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(54) **DEVICE AND METHOD FOR COATING A COMPONENT OR SEMI-FINISHED PRODUCT WITH A CHROMIUM LAYER**

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(57) **ABSTRACT**

The invention relates to a device for coating a component or semi-finished product with a chromium layer, the device comprising an undivided deposition cell, in which there is an anode and which is suitable for receiving a cathodically connected component, wherein: there is an electrolyte solution containing chromium(II) in the deposition cell; the device has an electrolytic cell, which is divided by a membrane disposed in the electrolytic cell into a cathode chamber, in which there is a cathode, and an anode chamber, in which there is an anode; the cathode chamber is connected to the deposition cell by means of a line and a pump disposed in the line; the pump can pump liquid from the cathode chamber into the deposition cell and/or can pump liquid from the deposition cell into the cathode chamber.

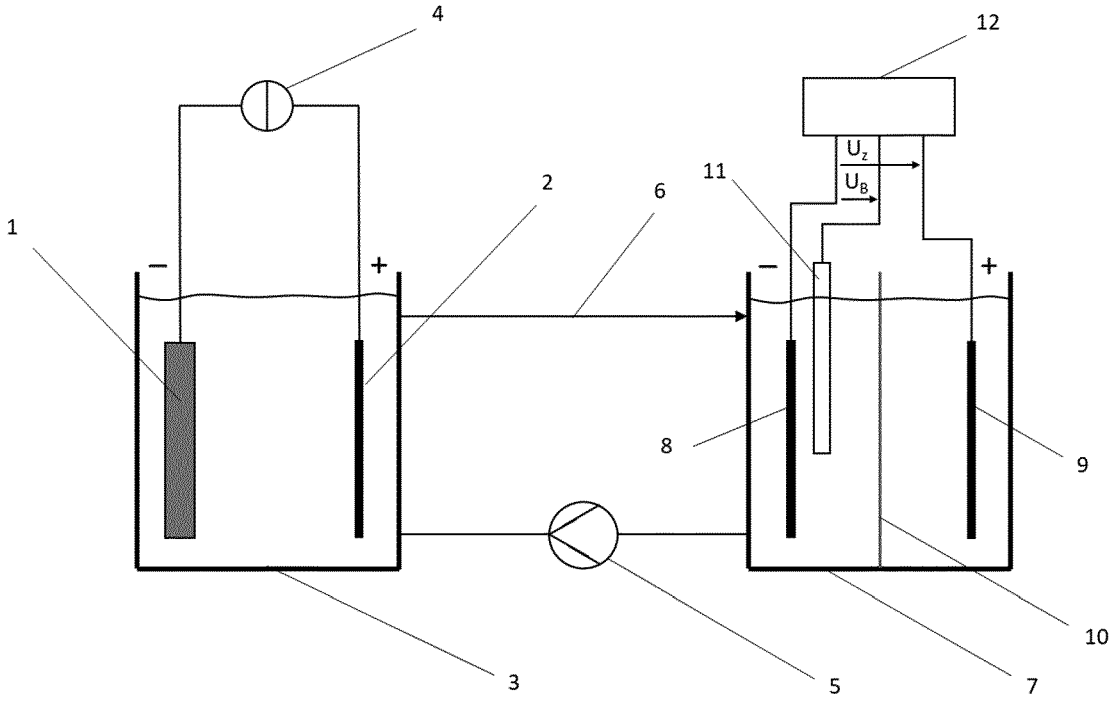

Fig. 1

DEVICE AND METHOD FOR COATING A COMPONENT OR SEMI-FINISHED PRODUCT WITH A CHROMIUM LAYER

FIELD OF THE DISCLOSURE

[0001] The invention relates to a device for coating a component or a semi-finished product with a chromium layer. Furthermore, the invention relates to a method for coating a component with a chromium layer.

BACKGROUND

[0002] It is well known from practice that decorative chromium layers and hard chromium layers are deposited onto a component from electrolyte solutions containing chromium (VI). The chromic acid used in this process is toxic and carcinogenic and has therefore been included in the lists of substances of very high concern (SVHC) of the EU Chemicals Regulation (REACH). For this reason, attempts have been made for many years to substitute chromium(VI)-containing electrolyte solutions with chromium(III)-containing electrolyte solutions.

[0003] A fundamental problem here is that stable complexes form in aqueous electrolyte solutions between chromium(III) ions and six water molecules, the so-called hexaaquachromium(III) complexes, which kinetically inhibit the reduction of the chromium(III) ion and thus the deposition of chromium. Therefore, complexing agents such as formates, oxalates or glycinates are usually added to the electrolyte solutions. The formation of these chromium complexes allows for a faster deposition of chromium.

[0004] During the reduction of the chromium(III) ion, first the chromium(III) ion is reduced to the chromium(II) ion and then the chromium(II) ion is reduced to the metallic chromium. With the reduction of the chromium(III) ion to the chromium(II) ion, the charge of the chromium cation and thus the stability of the chromaqua complex, but also of most other chromium complexes, decreases. The kinetic inhibition of chromium deposition is therefore caused in particular by the upstream reduction of the chromium(III) ion to the chromium(II) ion.

SUMMARY

[0005] Against this background, the invention was based on the object of creating a device and a process which make it possible to provide a component with a chromium layer on a technical scale without having to use electrolyte solutions containing chromium(VI) compounds, or at least to reduce the use of solutions containing chromium(VI).

[0006] This object is solved by the device according to claim **1** and by the method according to claim **5**. Advantageous embodiments are defined in the dependent claims and the description following herein.

[0007] The basic idea of the invention is to carry out the reduction of the chromium(III) ion to the chromium(III) ion and the chromium(III) reduction to the metallic chromium in two different electrochemical cells, the electrolyte solutions of which are mutually exchanged via a circulation system.

[0008] The device according to the invention has an undivided deposition cell in which an anode is located and which is suitable for receiving a cathodically connected component. Instead of a single anode, several anodes and additionally smaller auxiliary anodes can be arranged in the cell. This particularly achieves good uniformity of the coating of the component. The deposition cell can be an immersion basin. The use of an immersion basin allows single or multiple parts or even a larger number of parts to be immersed in drums or on racks. However, the deposition cell can also be a continuous cell in which the material is passed through a basin past one or more vertically, horizontally or radially arranged anodes. Furthermore, the deposition cell can also be combined with a reservoir and a pump to pump the electrolyte solution in a circuit to ensure good mixing of the electrolyte solution, especially between the component and the anode. The deposition cell can also be a coating cell in which the electrolyte solution is fed between the anode and the component surface, or semi-finished product surface, without the component, or semi-finished product, and/or the anode being in a basin. In this case, the cell is also combined with a pump and a reservoir for the electrolyte solution.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. **1** is a schematic representation of the device according to the invention.

DETAILED DESCRIPTION

[0010] The invention offers the advantage that conventional coating cells can be used for coating individual parts, but also for coating mass-produced goods and semi-finished products. For the coating of mass-produced goods, the use of rack and barrel processes is preferred. For the coating of semi-finished products such as wire, strip and tubes, continuous lines are preferably used. The invention can also be carried out with internal coating processes, e.g. for containers, tubes and bores. Here, the electrolyte solution is filled into the container or tube and an anode is introduced.

[0011] The deposition cell is an undivided cell. An undivided deposition cell is understood to be a space in which a liquid is located, whereby the space is not divided by a membrane into sub-cells which are only connected to each other via the membrane.

[0012] The deposition cell contains a liquid in which a chromium(II)-containing substance is dissolved. Depending on the chromium salts used, the liquid may also contain anions such as chloride, sulfate, hydrogen sulfate, fluoride, formate, oxalate, methanesulfonate, glycinate, citrate or acetate in addition to the dissolved chromium(II) ions. Furthermore, the liquid may contain at least one solvent such as water, ethylene glycol, acetic acid, dimethyl sulfoxide, formamide, dimethyl formamide or ethylene carbonate. To some extent, especially preferably during the deposition process, chromium(III) ions may also be present in the liquid, especially when the chromium(II) ions are oxidized at the anode of the deposition cell. Furthermore, the liquid may contain one or more acid buffers and/or one or more conducting salts such as sodium sulfate, sodium chloride, sodium methanesulfonate, potassium sulfate, potassium chloride, potassium sulfate, aluminum sulfate and boric acid or uncharged complexing agents such as ammonia, glycine, thiosulfate, diethanolamine, thiourea or urea and additives such as polyethylene glycol.

[0013] According to the invention, the device additionally has an electrolysis cell. The electrolysis cell is divided by a membrane arranged in the electrolysis cell into a cathode chamber, in which a cathode is located, and an anode chamber, in which an anode is located.

[0014] The electrolysis cell can be designed as a basin. In a preferred design, the cathode and anode are geometrically designed and aligned so that their distances from each other are the same everywhere and the membrane is arranged approximately centrally. In a particularly preferred design, the cathode, membrane and anode are made plane-parallel to each other and small distances in the range of 2 mm to 5 cm are selected between cathode and membrane and anode and membrane. If small distances are selected, it is advantageous to design both the cathode and anode chambers as flow-through cells. In this case, the electrolyte solution in the anode chamber may also be circulated by means of a pump. An electrolyte reservoir may also be provided in the electrolyte circuit. Several cells may also be combined to form a cell stack with separate inlets and outlets.

[0015] The membrane separating the cathode chamber from the anode chamber is preferably an anion exchanger. However, operation with a cation exchanger or diaphragm is also conceivable. For example, anion exchange membranes with a polymer backbone based on polyetheretherketones, polysulfones, polyphenylene ethers, polybenzimidazoles, fluoropolymers or polystyrene copolymers may be used. Trimethylammonium, pyridinium, sulfonium, phosphonium, guanidinium, imidazolium or piperidinium may be bonded to the polymer backbone as cationic functional groups.

[0016] The cathode located in the cathode chamber is preferably made of an electrically conductive material characterized by a high overvoltage for cathodic water decomposition. Particularly suitable are cathodes made of copper, lead, tin, titanium, lead-antimony alloys or carbon. Solid, but also porous electrodes such as metal foams or carbon tile can be used. Coatings of e.g. copper or carbon fleeces are conceivable. For example, bismuth, indium, lead, bismuth-lead, silver-lead, gold-lead or copper-lead are suitable.

[0017] The anode located in the anode chamber is preferably a titanium anode coated with iridium mixed oxide. However, other electrode materials such as platinized titanium, lead, lead-antimony, carbon or stainless steel may also be used. The liquid introduced into the anode chamber preferably contains the same solvent as the liquid of the cathode chamber and an acid whose anion is identical to an anion present in the electrolyte solution of the cathode chamber.

[0018] According to the invention, the cathode chamber is connected to the deposition cell via a line and a pump disposed in the line, wherein the pump is capable of pumping liquid from the cathode chamber into the deposition cell and/or liquid from the deposition cell into the cathode chamber. According to the invention, a method is conceivable which may be carried out with the device according to the invention, in which the direction of flow through the line is changed. The method according to the invention may be carried out in such a way that

[0019] in a first operating state, liquid is conveyed by means of the pump through the line from the cathode chamber into the deposition cell, and

[0020] in a second operating state, liquid is conveyed by means of the pump through the line from the deposition cell into the cathode chamber.

[0021] The method may consist of a sequence of the two operating states. However, other operating states may also be provided in which no liquid is conveyed through the line.

[0022] In another embodiment, the line with the pump arranged in it is only used to convey the liquid in one direction. There are conceivable embodiments in which liquid is conveyed by means of the pump through the line from the cathode chamber into the deposition cell. In such an embodiment, the cathode chamber may be connected to the deposition cell via an additional return line, with liquid flowing from the deposition cell into the cathode chamber via the return line. Embodiments are conceivable in which liquid is conveyed by the pump through the line from the deposition cell into the cathode chamber. In such an embodiment, the deposition cell may be connected to the cathode chamber via an additional return line, with liquid flowing from the cathode chamber into the deposition cell via the return line.

[0023] For deposition cells connected to a reservoir via lines and a pump, the exchange of electrolyte solution described above may also take place between the reservoir and the cathode chamber of the membrane cell.

[0024] The line may also be a channel.

[0025] The invention allows a high concentration of chromium(II) ions to be maintained in an undivided deposition cell. In this way, chromium deposition, which is strongly inhibited kinetically, may be accelerated and the current requirement (amount of charge in ampere-hours per mass of chromium deposited in kilograms) for chromium deposition in the deposition cell is reduced. Since a divided deposition cell can be dispensed with, complex-shaped parts may also be coated in an electrolyte solution containing chromium (II), in particular with the use of additional auxiliary anodes. Furthermore, chloride-containing electrolyte solutions may also be used in an undivided deposition cell, since only the chromium(II) ion is oxidized to the chromium(III) ion at the anode of the deposition cell due to the lower oxidation potential of the chromium(II) ion, thus avoiding oxidation of the chloride to the toxic chlorine. For the same reason, oxidation of the chromium(III) ion to chromium(VI) is also avoided. It is also a particular advantage that pulse current deposition of the chromium from the chromium(II)-containing electrolyte solution at high pulse current densities is made possible in the deposition cell. It is conceivable that this method could even be used to deposit fine-cracked chromium layers, which could previously only be produced from the toxic chromium(VI)-containing electrolyte solutions.

[0026] In a preferred embodiment, a liquid containing chromium(III) is present in the cathode chamber. The chromium(III)-containing liquid contains chromium(III) ions. The liquid in the cathode chamber may contain the same constituents as the liquid in the deposition cell, in particular if the liquids are constantly exchanged. The concentration of chromium(II) ions may be slightly higher in the catholyte. Furthermore, the pH (acid concentration) in the catholyte and in the deposition cell may be different.

[0027] In a preferred embodiment, a reference electrode is provided in the cathode chamber. This reference electrode may also be located outside the cathode chamber. In this case, the electrolyte solution of the reference electrode can be connected to the electrolyte solution in the cathode chamber via a capillary, the so-called Haber-Luggin capillary. The opening of the capillary in the cathode chamber is preferably positioned in the immediate vicinity of the cathode surface. Suitable reference electrodes include silver-

silver chloride electrodes, calomel electrodes, lead sulfate electrodes or mercury sulfate electrodes.

[0028] In a preferred embodiment, the device has a connector that may be electrically connected to the component to be coated and with which a potential can be applied to the component. The connector may be a terminal, for example. Depending on the deposition process, the electrical contact may also be made via racks with receptacles for the components (rack process), via discharge electrodes in drums (drum process), via current rollers in continuous processes, via sliding contacts or other contact-making discharge electrodes.

[0029] In a preferred embodiment, the device comprises a (first) current or voltage source having a first pole and a second pole. In a preferred embodiment, the anode of the deposition cell is electrically connected to the first pole of the first voltage source. In a preferred embodiment, a connector is provided that can be connected to the component to be coated and can be used to apply a potential to the component, the connector being electrically connected to the second pole of the first voltage source.

[0030] In a preferred embodiment, the device comprises a second current or voltage source having a first pole and a second pole. In a preferred embodiment, the anode of the anode chamber is electrically connected to the first pole of the second voltage source. In a preferred embodiment, the cathode of the cathode chamber is electrically connected to the second pole of the second voltage source.

[0031] The method according to the invention for coating a component with a chromium layer provides that the component to be coated is immersed in the chromium(II)-containing liquid present in the deposition cell of the device according to the invention, the component to be coated is connected cathodically and the anode is connected anodically, chromium deposition takes place in the deposition cell from the liquid on the cathodically connected component, the liquid in the deposition cell is pumped via the line into the cathode chamber or the liquid in the cathode chamber is pumped via the line into the deposition cell.

[0032] At the anode of the deposition cell, the chromium (II) cations can oxidize to chromium(III) cations. In a preferred embodiment, the electrolyte solution depleted in chromium(II) cations and enriched in chromium(III) cations in the deposition cell may be pumped into the cathode chamber. Both a constant liquid flow and an intermittent supply or discharge of the electrolyte solution are applicable. In a preferred embodiment, the liquid flow or the quantities of liquid exchanged may be dimensioned so that the concentration of chromium(II) ions in the deposition cell is only slightly lower than in the cathode chamber of the electrolysis cell.

[0033] For the reduction of chromium(III) cations in the electrolysis cell, the cathode potential of the cathode may be measured and adjusted against a reference electrode. The cathode potential may be adjusted by controlling the cell voltage or current. Thus, a cathode potential can be set that is small enough to reduce the chromium (III) ions to chromium (II) ions and large enough to avoid chromium deposition on the cathode of the electrolysis cell.

[0034] Depending on which chromium salt is used as the starting material, it may be appropriate to use a cation exchange membrane or an anion exchange membrane. This makes it easier to keep the electrolyte concentration and pH constant in the electrolyte circulation system or to avoid oxidation to toxic substances at the anode. The chromium (III) ions and chromium(II) ions are usually present in solutions as complexed chromium cations. Depending on the number of anions bound to the chromium cation and the charge numbers, the charge of the complexes is positive, neutral or negative. If the chromium(II) and chromium(III) complexes are completely or predominantly positively charged, an anion exchange membrane can be used to prevent or minimize the transfer of chromium ions into the anode chamber. If the chromium complexes are predominantly present as negatively charged ions, a cation exchange membrane may also be used. If no chloride-containing starting salt is used, a diaphragm electrolysis cell may also be used instead of a membrane electrolysis cell. It is also possible to use membrane electrolysis cells divided into three chambers by an anion and cation exchange membrane. A three-chamber cell with a cathode chamber, anode chamber and a central chamber without an electrode is suitable if anions of the electrolyte solution of the cathode chamber are not allowed to reach the anode in the anode chamber, where they can be oxidized to toxic substances. For example, chlorides of the electrolyte solution of the cathode chamber, if they reach the anode in the anode chamber, are oxidized to toxic chlorine gas. This can be avoided with a three-chamber cell whose central chamber is separated from the cathode chamber with an anion exchange membrane and the central chamber from the anode chamber with a cation exchange membrane. In this way, the chlorides can pass through the anion exchange membrane into the central chamber, but their transfer into anode chamber is almost completely avoided by the use of the cation exchange membrane.

[0035] The invention can also be applied to the electrodeposition of alloys containing chromium, such as zinc-chromium or chromium-iron electrodeposition. In addition, it may be used for electroplating iron or plating an alloy containing iron. The method may also be used for the galvanic chromium and iron extraction or recovery of these metals from salt solutions. For this purpose, the electrolyte solutions should contain appropriate metal salts in the solvent:

[0036] for zinc-chromium deposition: At least one additional salt containing zinc is required

[0037] for chromium-iron deposition: Additionally at least one ferrous salt

[0038] for iron deposition: At least one ferrous salt must be used instead of chromium-containing substances

[0039] ferrous alloys: Instead of chromium-containing substances, at least one ferrous salt and salts of the alloying partners must be used

[0040] The invention is described below with reference to a drawing which merely illustrates an exemplary embodiment of the invention in greater detail. It shows

[0041] FIG. **1** is a schematic representation of the device according to the invention.

[0042] The component **1** to be chromium-plated is cathodically connected by means of a current source **4** and an anode **2** in the deposition cell **3** in an electrolyte solution containing chromium(II) ions, so that chromium deposition takes place. The chromium(II) and chromium(III) ions, which are almost exclusively present as complexed chromium cations, are shown in the exemplary embodiment in simplified form only as Cr^{2+} and Cr^{3+} ions (cations), respectively. The anions of the electrolyte solution in the deposi-

tion cell and in the cathode and anode chambers of the electrolysis cell have also not been included.

[0043] On the component **1** to be chromium-plated take place preferentially the reduction of the chromium(II) ion to metallic chromium (equation 1) and, as a secondary reaction (equation 2), the water reduction with release of hydrogen:

$$Cr^{2+} + 2\,e^- \rightleftharpoons Cr\,(0) \quad 1)$$

$$H_2O + 2\,e^- \rightleftharpoons 1/2\,H_2 + OH^- \quad 2)$$

[0044] At anode **2** of deposition cell **3**, mainly chromium (II) ions, which are easily oxidized, are oxidized to chromium (III) ions (equation 3):

$$2\,Cr^{2+} \rightleftharpoons 2\,e^- + 2\,Cr^{3+} \quad 3)$$

[0045] The chromium salt is added to the electrolyte solution in electrolysis cell **7** as chromium (II) or chromium (III) salt and the chromium (III) cations are reduced to chromium (II) cations at cathode **8** of divided electrolysis cell **7** according to the following equation 4):

$$2\,Cr^{3+} + 2\,e^- \rightleftharpoons 2\,Cr^{2+} \quad 4)$$

[0046] The electrolyte solution from the cathode chamber of the electrolysis cell **7** is transferred to the deposition cell **3** via a line by means of a pump **5** and from there is returned to the cathode chamber of the electrolysis cell **7** via a return line **6**. The concentration of chromium(II) cations required for reactions 1) and 3) can be maintained in the deposition cell **3** by continuous or repeated recirculation of the electrolyte solution. To ensure that no chromium is deposited at the cathode **8**, the voltage Uz of the voltage source **12** must be controlled so that the voltage difference U_B between cathode **8** and a reference electrode **11** corresponds to a target voltage suitable for reducing the chromium(III) to chromium(II) but not to metallic chromium. The feasibility of such voltage control arises from the fact that the standard potential of the reaction in equation 1) is −0.913 V and that of the reaction in equation 3) is only −0.41 V.

[0047] The membrane **10** in the electrolysis cell **7** can be a cation or anion exchange membrane or a simple diaphragm is used. Depending on the selection of the chromium salt, it may be appropriate to use a cation or anion exchange membrane. If, for example, chromium(III) sulfate is used as the starting material, it makes sense to use an anion exchange membrane, since the sulfate anions supplied with chromium(III) sulfate are removed from the electrolyte circuit by means of the anion exchange membrane, i.e., transferred to the anode chamber. In this way, the electrolyte concentration can be kept constant despite constant replenishment of the chromium sulfate. At the same time, the chromium cations are almost completely retained by the anion exchange membrane and oxidation of the chromium cations to toxic chromium(VI) at anode **9** is avoided. At anode **9** in the anode chamber of electrolysis cell **7**, water can be oxidized with the release of oxygen and the increase in acid concentration according to the following equation 5):

$$H_2O \rightleftharpoons 1/2\,O_2 + 2\,H^+ + 2\,e^- \quad 5)$$

[0048] If chromium sulfate is used as the chromium salt for the method, it is expedient to introduce sulfuric acid in the anode chamber. Then the sulfuric acid generated in the anode chamber can be used to adjust the pH of the chromium-containing electrolyte solution. In addition to the chromium salt, complexing agents such as formate, glycinate or oxalate as well as other additives can be added to the coating electrolyte.

[0049] Pulsed current deposition of the chromium layer is also possible in the coating cell. For this purpose, a pulse current source or pulse reverse current source must merely be used instead of the direct current current source **4**. Chromium deposition with intermittent or pulse current reversal can also be carried out with this device.

1. A device for coating a component (**1**) or a semi-finished product with a chromium layer, having an undivided deposition cell (**3**) in which an anode (**2**) is located and which is suitable for receiving a cathodically connected component (**1**) or semi-finished product, wherein an electrolyte solution containing chromium(II) is located in the deposition cell,

wherein:

the device includes an electrolysis cell (**7**) which is divided by a membrane (**10**) arranged in the electrolysis cell (**7**) into a cathode chamber, in which a cathode (**8**) is located, and an anode chamber in which an anode (**9**) is located,

the membrane (**10**) is an anion exchange membrane and

the cathode chamber being connected to the deposition cell (**3**) via a line and a pump (**5**) disposed in the line, wherein the pump (**5**) is capable of pumping liquid from the cathode chamber into the deposition cell (**3**) and/or liquid from the deposition cell (**3**) into the cathode chamber.

2. The device of claim **1**, wherein a liquid containing chromium(III) is present in the cathode chamber.

3. The device according to claim **1**, wherein a reference electrode (**11**) is provided in the cathode chamber or is connected to the electrolyte solution in the cathode chamber via an electrolyte bridge.

4. The device according to claim **1**, wherein the cathode chamber is connected to the deposition cell (**3**) via an additional return line (**6**).

5. The device according to claim **1**, wherein a current source (**4**) in the form of a rectifier or a pulse current source or a pulse reverse current source is provided.

6. A method for coating a component (**1**) or a semi-finished product with a chromium layer using the device according to claim **1**, wherein,

the component (**1**) or semi-finished product to be coated is immersed in the chromium(II)-containing electrolyte solution present in the deposition cell (**3**),

the component (**1**) or semi-finished product to be coated is connected cathodically and the anode (**2**) is connected anodically,

chromium deposition takes place in the deposition cell (**3**) from the liquid on the cathodically connected component (**1**) or semi-finished product,

the liquid present in the deposition cell (**3**) is pumped via the line into the cathode chamber of the electrolysis cell (**7**), or the liquid present in the cathode chamber is pumped via the line into the deposition cell (**3**).

7. The method of claim **6**, wherein the potential of a cathode located in the cathode chamber is set in the cathode chamber with the aid of a reference electrode (**11**) located in the cathode chamber.

8. The method of claim **6**, wherein chromium(III) ions are reduced to chromium(II) ions at the cathode (**8**) and thus consumed chromium(II) ions are replenished.

9. The method of claim **6**, wherein coating is carried out with direct current or coating is carried out with pulsed current or intermittent or pulsed reverse current.

10. A method of use of a device for coating a component (**1**) or a semi-finished product with a chromium layer, wherein the device comprises:

an undivided deposition cell (**3**) in which an anode (**2**) is located and which is suitable for receiving a cathodically connected component (**1**) or semi-finished product, wherein an electrolyte solution containing chromium(II) is located in the deposition cell,

an electrolysis cell (**7**) which is divided by a membrane (**10**) arranged in the electrolysis cell (**7**) into a cathode chamber, in which a cathode (**8**) is located, and an anode chamber in which an anode (**9**) is located,

wherein the membrane (**10**) is a cation exchange membrane or a diaphragm and wherein the cathode chamber being connected to the deposition cell (**3**) via a line and a pump (**5**) disposed in the line, wherein the pump (**5**) is capable of pumping liquid from the cathode chamber into the deposition cell (**3**) and/or liquid from the deposition cell (**3**) into the cathode chamber.

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