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METHOD OF ELECTRODEPOSITING A CORROSION RESISTANT NICKEL-CHROMIUM COATING AND PRODUCTS THEREOF

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The invention relates to a method for improving the resistance to corrosion of nickel-chromium coatings.

Of late the working of the corrosion in nickel-chromium coatings has become better known. At first it was thought that corrosion was due to the nickel coating being too thin and to the presence of pores in this same nickel coating. It was thought that the chromium coating, as applied to the layer of nickel, having a thickness of 0.25μ , only served to make the nickel resistant against oxidation. However, for several years it has been known, that a galvanic action between chromium and nickel takes place, causing the nickel beneath the chromium to dissolve. It is this phenomenon which is the main factor, as has now become known, in causing corrosion to take place.

When the real nature of corrosion had in this way become known, the search for a method to replace the porous chromium layer by a compact chromium layer was on. These attempts eventually led up to the so-called crack-free chromium.

However, as any chromium layer is more or less of a porous nature, a crack-free chromium layer will therefore always show pores to a greater or lesser extent, caused by the chromium's ill-covering property. This is the reason why the micro-crack chromium has been developed. In this case one does not attempt to eliminate the galvanic action, but they are here produced on purpose. The micro-crack pattern of the chromium layer causes such a large surface of the nickel to be laid bare, that the current density of the corroding current is practically negligible, so that, for this very reason, a considerable improvement is achieved against the corrosion.

This improvement which will show on a bright nickel coating, both with crack-free chromium, as well as with micro-crack chromium, is in the order of magnitude of 5 to 10 times that of a normal chromium coating. This has been shown both in tests in the open air, as well as in the accelerated corrodokote-tests.

The micro-crack pattern can be made visible by means of copper-plating. Use is made here of the property that no copper precipitation takes place on chromium, but does so on nickel. After a test by microscope, where it is enlarged at least 200 times, the crack pattern becomes visible. The most delicate meshwork at present produced, will leave small islands between the cracks having a diameter of several microns.

The disadvantage, both of crack-free chromium, as well as micro-crack chromium is at present still found in the fact that thicker chromium coatings have to be applied in both cases.

Now the inventor has found that a considerable improvement in the corrosion resistance may be obtained if care is taken that the chromium coating on the nickel coating is precipitated in a microporous manner from the very first moment. This may be achieved either by precipitating the top layer of the nickel coating itself in a microporous manner (first case), or by seeing to it that the chromium per se will precipitate in a microporous manner (second case).

In the first case the ill-covering property of the chro-

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mium is made use of. If proper care is taken that the depth of the openings in the nickel layer is for example 2-3 times as much as the diameter of these openings, the bottom parts of these openings will stay free of chromium, causing a microporous structure.

In order to bring this microporous structure about, use is made of colloidal particles as found in an emulsion, according to the invention. Their size lies between 0.01 and 0.1μ .

Nickel-plating and chromium-plating in an emulsion has been unknown up to now. On the contrary, so far every care was taken to keep a bath free from any organic impurities.

In a bright nickel-chromium plating the method according to the invention may be applied by having this new "emulsion-plating" take place either in a nickel bath (first case) or in a chromium bath (second case).

In order to eliminate the influence which the emulsifying oil, wax or resin has on the brightness of the nickel layer, a very short nickel coating is applied after the normal bright nickel in an emulsion bright nickel bath of let us say $\frac{1}{4}$ - 2μ . This will cause a micro-porous layer on top of the bright nickel, with pores having a diameter in the order of magnitude of the colloidal particles with the result that the chromium plating taking place hereafter will have a microporous structure in the order of magnitude of 0.25μ .

It would also be possible to apply a normal bright nickel coating and to chrome it with an emulsifying chromium bath afterwards, in which case (second case) the colloidal particles in the chromium bath will themselves see to it that no chromium will precipitate locally.

The improvement in the corrosion resistance found by means of the corrodokote test, is in the order of magnitude of 15 to 20 times that of a normal chromium coating.

In applying the emulsion plating with the aid of an emulsion chromium bath (second case), the strongly oxidizing property has to be taken into account, as well as the high temperature of the chromium bath. Which means that oils, waxes, resins and emulsifying agents have to be applied which cannot oxidise. Specially suited to this purpose appear in this case the not water soluble halogenfluoro carboxylic acid oils and waxes which cannot be oxidised even in a concentrated sulfuric acid. As emulsifying agents the water soluble fluoro carboxylic acids or the fluoro sulfonic acids which are oxidation resistant as well, may be applied.

Example 1

An object is bright nickel plated until its plating has a thickness of 40μ , in the following nickel bath:

Nickel sulfate	-----g./l.	300
Nickel chloride	-----g./l.	60
Boric acid	-----g./l.	40
Butynediol sulfonic acid (brightener)	-----mg./l.	50
Saccharine (brightener)	-----g./l.	2
Sodium allyl sulfonate (brightener)	-----ml./l.	2

It is left in the nickel bath for 40 min. with a current density of 5 A./dm^2 and at a temperature of 60°C .

Without an intermediate washing the object is consequently hung in a second bright nickel bath having the same composition, to which, however, the following substances have been added:

Liquid paraffin (paraphinum liquidum)	-----ml./l.	8
Sodium lauryl sulfate	-----g./l.	1

It is left in this bath for 2 min. with a current density of 2 A./dm^2 and at a temperature of 60°C .

The average layer thickness of this layer of nickel as strewn with micropores amounts to 0.8μ .

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After a thorough washing of this object it is finally chromium-plated in a chromium bath of the normal composition:

	G./l	
Chromic acid -----	300	5
Sulfuric acid -----	3	

The chromium plating takes place for 1 min. with a current density of 15 A./dm.² and at a temperature of 40° C.

If the object thus bright nickel- and chromium-plated is copper-plated electrolytically, so as to be able to determine the microporous structure when magnifying it at least 200 times, one will find a delicately distributed microporous structure, and when taking the corrodokote test, an improvement in the corrosion is found of 14 times in proportion to the normal bright nickel-chromium coating.

Example 2

An object is bright nickel-plated in a normal bright nickel bath until the layer has reached a thickness of 40 μ . Hereafter the object is chromium-plated in the following bath:

	G./l	
Chromic acid -----	300	25
Sulfuric acid -----	3	
Cl(CF ₂ —CFCl) _x Cl (molecular weight 780) -----	10	
Perfluoro laurylsulfonic acid -----	4	

The last mentioned substance is the emulsifying agent.

The chromium-plating is done by blowing in with air for 2 min. with a density of current of 20 A./dm.² and at a temperature of 40° C. The object will emerge from the chromium bath highly bright.

After copper-plating it so as to be able to appreciate the micro-porous structure, the structure, on magnifying it 500 times, appears to be finely divided and open.

The corrodokote-test will show an improvement of 18 with respect to the normal chromium-nickel coating.

What I claim is:

1. A method of producing a micro-porous chromium plating on an object comprising the steps of electroplating a layer of nickel on said object from a nickel electroplating bath and electroplating a layer of chromium on said nickel layer from a chromium plating bath, one of said

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plating baths being an emulsion whereby the chromium layer which is produced is micro-porous, the emulsified liquid particles of said emulsion being oxidation resistant under the electroplating conditions.

2. A method according to claim 1 wherein said nickel plating bath is the emulsion.

3. A method according to claim 2 wherein the emulsified liquid particles in said emulsion are selected from the class consisting of oils, resins and waxes.

4. A method according to claim 3, wherein before said layer of nickel is electroplated on said object from said emulsified nickel plating bath the object is electroplated with nickel from a conventional nickel plating bath.

5. The method according to claim 4, wherein said emulsified particles are liquid paraffin.

6. A method according to claim 5 wherein the nickel layer electroplated from said emulsified nickel plating bath is about from 1/2 to 2 microns thick.

7. A method according to claim 6 wherein both of said nickel plating baths are bright nickel plating baths.

8. A method according to claim 1 wherein said chromium plating bath is the emulsion.

9. A method according to claim 8 wherein the emulsified liquid particles in said emulsion are selected from the class consisting of oxidation-resistant oils, resins and waxes.

10. A method according to claim 9 wherein said emulsified liquid particles have the formula Cl(CF₂—CFCl)_xCl and a molecular weight of about 780.

11. A method according to claim 10 wherein said nickel electroplating bath is a bright nickel electroplating bath.

12. The product produced by the method of claim 2.

13. The product produced by the method of claim 8.

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