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PROCESSES FOR IMPROVING THE CORROSION RESISTANCE
OF NI-CO-METAL COATINGS CONTAINING BORON
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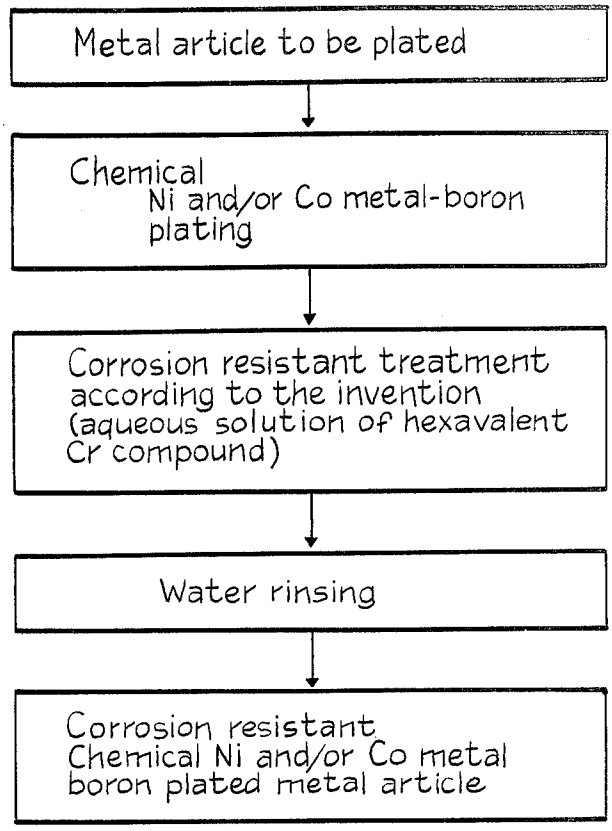

INVENTORS
HEINZ-GÜNTER KLEIN
EBERHARD ZIRNGIEBL

BY Burgess, Dinklage & Sprung
ATTORNEYS

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PROCESSES FOR IMPROVING THE CORROSION RESISTANCE OF NI-CO-METAL COATINGS CONTAINING BORON

Heinz-Günter Klein, Cologne-Deutz, and Eberhard Zirngiebl, Cologne-Flittard, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany

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Ni-Co-metal-boron coatings are formed by chemical plating of metal surfaces in plating baths containing as essential components the metal salts, complex formers and, as a reducing agent, boron-hydrogen compounds with one to four hydrogen atoms linked directly to boron. Nothing is so far known from publications about the corrosive behavior of these metal-boron layers, for example nickel-boron or cobalt-nickel-boron layers, etc.

The metal-boron coatings do not display any pores under the microscope or interference microscope, the ferr-oxyl test, however, indicates the existence of active points so that pitting and further corrosion cannot be completely excluded, under certain conditions.

The object of the invention is to provide a process for improving the corrosion resistance of chemically deposited Ni-Co-metal coatings containing boron, characterized by after-treating the chemically plated metal surfaces with aqueous solutions containing a hexavalent chromium compound, preferably chromic acid and, if desired, phosphoric acid or its salts.

The process is illustrated by the flow diagram shown in the drawing.

The duration of the after-treatment, the concentration of the hexavalent chromium compounds as well as the bath temperature can be varied within a wide range. The temperature of the after-treatment bath can lie between room temperature and boiling temperature, the concentration of, for example chromic acid can be 1 to 300 g./liter. As an addition to the bath, in order to shorten the duration of stay, 0.1 to 2% phosphoric acid are sufficient.

In order to achieve a good protection against corrosion a coating of 5 μ of a NiB alloy, containing 90% Ni and 10% B, an after-treatment of 5 minutes at 40° C. in a

bath of the composition 200 g./liter CrO_3 and 5 g./liter H_3PO_4 is technically satisfactory. For a coating of 10 μ a duration of stay of 8 minutes at 65° C. in the same bath is required. Investigations of the coatings carried out subsequent to the after-treatment show that the active points detected in the ferr-oxyl test have completely disappeared. The corrosive behavior of the surfaces treated according to this invention surpasses that of objects metallized by galvanic methods as well as of those metallized using alkali metal hypophosphite as a reducing agent.

The following examples are given for the purpose of illustrating the invention:

Example 1

In a chemical plating bath of the following composition:

30 g./liter of nickel chloride
40 g./liter of sodium hydroxide
50 g./liter of ethylene diamine
0.6 g./liter of sodium borohydride
1 g./liter of thiodiglycollic acid
10 mg./liter of lead chloride

iron plates were coated with a nickel-boron layer having the composition 90–92% Ni and 8–10% B. The area of one plate was 1 dm., the thickness of the coating about 15μ.

The after-treatment of the plates, in order to improve the corrosive behavior, was carried out by immersing them into an aqueous solution of 200 g./liter CrO_3 at 85° C. The residing time of the plates in the bath was 10 minutes. Subsequently, the plates were rinsed with water and subjected to the corrosion test.

The corrosion test was carried out using the corrosion apparatus "Testor" of the Firma Köhler, Lipperode, at 50° C. and 100% relative humidity of the air. The samples were suspended from glass hooks in the apparatus. During the test period a thin layer of condensed water was always present on the sample surface. The duration of the test was 15 days. The samples were examined first at short intervals, later at longer intervals and the degree of rusting was estimated as a percentage of the total surface. The individual degrees of rusting in proportion to the period of testing are shown in the table.

Sample No.	G.-deposit Ni-B/dm.²	After-treated	Rust as percent of surface						
			1 h.	5 h.	1 day	3 days	5 days	10 days	15 days
139	1.0834 (ca. 15μ)	No	0	0.2	25	40	50	50	50
28	1.0968 (ca. 15μ)	Yes	0	0	0	0	0	0	0.1
30	1.0409 (ca. 15μ)	No	0	0.5	5	20	40	40	40
74	1.0004 (ca. 15μ)	Yes	0	0	0.1	0.1	0.1	0.1	0.1
27	1.1424 (ca. 15μ)	No	0	0	1	5	10	15	20
56	1.0494 (ca. 15μ)	Yes	0	0	0	0	0	0	0
7	1.0160 (ca. 15μ)	No	0	0.2	1	3	5	8	10
111	1.0968 (ca. 15μ)	Yes	0	0	0	0	0	0	0

Example 2

In a chemical plating bath of the following composition:

15 g./liter of cobalt chloride
15 g./liter of nickel chloride
5 g./liter of ammonium chloride
20 g./liter of sodium acetate
50 mg./liter of thiodiglycollic acid
3.5 g. of N-diethyl-borazane dissolved in 50 ml.

methanol iron plates were provided with a Co-Ni-B coating. The iron plates had an area of 1 dm.² each. The composition of the coating was approximately 47% Co, 51% Ni and 2% B. The after-treatment of the plates as well as the corrosion test were carried out as described in Example 1.

(a) 100 g./liter of potassium dichromate
(b) 100 g./liter of potassium dichromate
10 ml./liter phosphoric acid D 1.84

The corrosion test was carried out as described in Example 1. The following values were obtained:

G. Ni-B/dm.²		Residing time	Bath	Rust after 12 days	
		a	b	a	b
2.0410	(ca. 32μ)	15		1 rust spot	
2.0624	(ca. 32μ)		15		
2.0103	(ca. 32μ)	30		1 rust spot	
2.0539	(ca. 32μ)		30		
1.9902	(ca. 32μ)	45			
1.9974	(ca. 32μ)		45		
2.1358	(ca. 32μ)	60			
2.1119	(ca. 32μ)		60		

Sample No.	G.-deposit Co-Ni-B/dm.²	After-treated	Rust as percent of surface									
			Hours			Days						
			1	3	5	1	3	5	7	9	11	15
220	0.5048 (ca. 8μ)	No	0	0.2	0.8	1	5	10	20	45	55	70
227	1.0052 (ca. 15μ)	No	0	0	0.2	0.5	1	4	7	10	15	20
72	1.5070 (ca. 23μ)	No	0	0	0	0.2	0.5	0.8	1	3	7	10
11	0.5281 (ca. 8μ)	Yes	0	0	0.2	0.6	1	4	8	12	16	20
233	1.0740 (ca. 15μ)	Yes	0	0	0	0.2	0.3	0.4	0.5	0.6	0.7	0.8
225	1.5166 (ca. 23μ)	Yes	0	0	0	0	0	0	0	0	0	0.1

Example 3

Iron plates were provided with a N-B layer as described in Example 1. The after-treatment of the iron plates was carried out at 60° C. and with varying stays in aqueous solutions of

(a) 200 g./liter CrO_3
(b) 200 g./liter CrO_3
10 ml./liter phosphoric acid D 184

The corrosion test was carried out as described in Example 1. The following values were obtained:

G. Ni-B/dm.²		Residing time	Bath	Rust in percent of surface after 15 days	
		a	b	a	b
0.9882	(ca. 15μ)	10		0.1	
1.1400	(ca. 15μ)		10		<0.1
1.0376	(ca. 15μ)	20		0.1	
1.0184	(ca. 15μ)		20		<0.1
1.1716	(ca. 15μ)	30		<0.1	
1.0216	(ca. 15μ)		30		0
0.9722	(ca. 15μ)	45		<0.1	
1.0264	(ca. 15μ)		45		0
1.1665	(ca. 15μ)	60		<0.1	
1.0486	(ca. 15μ)		60		<0.1
0.9604	(ca. 15μ)	90		0	
1.1020	(ca. 15μ)		90		0
0.9795	(ca. 15μ)	120		0	
1.0130	(ca. 15μ)		120		0

The samples were subsequently suspended for 150 hours in an aerosol chamber with 0.3% NaCl spray. During the duration of the experiment no further rust formation occurred.

Example 4

Iron plates were provided with a Ni-B layer as described in Example 1. The after-treatment of the plates took place at 65° C. and with varying stays in aqueous solutions of

A non-after-treated iron plate having a Ni-B coating of 2.0540 g. Ni-B/dm.² showed after 12 days 4% rust (expressed as a percentage of the surface).

We claim:

1. A process for improving the corrosion resistance of metal coatings containing boron and a metal selected from the group consisting of Ni, Co, and Ni-Co-systems chemically deposited from a plating solution containing as essential ingredients a metal selected from the group consisting of Ni, Co, and Ni Co-systems and a borohydride which comprises treating the chemically plated surfaces with an aqueous solution containing a hexavalent chromium compound, the chromium compound being present in an amount between 1 to about 300 g./l. of chromic acid.

2. A process according to claim 1, wherein said aqueous solution additionally contains a member selected from the group consisting of phosphoric acid and soluble salts thereof, the phosphoric acid being present in an amount between about 1 and 20 g./l. of aqueous solution.

3. A process according to claim 1, which comprises effecting said treatment with said aqueous solution at a temperature between about 18 and about 100° C.

4. A process according to claim 1, which comprises effecting said treatment with said aqueous solution at a temperature of 40° C. and wherein said aqueous solution contains 200 g./l. of chromic acid and 5 g./l. phosphoric acid.

5. A process according to claim 1, which comprises effecting said treatment with said aqueous solution at a temperature of 85° C. and wherein said aqueous solution contains 200 g./l. of chromic acid.

6. A process according to claim 1, which comprises effecting said treatment with said aqueous solution at a temperature of 60° C., wherein said aqueous solution contains 200 g./l. chromic acid and 10 ml./l. phosphoric acid (D 1.84).

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JOSEPH B. SPENCER, *Primary Examiner.*

RICHARD D. NEVIUS, *Examiner.*