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(71) Applicant (for all designated States except US): **ENTHONE INC.** [US/US]; 350 Frontage Road, West Haven, Connecticut 06516 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **HORSTHEMKE, Helmut** [DE/DE]; Dürener Straße 29, 42697 Solingen (DE).

(74) Agents: **FLEISCHUT, Paul, I.J.** et al.; Senniger Powers LLP, 100 North Broadway, 17th Floor, St. Louis, Missouri 63102 (US).

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(54) Title: METHOD FOR GALVANIC DEPOSITION OF HARD CHROME LAYERS

(57) Abstract: The present invention concerns a method for galvanic deposition of a hard chrome layer on a substrate surface at high rates of deposition. According to the invention, the substrate surface being coated makes contact at reduced pressure relative to the ambient pressure with a chromium-containing electrolyte suitable for galvanic deposition and a relative motion between substrate surface and electrolyte is produced during the depositing of the chrome layer on the substrate surface.



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METHOD FOR GALVANIC DEPOSITION OF HARD CHROME LAYERS

FIELD OF THE INVENTION

The present invention concerns a method for deposition of a hard chrome layer on a substrate surface. In particular, the present invention concerns a method for deposition of hard chrome layers at high rates of deposition.

BACKGROUND OF THE INVENTION

Hard chrome layers are widespread as coatings on technical parts. Thus, for example, it is known how to provide valve bodies, bushings, brake pistons or axle hubs with hard chrome layers. The deposited chrome layer serves, on the one hand, as corrosion protection for the substrate surface located underneath, and on the other hand also as a protective layer against friction and wear, since the deposited hard chrome layers have great hardness.

For galvanic deposition of chrome layers, the substrate surfaces being coated after a suitable pretreatment to prepare the surface are brought into contact with an electrolyte having at least the metal (chromium) being deposited, while a deposition voltage is applied between the cathodically contacted substrate surface and an anode. As a result, the chromium dissolved in the electrolyte is deposited as a layer on the substrate surface.

The layers so deposited can have tensile or compressive internal stresses. Compressive internal stresses can lead to microcracks in the deposited layers, which means that the layers are not continuously closed, but rather possess a network of microcracks.

Tensile internal stresses, on the other hand, can lead to deep cracks in the deposited layers, into which moisture or corrosive substances can migrate and thus lead to corrosion effects in the substrate surface underneath the chrome layer, ultimately resulting in damaging of the chrome layer, even a flaking off.

Furthermore, the tensile internal stress found in such layers is detrimental to many applications, such as the chrome plating of axle hubs, since this has negative impact on the fatigue strength under reversed bending stresses of the substrate or the structural part. Furthermore, it is presumed that the unavoidable occurrence of gaseous H₂ during the deposition of chrome layers leads to an incorporation of hydrogen in the layer and the substrate, which in turn can lead to formation of cracks in the layer and a damaging of the substrate.

In order to relieve the deposited chrome layers of the tensile internal stresses occurring in them, the coated substrate surfaces undergo subsequent machining according to the prior art, e.g., by grinding or honing, in order to do away with the internal tensile stresses occurring in the layers. Besides the fabricating expense which this entails, the machining can also lead to a damaging of the deposited chrome layers, which ultimately reduces their property as a corrosion protection layer drastically.

Although chromium in itself is a relatively non-noble metal in chemical respect, thanks to the formation of a thin oxide layer on the surface and the concomitant very positive potential chromium layers act to protect against corrosion and exhibit corrosion protection properties comparable to noble metals such as gold, silver or platinum in regard to their corrosion and tarnish protection.

In the industrial fabrication of galvanically coated mass-produced articles such as valves for four-stroke internal combustion engines, shock absorbers, axle hubs or similar mechanical parts it is necessary to deposit chrome layers with a sufficiently high rate of deposition on substrate surfaces in order to ensure an economically reasonable production process. Higher rates of deposition are generally achieved by setting higher current densities in the galvanic deposition process. However, the formation of hydrogen at the cathode occurs as one side reaction in the galvanic deposition of chrome layers. Since the substrate surfaces being coated serve as the cathode in the galvanic coating processes, the resulting hydrogen can lead to the formation of bubbles on the substrate surfaces, which strongly affects the outcome of the galvanic chrome deposition. Thus, pores or flaws can form due to the resulting hydrogen bubbles, which quite adversely affect the corrosion protection properties of the deposited chrome layers.

Increasing the current density to achieve sufficiently high speeds of deposition also results in a greatly intensified formation of hydrogen on the substrate surfaces.

However, the network of cracks occurring in galvanically deposited chrome layers due to internal compressive stresses does not have merely negative influence on the corrosion protection property of the deposited layer, but instead leads positively to improved properties of the so coated moving parts, since lubricants for reducing the frictional resistance between moving parts can become embedded in the microcracks, and thus they have a depot effect for the lubricants. This capability of the layers is known as oil carrying capacity and it is absolutely desirable for such mechanical parts. For example, this is important in the case of piston rings, to maintain the fire stability.

GB 1 551 340 A discloses the depositing of a hard chrome layer on a substrate surface at a temperature of 60° C and a current density set at 80 A/dm² in a low-pressure chamber with chromium deposition electrolytes flowing through it.

US 2,706,175 A discloses a device for coating the insides of hollow cylinders, wherein a chrome layer is deposited under low pressure.

EP 1 191 129 A discloses a method for depositing a hard chrome layer under low pressure, wherein electrolyte and substrate move with a velocity of 0.4 m/sec relative to each other.

US 2001/054557 A1 discloses a method for the galvanic deposition of hard chrome layers, in which the chrome layer is likewise deposited under low pressure at a current density of 30 to 40 A/dm² and a pulse frequency of 5 to 700 Hz.

EP 0 024 946 A discloses a method for depositing of hard chrome layers at low pressure with a current density in the range of 200 A/dm² and the addition of a relative motion between electrolyte and substrate being coated.

US 5,277,785 discloses a method and a device for depositing of hard chrome layers by means of a brush deposition.

SUMMARY OF THE INVENTION

Taking into account the above remarks, it is therefore the problem of the present invention to indicate a method for the depositing of hard chrome layers by which hard chrome layers with high corrosion resistance and good mechanical properties can be deposited at high rate of deposition.

Briefly, therefore, in one aspect the invention is directed to a method for galvanic depositing of a hard chrome (i.e., chromium-based) layer on a substrate surface, having the steps of making contact between the substrate surface being coated and a chromium-containing electrolyte suitable for galvanic deposition; and applying a voltage between the substrate surface being coated and a counterelectrode for the galvanic deposition of a hard chrome layer on the substrate surface; wherein the deposition occurs in a container essentially gas-tight to the surroundings, and at least during the applying of the voltage a low pressure is established in the container essentially gas-tight to the surroundings and wherein substrate surface and chrome-containing electrolyte are moved with a velocity of 0.1 m/s to 5 m/s, preferably > 1 m/s to 5 m/s relative to each other.

Other objects and features will be in part apparent and in part pointed out hereinafter.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

This application claims priority from European application 08018462.5 filed 22 October 2008, the entire disclosure of which is incorporated by reference.

This problem is solved by a method for galvanic depositing of a hard chrome layer on a substrate surface having the steps:

- making contact between the substrate surface being coated and a chromium-containing electrolyte suitable for galvanic deposition;
- applying a voltage between the substrate surface being coated and a counterelectrode for the galvanic deposition of a hard chrome layer on the substrate surface,
- wherein the deposition occurs in a container essentially gas-tight to the surroundings, and at least during the applying of the voltage a low pressure is

established in the container essentially gas-tight to the surroundings and wherein substrate surface and chrome-containing electrolyte are moved with a velocity of 0.1 m/s to 5 m/s, preferably > 1 m/s to 5 m/s relative to each other, characterized in that a second hard chrome layer is deposited on a first deposited hard chrome layer, and for the depositing of the first hard chrome layer a pulsed current is applied between substrate surface and counterelectrode, and for the depositing of the second hard chrome layer a direct current is applied to the first hard chrome layer.

The reduction of the pressure relative to ambient pressure during the galvanic deposition leads to an improved detachment of the hydrogen bubbles on the substrate surface that are formed during the galvanic separation process. This detachment is supported by the relative movement between substrate surface and electrolyte. Together, this leads to the depositing of a hard chrome layer which is also essentially free of pores or flaws, even at high deposition current densities.

By suitable measures, such as pumps, an appropriate low pressure can be created. Advantageously, the pressure difference to be established lies in a range of 10 mbar to 800 mbar, preferably 20 mbar to 200 mbar.

In the method of the invention, a second hard chrome layer is deposited on a first deposited hard chrome layer, wherein for the depositing of the first hard chrome layer a pulsed current is applied between substrate surface and counterelectrode, and for the depositing of the second hard chrome layer a direct current is applied to the first hard chrome layer.

In one embodiment of the method of the invention, a first hard chrome layer is deposited, having no internal stresses and being free of microcracks thanks to the pulsed current applied. By subsequent applying of a direct current between the substrate surface being coated and the counterelectrode, a second hard chrome layer is deposited on the already deposited first hard chrome layer free of cracks and internal stresses, the second layer having internal tensile stress and the mechanically desirable microcracks.

The resulting compound layer structure has excellent corrosion resistance and furthermore excellent mechanical properties as running or sliding surfaces, thanks to the microcracks occurring in the upper chrome layer.

For the depositing of the first chrome layer, the pulsed current can be applied with a pulse frequency of 5 Hz to 5000 Hz, preferably 50 Hz to 1000 Hz. A current density between 25 A/dm² and 1000 A/dm², preferably 50 A/dm to 500 A/dm², is adjusted for this.

For the depositing of the second chrome layer, a direct current can be adjusted with a current density in the range between 25 A/dm² and 1000 A/dm², likewise with a preferred range between 50 A/dm² and 500 A/dm².

According to the invention, the substrate surface being coated makes contact with the chromium-containing electrolyte at a temperature between 30°C and 85°C, and the electrolyte can have a pH value in the range of $\leq$ pH 3, preferably $\leq$ pH 1.

According to the invention, the chromium-containing electrolyte can have a conductivity K of 200 mS/cm to 550 mS/cm (at 20°C).

Advantageously, the method can be carried out with only one electrolyte in a single coating cell.

According to the invention, a relative motion can be produced at least temporarily between the electrolyte and the substrate surface being coated. According to the invention, the relative motion can lie in a range between 0.1 m/s and 5.0 m/s.

To produce the relative motion between electrolyte and substrate surface, the substrate surfaces can be moved or the electrolyte can be appropriately delivered. Stirring devices or pumps are suitable for the delivery of the electrolyte.

Relative motion between electrolyte and substrate surface so produced encourages a detachment of the forming hydrogen bubbles, in addition to the low pressure applied.

In an especially advantageous embodiment of the method of the invention, the substrate surface being coated makes contact with the electrolyte in a cell, in which the chromium-containing electrolyte flows in from below and can flow away across a spillway, and a sufficient flow velocity is adjusted to sustain the detachment of the resulting hydrogen bubbles.

To carry out the method of the invention, a coating reactor is especially suitable, having the shape of a cylinder and being outfitted with a cylindrical inner anode of platinum-coated metal, such as platinum-coated titanium, niobium or tantalum. At the top and bottom of the coating reactor, there can be supports for the structural part being chrome plated. A coating reactor of this kind is particularly suitable for the coating of cylindrical parts. At least one of the two supports serves to supply current to the part being coated and is accordingly configured as an electrical contact.

By means of a suitable pump, an electrolyte is suctioned from a reservoir tank through the reactor to the top part of the reactor and from there back to the reservoir tank. In the reservoir tank, the electrolyte can be degasified by means of suitable devices. The gas mixture separated in this way is taken to the outside via a drop separator. Alternatively, a separate degasification tank can be provided.

Devices for temperature control of the electrolyte can be provided in the reservoir tank, such as heating and/or cooling systems. The reservoir tank can be connected via dispensing pumps to other reservoir tanks, which contain compositions to supplement the electrolyte located in the reservoir tank, insofar as a further dispensing of the electrolyte is needed. To reduce the volume, the electrolyte heated by the applied deposition voltage can be taken across

an evaporator unit, where water is removed from the electrolyte while cooling it at the same time.

Advantageously, such a reactor configured according to the invention is outfitted with at least one movable end face, facilitating the bringing up and taking away of the part being coated. Furthermore, the usual handling systems and seals can be provided for an automation of the process.

In one embodiment of such a coating reactor, the part being coated in the reactor can be rinsed with rinse water or steam, or at least prerinsed. For this, the supply of electrolyte to the reactor can be interrupted and replaced by rinse water or steam. In the case of a simple prerinsing of the coated part in the reactor, the final rinsing can occur in a second reactor, which is basically identical in design to the first reactor, but does not have any anode or current supply.

The method of the invention shall be presented hereafter in the context of sample embodiments, although the notion of the invention cannot be confined to the sample embodiments.

EXAMPLES

Example 1:

A workpiece being chrome plated (piston rod of steel type CK 45) was brought into contact in a reactor configured according to the invention with an electrolyte for deposition of a hard chrome layer, having 370 g/l of chromic acid and 5.3 g/l of sulfuric acid, the electrolyte flowing into the respective reactor from the bottom and it was taken away across a spillway at the top of the reactor. The relative velocity established in this way between the substrate surface of the workpiece being coated and the electrolyte was 4 m/s. The electrolyte had a temperature of 70°C. By suitable devices, a pressure of 50 mbar was established inside the reactor. After an appropriate conditioning and activation of the workpiece by applying a suitable current ramp, a hard chrome layer was then deposited by adjusting a current density of 235 A/dm² in the space of 300 seconds. The substrate was then rinsed.

The obtained chrome layer had a layer thickness of 11 µm, it had around 40 cracks per cm, and it had a corrosion resistance in the neutral salt spray test of less than 100 h.

Example 2:

A workpiece being chrome plated was brought into contact with an electrolyte in a reactor configured according to the invention, as in example 1. The electrolyte contained 370 g/l of chromic acid, 5.3 g/l of sulfuric acid, and 6 g/l of methane sulfonic acid. The deposition conditions corresponded to example 1. A shiny chrome layer with a layer thickness of 11 µm was obtained, which had around 250 cracks/cm and a corrosion resistance in the neutral salt spray test of less than 100 h.

Example 3:

A workpiece being chrome plated was brought into contact with the electrolyte per example 2 under the conditions mentioned in example 2, wherein a pulsed current with a current density during the pulse of 235 A/dm², a frequency of 1000 Hz and an On time of 50% was applied for 400 seconds.

A shiny, crack-free chrome layer with a layer thickness of 11 µm was obtained, which had 0 cracks/cm and a corrosion resistance in the neutral salt spray test of more than 500 h.

Example 4:

A workpiece being chrome plated was coated under the deposition conditions per example 3, at first applying a pulsed current with a current density of 235 A/dm² during the pulse, a frequency of 1000 Hz and an On time of 50% for 400 seconds and then applying a direct current in the same electrolyte with a current density of 235 A/dm² for 100 seconds, other conditions being equal.

The obtained shiny chrome layer had a layer thickness of 17 µm and around 25 cracks/cm, with a corrosion resistance in the neutral salt spray test of more than 500 h.

When introducing elements of the present invention or the preferred embodiments(s) thereof, the articles "a", "an", "the" and "said" are intended to mean that there are one or more of the elements. The terms "comprising", "including" and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements.

In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

As various changes could be made in the above compositions and processes without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

CLAIMS

1. Method for galvanic depositing of a hard chrome layer on a substrate surface, having the steps:

- making contact between the substrate surface being coated and a chromium-containing electrolyte suitable for galvanic deposition;
- 5 - applying a voltage between the substrate surface being coated and a counterelectrode for the galvanic deposition of a hard chrome layer on the substrate surface,

wherein the deposition occurs in a container essentially gas-tight to the surroundings, and at least during the applying of the voltage a low pressure is established in the container essentially gas-tight to the surroundings and wherein substrate surface and
10 chrome-containing electrolyte are moved with a velocity of 0.1 m/s to 5 m/s, preferably > 1 m/s to 5 m/s relative to each other.

2. Method according to claim 1, wherein a second hard chrome layer is deposited on a first deposited hard chrome layer, and for the depositing of the first hard chrome layer a pulsed current is applied between substrate surface and counterelectrode, and for the depositing of the second hard chrome layer a direct current is applied to the first hard chrome layer.

3. Method according to claim 1, wherein a pressure difference of 10 mbar to 800 mbar, preferably 20 mbar to 200 mbar, is established relative to ambient pressure.

4. Method according to one of claim 2 and 3, wherein a pulsed voltage with a frequency of 5 Hz to 5000 Hz, preferably between 50 Hz and 1000 Hz, is applied for the depositing of the first hard chrome layer.

5. Method according to one of the preceding claims, wherein for the depositing of the hard chrome layer a current density between 25 A/dm² and 1000 A/dm², preferably between 50 A/dm² and 500 A/dm², is adjusted.

6. Method according to one of the preceding claims, wherein the substrate surface being coated makes contact with the chromium-containing electrolyte at a temperature between 30°C and 85°C.

7. Method according to one of the preceding claims, wherein a pH value is adjusted in the electrolyte in a range of ≤ pH 3, preferably ≤ pH 1.

8. Method according to one of the preceding claims, wherein the substrate surface being coated makes contact with the electrolyte in a cell, into which the chromium-containing electrolyte flows from below and flows away across a spillway.

9. Method for galvanic depositing of a hard chrome layer on a substrate surface, having the steps:

- making contact between the substrate surface being coated and a chromium-containing electrolyte suitable for galvanic deposition;
- 5 - applying a voltage between the substrate surface being coated and a counterelectrode for the galvanic deposition of a hard chrome layer on the substrate surface,

wherein the deposition occurs in a container essentially gas-tight to the surroundings, and at least during the applying of the voltage a low pressure is established in the
10 container essentially gas-tight to the surroundings and wherein substrate surface and chrome-containing electrolyte are moved with a velocity of 0.1 m/s to 5 m/s, preferably > 1 m/s to 5 m/s relative to each other;

wherein a second hard chrome layer is deposited on a first deposited hard chrome layer, and for the depositing of the first hard chrome layer a pulsed current is applied between
15 substrate surface and counterelectrode, and for the depositing of the second hard chrome layer a direct current is applied to the first hard chrome layer.

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2009/061683

A. CLASSIFICATION OF SUBJECT MATTER

INV. C25D5/00 C25D5/04 C25D5/08 C25D5/12 C25D5/18
C25D21/00 C25D21/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *I* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Haering, Christian

INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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