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METHOD FOR COVERING OBJECTS WITH A DECORATIVE BRIGHT-NICKEL/CHROMIUM COATING, AS WELL AS OBJECTS COVERED BY APPLYING THIS METHOD

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The invention relates to a method for covering objects with a decorative bright nickel/chromium coating, as well as objects covered by applying this method.

Of late an attempt has been made to improve the resistance to corrosion of bright nickel/chromium coatings by applying a layer of so-called micro-crack chromium to the nickel layer. For, in a micro-crack pattern in the chromium layer the largest possible portion of the underlying nickel layer will be set free, so the corroding current, caused by the galvanic action, is minimal per surface unit.

So far the only method for applying a layer of micro-crack chromium in practical usage is the "duplex method," in which a so-called crack-free chromium layer is applied to the nickel layer to begin with, and after this a chromium layer, showing cracks, is applied in a second bath. By the high inner tension of the first chromium layer this will crack to a micro-crack pattern while being chrome-plated in the second bath (AES Proceedings 47 (1960), 214-225).

This disadvantage of this method is that firstly the precipitation of chromium on chromium is hard to achieve, and secondly it takes longer to cover with chromium plate (in the order of magnitude of 7 to 14 min.), whereas formerly, so before the duplex method was applied, it would take only from 1 to 2 minutes to cover with a chromium coating in a normal chromium bath.

The inventor has now found that a more delicate open structure of the chromium coating of the bright nickel may be achieved by applying a very thin metal layer between the bright nickel layer and the chromium layer from a galvanic bath containing solid matter in suspended condition.

The bright nickel layer is thus covered by a thin metal layer in which solid matter, as conductive as or less conductive than graphite, is embedded, so that later on no chromium layer can precipitate on the non- or ill conducting "places," as formed by the solid particles, so an interruption in the chromium layer takes place.

In this manner a microporous chromium layer will originate at once, from the very start, whereas so far the delicate mesh-work in the micro-crack chromium layers would only come into being at a height of the layer of 0.5-0.7 μ by the cracking of the layer, owing to the inner tension of the first chromium layer.

In principle any type of galvanic bath may be taken for the application of the thin intermediate metal layer. Preferably, however, an intermediate layer is applied from a galvanic bath, producing a metal layer no less anodic than the ground nickel coating and no more cathodic than the chromium coating.

Therefore, the invention relates to a method for covering objects with a decorative bright nickel/chromium coating, characterized in that, after the bright nickel plating and before the chromium plating takes place, an intermediate metal layer is applied electrolytically, keeping a solid, non- or less conductive substance embedded.

Preferably, according to the invention, a metal intermediate layer is applied in this case, consisting of nickel, silver or of a metal (including elements and alloys),

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found in the electrochemical series between these metals (nickel and silver).

In this way an earlier corroding away of the intermediate layer is prevented on the one hand, which would mean that the chromium layer would lose its adhering power, while on the other hand it would cause the chromium layer itself to first corrode away. This is the reason why an intermediate layer of, let us say, zinc or iron cannot be applied.

As the corrosion proof chromium (II)-oxide of the top chromium layer is as cathodic as silver, metals more cathodic than silver are less desirable. Therefore, as mentioned before, metals, such as silver, nickel, and the metals found between these two in the electrochemical series, are preferably applied.

For a practical electrochemical series we would refer to F. Todt, "Korrosion und Korrosionsschutz," second edition, De Gruyter Berlin, 1961, page 1202.

As metals (including elements and alloys) found between nickel and silver in the electrochemical series, and which can be produced galvanically, antimony, bismuth, monel, etc. may be applied.

The height of the intermediate metal layer only has to be sufficient to embed the solid matter.

When the height of the layer is 0.1 μ , a favourable influence will already be noticed when particles of solid matter of the same size are applied. A height of the layer of 0.5 to 1 μ is amply sufficient. A greater height of the layer will produce no adverse effect whatsoever, looking at it from the point of view of protection against corrosion. However, owing to the fact that the solid particles unfavourably influence the burnish, its second object (not counting the resistance against corrosion), i.e. the shining appearance of the bright nickel/chromium coating, is met by taking the height of the intermediate layer not more than a few microns.

The particles produced in the solid-matter bath may be made up out of aluminum oxide, silicon carbide, chromous oxide, ceric oxide, diamond powder and any other solid matter which is sufficiently fine and does not dissolve in the bath. The particles have to be of as small as size as possible causing the intermediate metal layer to be as thin as possible.

In an intermediate nickel layer with a height of the layer of 0.1 μ no particles, to give an example, can be applied of the order of magnitude of 10 μ . Preferably, the size of the particles has to be taken as small as is possible, as particles of a larger size will easily cause a rough precipitation. On the other hand the application of particles of a smaller diameter will increase the resistance to corrosion even more, the more so as a sealing-off effect will be produced by the solid particles on the dangerous pores which will act upon the ground layer of nickel.

Therefore, the size of the particles should be kept below 10 and preferably even below 1 μ . The solid matter may even have the size of colloidal magnitude, as will be the case for instance in colloidal graphite. The fact that graphite is a semi-conductor does not present any difficulties.

The height of the chromium layer to be applied later on should also be adapted to the size of the solid particles, so there will be no risk of the very fine pores closing up when the chromium layer is too thick.

Another possibility is found in the precipitation being produced in the galvanic bath itself, which is to produce the intermediate layer. To this purpose barium chloride or hydrogen sulfide may be added for example to a solution of nickel sulfate, so a very fine precipitation of barium sulfate or of nickel sulfide will be produced. These two substances are in this case non-soluble in a solution of acid.

Other precipitations are also possible, such as silver chloride from silver carbonate and nickel chloride.

As silver chloride is soluble in a silver bath containing potassium cyanide, potassium sulfide for example produces a satisfactory addition in the case of a silver bath is applied as a bath to produce the intermediate layer, as in this way the non-soluble silver sulfide will come into being.

The group of positively charged metal hydroxide sols which is stable in acid surroundings, and the parts of which are of a colloidal size, are extremely well-suited to be applied in acid baths for an intermediate treatment (iron-hydroxide, indium-hydroxide, aluminium-hydroxide, thorium-hydroxide).

In applying metal-hydroxides the metal-salts are added in an aqueous solution, to which purpose sulfates and chlorides are specially suited. In this case hydroxide is produced in said bath.

One condition, however, comes first. Namely, that the ions remaining in the solution owing to the solubility product of the substances precipitated are not harmful to the galvanic bath to which they are applied. This is the reason why preferably lead-chromate, lead-sulfide and mercury-sulfide are not applied.

The particles are kept suspended by blowing in air, or by applying a stirrer. In baths using a humidifier no air can be blown in because of too large a formation of foam.

A favourable influence on the resistance to corrosion will already be found from a percentage of 2 g./l. of solid matter onwards. A percentage of 100 to 200 g./l., however, is in this respect the optimum percentage. We would observe here, that larger concentrations of e.g. 400 g./l. can also be used, but in that case the objects treated will emerge from the bath covered by matter adhering to it.

The above method is easily applied to existing installations when an intermediate nickel layer is made use of, as in general a nickel-saving bath will be used after the nickel-plating, in which this treatment is easily realized. Possible difficulties with the bright nickel adhering to the bright nickel, as will take place in some of the kinds of bright nickel baths, may be taken away by an activating intermediate treatment or by adding fluoride or fluoroborate to the second bright nickel bath.

Example 1

An iron object is nickel-plated for 10 min. at 5 a./dm.² at 60° C. in the following bath, having a pH of 4, in which the object is moved by cathodic motion:

Nickel-sulfate, NiSO ₄	g./l.	250
Nickel-chloride, NiCl ₂	g./l.	60
Boric acid, H ₃ BO ₃	g./l.	40
Saccharine, C ₆ H ₄ SO ₂ NHCO	g./l.	2
Butyndiol, HOC≡COH	mg./l.	150
Sodium lauryl sulfate, Na[CH ₃ (CH ₂) ₁₀ CH ₂]SO ₄	g./l.	0.3

After this treatment the object is nickel-plated, without an intermediate washing, in a bright nickel bath of the same composition, however, by adding 100 g./l. of silica, the particles of which have the size of 0.2μ for 1 min. at 5 a./dm.², causing a layer of 1μ to come into being.

The solid matter is kept suspended in this bath by a stirrer. When the object in question is consequently chromium-plated, this can be done in the ordinary way, e.g. in a bath, containing 300 g./l. CrO₃ and 3 g./l. H₂SO₄, by plating for 1 min. at 15–20 a./dm.² at 40° C. A strongly increased resistance to corrosion will then be observed in respect to an analogous object being covered in a similar bath under similar circumstances by a bright nickel layer and a chromium layer though without an intermediate nickel layer.

Example 2

An object made of "Zamac" (an aluminium-copper-magnesium-zinc alloy) covered by a layer of 8μ of copper, is nickel plated for 15 min. at 4 a./dm.² at 60° C. in the following bright nickel bath, having a pH of 3.5 which is kept in agitation by blowing air into it.

Nickel-sulfate, NiSO ₄	g./l.	270
Nickel-chloride, NiCl ₂	g./l.	45
Cobaltic-sulfate, Co ₂ (SO ₄) ₃	g./l.	3
Boric acid, H ₃ BO ₃	g./l.	40
Formic acid, HCOOH	g./l.	20
Formalin, 40% HCHO	ml./l.	3

After this the object is treated for half a minute with 4 a./dm.² without an intermediate washing (producing a layer of 0.4μ) in a bright nickel bath of similar composition, this time, however, 140 g./l. of silicon carbide, having particles of the size of 0.1 to 0.2μ, is added. These particles are kept suspended by blowing in air.

After chromium plating in the above mentioned way takes place for 1 min. at 20 a./dm.² in a normal sulfuric acid chromium bath a highly increased resistance against corrosion is obtained compared to an object as bright nickel-plated/chromium-plated in the same baths without the intermediate nickel layer.

Example 3

An object is nickel-plated with a bright nickel layer according to Example 1. After an intermediate washing the object is silver-plated in a silver bath of the following composition:

	G./l.	
Silver cyanide, AgCN		40
Potassium cyanide, KCN		120
Potassium hydroxide, KOH		50

The silver bath also contains 150 g./l. of aluminium oxide with its particles having a size of 0.3μ. The silver-plating takes place for 20 sec. at 40° C. at 4 a./dm.², producing a layer of about 0.8μ.

After rinsing the object is chromium-plated for 1 min. at 20 a./dm.² in the normal sulfuric acid/chromium bath.

In comparison to an object treated in a similar way, without the silver intermediate layer though, the resistance to corrosion is found highly increased.

Example 4

An object is nickel-plated in a bright nickel bath according to Example 1. Without an intermediate washing the object is then nickel-plated for 0.5 min. at 5 a./dm.² in the following bath, producing a layer of 0.5μ.

Nickel-sulfate, NiSO ₄	g./l.	400
Boric acid, H ₃ BO ₃	g./l.	40
Barium chloride, BaCl ₂	g./l.	100
Saccharine, C ₆ H ₄ SO ₂ NHCO	g./l.	2
Butyndiol, HOC≡COH	mg./l.	150
Sodium lauryl sulfate, Na[CH ₃ (CH ₂) ₁₀ CH ₂]SO ₄	mg./l.	0.3

The addition of barium chloride takes place in an aqueous solution, slowly and by stirring well. The organic substances are added after the barium sulfate has formed a precipitation, this in connection with the high absorption capacity of barium sulfate.

The precipitation of barium sulfate is kept suspended by means of a stirrer.

The object thus nickel-plated and then chromium-plated in the normal sulfuric acid/chromium bath for 1 min. at 20 a./dm.² has a very considerable resistance to corrosion.

The layer of chromium-plating has a thickness of about 0.15μ.

What I claim is:

1. A method of coating an object with a bright nickel/chromium coating comprising providing an object hav-

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ing thereon a bright nickel plating, applying thereto an intermediate metal layer containing particles, said particles having a conductivity not exceeding the conductivity of graphite and plating chromium over said intermediate layer.

2. A method according to claim 1, wherein the metal of said intermediate layer is a metal between nickel and silver, inclusive, in the electrochemical series.

3. A method according to claim 1, wherein the size of said particles does not exceed 10 microns.

4. A method according to claim 3, wherein the thickness of said intermediate layer does not exceed a thickness of the order of about a few microns.

5. A method according to claim 4, wherein the size of said particles does not exceed about 1 micron.

6. A method according to claim 5, wherein the thickness of said layer is between about .5 to 1 micron.

7. A method of coating an object with a decorative bright nickel/chromium coating comprising plating an object with a bright nickel plating, electrolytically depositing thereon an intermediate metal layer containing particles, said particles having a conductivity not exceeding the conductivity of graphite, said intermediate layer being deposited from a plating bath containing said particles, and plating chromium over said intermediate layer.

8. A method according to claim 7, wherein the concentration of said particles in said bath is about 100-200 grams per liter.

9. A method according to claim 8, wherein said plating bath containing said particles is a bright nickel plating bath.

10. A method of coating an object with a decorative bright nickel/chromium coating comprising plating an object with a bright nickel plating, electrolytically depositing thereon an intermediate metal layer containing particles from a plating bath containing said particles, said particles having a conductivity not exceeding the conductivity of graphite, the size of said particles not exceeding about 1 micron with the thickness of said intermediate layer being between about .5 to about several

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microns, and plating chromium over said intermediate layer.

11. A method according to claim 10, wherein the metal of said intermediate layer is a metal between nickel and silver, inclusive, in the electrochemical series.

12. A method according to claim 11, wherein said plating bath is a bright nickel plating bath containing about 100-200 grams per liter of said particles.

13. An object comprising a base having thereon a bright nickel coating, an intermediate metal layer over said coating, said intermediate layer having therein particles having a conductivity not exceeding the conductivity of graphite, and a plated chromium layer over said intermediate layer.

14. An object according to claim 13, wherein the size of said particles does not exceed about 10 microns.

15. An object according to claim 14 wherein the size of said particles does not exceed about 1 micron and the thickness of said intermediate layer is between about .5 to 1 micron.

16. An object according to claim 15, wherein the metal of said intermediate layer is a metal between nickel and silver, inclusive, in the electrochemical series.

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