposed or consumed in the course of the surface treatment process and has therefore to be completed in the process solution, such that during contacting the process solution with the charged ion exchanger resin the substance is transferred into the process solution on the understanding that the amount of substance that has been decomposed or consumed in the surface treatment process will be at least partially completed in the process solution.

The method according to the invention is in particular adapted for the purification of electrolytes for the galvanic or autocatalytic coating of a surface with a metal layer.

The polymer resin that can be used in the method according to the invention is advantageously a resin from the group consisting of divinylbenzene/styrene copolymerisate.

The polymer resin used in the method according to the invention can be regenerated by means of one or more regeneration solutions of the group comprising water, an alkaline aqueous solution, an alcoholic aqueous solution, an alkaline alcoholic solution, an acidic solution or an acidic alcoholic solution.

Furthermore, the regeneration solution can comprise an oxidizing agent or a reducing agent for the regeneration of the polymer resin.

Advantageously at least one regeneration solution comprises hydrogen peroxide as oxidizing agent.

The regeneration solution can comprise the oxidizing or reducing agent in a concentration comprised between about 0.1 and about 10% by mass, preferably between 1 and 5% by mass, more preferably between 1.5 and 3% by mass.

Due to the treatment of the polymer resins charged with organic contraries with a regeneration solution that contains an oxidizing agent, the organic contraries are oxidized. It has been found that the oxidized organic contraries are no more adsorbed by the used polymer resins. Hereby, the solution that contains the oxidizing agent can advantageously be used several times for the regeneration of the polymer resins, which is another economic and ecologic advantage of the method according to the invention.

The ion exchanger resin that can be used in the method according to the invention can be brought into contact with a saccharine bearing solution after regeneration and before contacting with the process solution, wherein the ion exchanger resin is charged with saccharine. Furthermore, the adsorbent resins can also be charged with suitable coating active substances.

Process solutions can be continuously purified by means of the method according to the invention. Furthermore, the method according to the invention can be combined with other methods for the purification of process solutions that are known from the state of the art, such as filtration, dialysis, electrodialysis, UV-H₂O₂, UV.H₂O₂ oxidation, extraction, crystallisation, precipitation.

With respect to the device, the aim is achieved by a device for the purification of a process solution in the surface treatment, in particular an electrolyte for the galvanic or autocatalytic deposition of a metal layer on a substrate, comprising at least two units for accommodating a polymer resin, that is characterized in that the units for accommodating a polymer resin are in fluidic communication such that the process solution successively flows through the units for accommodating a polymer resin or partial flows of the process solution respectively flow through the units in parallel, wherein the units accommodate polymer resins that are different with respect to their physical-chemical properties.

In one embodiment of the device according to the invention, a unit for accommodating a polymer resin accommodates a ion exchanger resin.

Furthermore, the units for accommodating an adsorbent resin and/or a ion exchanger resin can be in fluidic communication with at least one reservoir of a regeneration solution, such that for the regeneration of the resins the regeneration solution successively flows through the units or partial flows of the regeneration solution respectively flow in parallel through the units.

The unit for accommodating an adsorbent resin at least receives one adsorbent resin of the group consisting of polyacrylate, polystyrene, polyacrylamide and divinylbenzene/styrene copolymerisates.

According to the invention, the unit for accommodating a ion exchanger resin receives at least one ion exchanger resin of the group consisting of strongly acid, strongly basic, moderately acid, moderately basic, weak acid or weak basic ion exchanger resins.

Fig. 1 shows an embodiment of the device according to the invention.

In fig. 1 an embodiment of the device according to the invention is represented. A process solution to be purified is withdrawn from a process bath and supplied via a supply 4 to the device 14 for the treatment of the process solution. The device 14 comprises two units 1 and 2 for accommodating an adsorbent resin and a unit 3 for accommodating a ion exchanger resin. The supply 4 is in fluidic communication with the units 1, 2 and 3 such that the process solution withdrawn from the process bath can flow through the units 1, 2 and 3 at least partially in parallel and/or successively and can then be returned to the process bath via a return 5. The units 1, 2 and 3 comprise a feeding pipe 10 for an acid regeneration solution as well as supplies 11, 12 and 13 for a solution that contains an oxidizing agent, an alkaline regeneration solution and rinsing water. Furthermore, the units 1, 2 and 2 comprise returns 10a, 11a and 12a for the corresponding regeneration solutions. Hereby, the adsorbent and ion exchanger resins in the units 1, 2 and 3 can be brought into contact with the regeneration solutions and/or the oxidizing agent solution independently from each other for regeneration and the solutions can be separately collected after contact with the adsorbent resin and/or the

ion exchanger resin. Thus, the regeneration solutions can be used several times for the regeneration of the adsorbent resin and/or ion exchanger resin.

Example:

An electrolyte for the currentless deposition of nickel layers on substrate surfaces is withdrawn from the coating bath and supplied to a device according to the invention. The device according to the invention comprises a column filled with divinylbenzene/styrene copolymerisate adsorbent resin as well as a column filled with an acid ion exchanger resin. The nickel electrolyte withdrawn from the process bath is successively brought into contact with the adsorbent resin and the ion exchanger resin by means of a pump, wherein the adsorbent resin adsorbs the organic decomposition products that are present in the nickel electrolyte and the ion exchanger resin receives the parasitic ions that are present in the electrolyte, such as aluminium ions, and replaces them by hydrogen ions.

Partial flows of the process solution can also respectively flow in parallel through the adsorbent column and the ion exchanger column by means of suitable fluidic communications. This also enables a bypass of the adsorbent column, in order to be able to regenerate the adsorbent resin separately from the ion exchanger resin in case of need.

For regeneration, the adsorbent column and the ion exchanger column are connected in the above described manner to corresponding reservoirs of different regeneration solutions. The adsorbent polymer can be regenerated by means of the following regeneration procedure:

1. rinsing with water
2. regeneration with a 2.5% H₂O₂/2.5% HCl solution for about 2 hours
3. regeneration with a 6% NaOH solution.

In a last step the alkaline regenerated adsorbent resin can be acidified with a weak sulphuric acid solution in order to prevent a precipitation of nickel salts. After the steps 2. and/or 3., rinsing steps can optionally follow.

Other examples of surface treatment processes for which the method according to the invention and the device according to the invention can be used, are for example the deposition of a bright nickel layer or a semi-bright nickel layer on substrates as they are known from the *Taschenbuch für Galvanotechnik*, 13th edition 1988 or pulse reverse plating copper baths as they are known from EP 05009183.

The invention can also be applied to an acid tin/silver bath for the electrolytic deposition of lead-free silver alloy layers, which is operated with an insoluble anode. Herein, decomposition products are generated which have to be removed. A cation exchanger that is used in combination with adsorbent polymers can be previously or afterwards periodically charged with tin. The acid tin bath elutes tin from the cation exchanger which otherwise had to be dosed again. Thanks to the elution from the cation exchanger no additional contrary anions are introduced, i.e. the anion load is not increased. The adsorbent resin can be regenerated with H_2O_2 and NaOH, as in the other examples.

The method according to the invention as well as the device according to the invention can also be used for the electrolytes for the deposition of bronze that are known from EP 1 408 141 A1.

Since the method according to the invention and the device according to the invention are realized as multi-column system, it is assured that the individual adsorbent polymers and the ion exchanger polymers can be regenerated separately from each other and can thus be widely adapted to the electrolyte with respect to their adsorption or ion exchange properties. Furthermore, smaller volumes of regeneration solution and rinsing solution are required due to the use of the method according to the invention and the device according to the invention.

List of reference numerals

- 1 adsorption column
- 2 adsorption column
- 3 ion exchanger column
- 4 supply from process bath
- 5 return to process bath
- 6 bypass
- 7 pipe
- 8 pipe
- 9 pipe
- 10 supply acid regeneration solution
- 10a return acid regeneration solution
- 11 supply oxidizing agent bearing solution
- 11a return oxidizing agent bearing solution
- 12 supply alkaline regeneration solution
- 12a return alkaline regeneration solution
- 13 supply water
- 14 device for the purification of a process solution

Claims

1. A method for the purification of a process solution that can be used in the surface treatment, in particular an electrolyte for the galvanic or autocatalytic deposition of a metal layer on a substrate, by means of a polymer resin which is able to adsorb impurities from the process solution and thus to at least partially remove the impurities from the process solution,
characterized in that
the process solution is successively brought into contact with at least two polymer resins or partial flows of the process solution are in parallel brought into contact with at least two polymer resins, wherein the polymer resins differ from each other with respect to their physical-chemical properties.
2. A method according to claim 1, characterized in that the polymer resins are able to at least partially remove organic and/or inorganic impurities from the process solution.
3. A method according to one of the preceding claims, characterized in that the polymer resins are brought into contact with the process solution in individual separated receiving units of the polymer resins.
4. A method according to one or more of the preceding claims, characterized in that the polymer resins are regenerated by means of at least one suitable regeneration solution.
5. A method according to one or more of the preceding claims, characterized in that at least one polymer resin is able to at least partially remove organic impurities from the process bath and at least one polymer resin is a ion exchanger resin that is able to at least partially remove inorganic impurities from the process solution.

6. A method according to claim 5, characterized in that at least the ion exchanger resin is charged with a substance contained in the process solution before being contacted with the process solution, which substance is at least partially transferred into the process solution when the process solution is contacted with the ion exchanger resin.
7. A method according to one or more of the preceding claims, characterized in that the process solution is an electrolyte for the galvanic or autocatalytic coating of a surface with a metal layer.
8. A method according to one or more of the claims 4 through 7, characterized in that the regeneration solution comprises an oxidizing agent or a reducing agent.
9. A method according to one or more of the preceding claims, characterized in that the process solution is continuously purified by means of the method.
10. A method according to one or more of the preceding claims, characterized in that the method is combined with at least one other method for the purification of process solutions.
11. A device for the purification of a process solution in the surface treatment, in particular an electrolyte for the galvanic or autocatalytic deposition of a metal layer on a substrate, comprising at least two units for accommodating a polymer resin, characterized in that the at least two units for accommodating a polymer resin are in fluidic communication such that the process solution successively flows through the units for accommodating a polymer resin or partial flows of the process solution respectively flow through the units in parallel, wherein the units for accommodating a polymer resin accommodate polymer resins that are different with respect to their physical-chemical properties.

12. A device according to claim 11, characterized in that at least one unit for accommodating a polymer resin receives a ion exchanger resin.
13. A device according to one or more of the claims 11 and 12, characterized in that the units for accommodating a polymer resin are in fluidic communication with at least one reservoir of a regeneration solution, such that for the regeneration of the resins the regeneration solution can successively flow through the units for accommodating a polymer resin or partial flows of the regeneration solution can respectively flow in parallel through the units.
14. A device according to one or more of the claims 11 through 13, wherein the units for accommodating an adsorber resin at least accommodates one polymer resin of the group consisting of polyacrylate, polystyrene, polyacrylamide and divinylbenzene/styrene copolymerisates.
15. A device according to one or more of the claims 11 through 14, wherein the unit for accommodating a ion exchanger resin receives at least one ion exchanger resin of the group consisting of strongly acid, strongly basic, moderately acid, moderately basic, weak acid or weak basic ion exchanger resins.
16. Use of a device according to one or more of the claims 13 through 15 for carrying out a method according to one or more of the claims 1 through 10.