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**PROTECTIVE AND DECORATIVE
NICKEL COATINGS**

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The present invention relates to the provision of decorative and protective metallic coatings and, more particularly, to the provision on metallic surfaces of bright composite electrodeposited coatings which have substantially improved resistance to the destructive influences of industrial and marine atmospheres and which exhibit an attractive and decorative surface appearance for long periods of time during use.

As is well known to those skilled in the art, many proposals have been made in an endeavor to provide metallic coatings capable of providing appreciable resistance to corrosive attack when subjected to various atmospheres while retaining a pleasing and decorative surface appearance. The bright metallic appearance and, particularly, the retention thereof, of parts of many manufactured articles, e.g., automobiles, household equipment, metal furniture, etc., is often a paramount consideration in their usefulness and pleasure afforded the user. However, the various metals and metal combinations which have been proposed in attempts to satisfy commercial needs have proven unsatisfactory in many applications.

Electrodeposited chromium is pleasing in appearance and offers a degree of resistance to corrosive atmospheres but fails to provide sufficient protection for underlying metals, e.g., ferrous metals, chiefly on account of the inherent porosity characterizing chromium electrodeposits. Electrodeposited nickel may also have a bright and pleasing appearance but nickel deposits on basis metals are characterized by fogging in industrial atmospheres and then by pitting at myriads of points on the surface. It has been proposed heretofore to employ composite electrodeposited metal coatings, such as nickel-chromium and copper-nickel-chromium coatings wherein the chromium is the outer layer of the composite, on ferrous metals to provide an improved combination of corrosion resistance and pleasing appearance while using a commercially practicable thickness of coating in the neighborhood of about 1 mil. However, the corrosion resistance of these prior composite coatings on steel is still unsatisfactory in applications requiring relatively long exposure to weathering in industrial atmospheres, marine atmospheres and other corrosive media. For example, in the commercially used conventional nickel-chromium composite, the thickness of which is generally about 1 mil for economic reasons, chromium reduces the fogging tendency of nickel but the chromium layer is thin and not impervious to atmospheric and other corrosive effects and, as a consequence thereof; exposure to atmospheres containing detrimental and corrosive substances, e.g., sulfur dioxide, leads to pitting and/or perforation of the composite coating. When these pits and/or perforations penetrate through the coating to the basis metal, e.g., steel, the latter corrodes and unsightly corrosive products exude to the surface to mar its outward appearance. The protective value of conventional composite nickel-chromium coatings increases with increasing thickness of the nickel deposit, but commercially this has not proved to be a panacea for rust spotting of the plated metal, e.g., steel, exposed to weather.

It has been proposed to employ other composite electrodeposited coatings such as those containing a copper-tin alloy or a copper-zinc alloy layer as a substitute for the

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nickel layer in the usual nickel-chromium composites. When subjected to weathering, these substitute composites have been found to lose their decorative appearance more quickly than the conventional composites. Electrodeposited composite coatings such as nickel-copper-nickel have been widely suggested for purposes of protecting steel from corrosive effects but it has been found that this type of coating is adversely affected by atmospheric attack and that the corrosion products of copper are themselves highly corrosive to the coating. Coatings which are customarily used without a surface finish of chromium, such as zinc and cadmium coatings, although bright when freshly prepared become dull rapidly through weathering and/or wear.

Although many attempts were made to overcome the foregoing difficulties and other difficulties, none, as far as we are aware, was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that bright, decorative and protective composite electrodeposited coatings which, when compared with conventional coatings of the same magnitude of thickness, manifest a markedly higher order of resistance to atmospheric attack, better protect the ferrous metal base from corrosion and longer retain a pleasing surface appearance during use can be obtained when metal of a selected class is interposed between layers of nickel in the fashion of a sandwich, the outermost nickel layer advantageously being provided with a layer of chromium.

It is an object of the present invention to provide composite electrodeposited coatings which are bright and decorative and exhibit an improved high degree of corrosion resistance when exposed to atmospheric attack.

Another object of the invention is to provide metallic surfaces including metals and/or alloys with composite electrodeposited coatings characterized by a high degree of resistance to corrosion when subjected to weathering and which retain a decorative and pleasing surface appearance for relatively long periods of time during use.

The invention also contemplates providing bright, decorative and protective composite electrodeposited coatings on metallic surfaces including metals and/or alloys which, when compared to conventional composite coatings of comparable thickness, manifest an improved order of resistance to perforation by corrosive atmospheres, better protection of the metallic surface from corrosion and longer retention of a decorative and pleasing surface appearance during use.

The invention further contemplates providing a process for accomplishing the foregoing objects.

Other objects and advantages will become apparent from the following description.

Generally speaking, the composite electrodeposited coatings provided in accordance with the present invention are comprised of a plurality of electrodeposited nickel layers and a layer of electrodeposited dissimilar metal selected from the group consisting of cobalt, alloys of cobalt with up to 20% tungsten and up to 90% nickel, tin, lead, silver and palladium interposed between said layers of nickel. Binary alloys of cobalt with about 10% to 20% tungsten and about 50% to 90% nickel may advantageously be employed in the interposed or intermediate layer. A relatively thin layer of chromium having a thickness of about 10 to 20 micro-inches is advantageously deposited on the outermost layer of nickel to contribute stain resistance to the composite coating. When the composite coatings of the present invention are electrodeposited on a metallic base, including metals and/or alloys, it has been found that the coatings are more resistant to atmospheric and other corrosive effects and retain a pleasing protective surface appearance longer during use than do known bright coatings of the same

order of thickness, e.g., the conventional nickel-chromium and copper-nickel-chromium electrodeposits. It is important within the concepts of the present invention in order to insure the attainment of highly satisfactory results that the respective thicknesses of each of the electrodeposited metal layers comprising the composite coating be controlled with the following ranges:

	Mils
Basis layer of electrodeposited nickel.....	0.1 to 2
Intermediate electrodeposited layer of dissimilar metal.....	0.01 to 0.3
Outer layer of electrodeposited nickel.....	0.1 to 2

The composite coating must in all cases be at least 0.25 mil thick.

In carrying the invention into practice, it is advantageous in order to achieve optimum results to control the thicknesses of the respective intermediate layers or deposits over the following ranges: cobalt, about 0.01 to about 0.1 mil; cobalt-nickel alloy, about 0.1 to about 0.3 mil; cobalt-tungsten alloy, about 0.05 to about 0.2 mil; tin, about 0.05 or 0.1 to about 0.3 mil; lead, about 0.1 to about 0.3 mil; silver, about 0.05 to about 0.2 mil; and palladium, about 0.05 to about 0.2 mil. When intermediate or interposed layers of the aforementioned kinds and thicknesses are employed, superior results are obtained using a basis nickel layer having a thickness of about 0.1 to 1 mil and an outer nickel layer having a thickness of about 0.1 to 2 mils. In general, for best protective effects, thicker outer nickel layers should be employed when the basis nickel layer has a thickness in the lower portion of the range described. For example, when the basis nickel layer is only about 0.2 mil or 0.1 mil, or even as thin as about 0.05 mil, the outer nickel layer should be at least about 0.5 mil or, more advantageously, about 0.6 or 0.75 or 1 mil thick. The total thickness of nickel in the two layers should be at least about 0.5 mil but most advantageously is at least about 1 mil, particularly when the coating is to be subjected to outdoor exposure. When composite coatings having layer thicknesses within the foregoing preferred ranges are employed, we have found that the results obtained are not only markedly superior to the results obtained utilizing conventional composites having a single layer of nickel, e.g., nickel-chromium composites, of comparable thickness, e.g., about 1 mil, but are comparable and often superior to conventional composites, e.g., nickel-chromium, of twice the thickness, e.g., about 2 mils. When intermediate, or interposed, layers (sandwiched between the nickel layers) comprised of cobalt, cobalt-nickel alloy or cobalt-tungsten alloy are employed in accordance with the invention, the resulting coatings are superior in corrosion resistance to conventional nickel-chromium coatings having the same thickness of nickel, and it is thus advantageous to use these metals for the intermediate layer to obtain the most satisfactory results. In many applications, composite coatings within the invention are superior for decorative and protective purposes to conventional nickel-chromium coatings having twice the thickness of nickel. The effectiveness of composite coatings having an interposed layer of cobalt or a cobalt-containing alloy increases as the thickness of the intermediate layer is increased up to 0.1 mil. When the thickness of the interposed cobalt and cobalt-containing alloy layers falls below the minima set forth herein, the beneficial influence of the composite coating is lost and the protective value of the composite coating drops to that of a single layer of nickel having the same thickness.

The nickel layers contemplated by the invention may be made of electrodeposited nickel obtained from plating baths of the conventional Watts type, or may be made of bright or semi-bright nickel deposited from baths containing the usual brighteners and/or levelers for enhancing the smoothness and appearance of the nickel electrodeposit. Nickel plating baths for producing nickel deposits satisfactory for use in the present invention contain

up to 400 grams per liter of nickel sulfate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$), up to 400 grams per liter of nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and up to 50 grams per liter (preferably 10 to 40 grams per liter) of a buffer such as boric acid. Those skilled in the art know that the essential ingredients of the Watts-type nickel plating bath are nickel sulfate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) and nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) which may be present in the bath in amounts of about 100 to about 400 grams per liter and of about 10 to about 60 grams per liter, respectively. The bath is operated in the pH range of about 1.5 to 6. Usually a buffering agent such as boric acid is included in the bath in an amount of up to about 50 grams per liter, e.g., about 10 to about 40 grams of boric acid per liter. A small amount (e.g., about 0.2 gram per liter) of a wetting agent such as a sodium lauryl sulfate is usually included in the bath to prevent undesirable pitting. Cathode current densities of about 20 to about 100 amperes per square foot are usually employed and the operating range of bath temperatures is about 115° to about 160° F. Nickel deposited from the Watts-type bath generally will require buffing before application of the final chromium plate to insure a fully bright appearance. Plating baths for plating bright nickel are of generally similar composition to the Watts-type bath and may, for example, contain about 25 to 300 grams per liter of nickel sulfate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) and 30 to 225 grams per liter of nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), with up to 50 grams per liter of boric acid as a buffer. Bright nickel baths include combinations of addition agents for producing a more lustrous and brighter deposit than is obtainable with the Watts-type bath. These addition agents generally include a combination of a wetting agent, a leveling and/or smoothing agent, a luster-producing agent and a stress-reducing agent. Bright nickel plating baths are discussed in *Modern Electroplating*, John Wiley and Sons, Inc., New York, 1953, at pages 311 to 318, and in many U.S. patents, including, e.g., Patents Nos. 2,191,813, 2,389,135, 2,524,619, 2,647,866 and 2,648,628.

Plating baths for producing semi-bright nickel are generally similar in composition to Watts-type baths and bright nickel baths and contain a leveling agent, such as coumarin and derivatives thereof, which contributes a leveling and scratch-covering property to the plate without introducing a high level of stress therein as may be the case with bright nickel. Semi-bright nickel plates are not as bright as the bright nickel plates but are more easily buffed than conventional Watts-type plates and are characterized by a high degree of smoothness. Nickel electrodeposits from the Watts-type bath generally have a hardness of about 140 to 160 Vickers, while bright nickel electrodeposits generally have a higher hardness which may be as high as about 500 Vickers.

Modern production conditions favor the use of bright or semi-bright nickel deposits since these deposits require no buffing or very little buffing as compared to the conventional gray or Watts-type nickel deposits. A particular embodiment of the invention wherein a satisfactory composite coating upon an underlying metal, e.g., steel, is provided without any mechanical polishing operation, e.g., buffing, includes the following steps: (1) prepare the underlying metal for plating, (2) deposit a layer of gray or Watts-type nickel thereon in a thickness as hereinbefore described, (3) deposit an intermediate layer of metal of the hereinbefore-described kind and thickness, (4) deposit a bright outer nickel layer of the hereinbefore-described thickness and (5) deposit an outer chromium layer over the said bright nickel layer. The aforescribed outer nickel layer may advantageously comprise a layer of semi-bright nickel applied over the intermediate layer in sufficient thickness to provide a good leveling action, e.g., about 0.5 mil, and a layer thereover of bright nickel to provide a bright finish upon which the final chromium layer may be applied. Alternatively, layers of bright nickel may be employed in accordance with the invention.

The invention also contemplates multi-layer coatings

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having a plurality of electrodeposited intermediate layers of the kind and thickness described hereinbefore and having a plurality of electrodeposited nickel layers having thicknesses as aforescribed. As an example, a multi-layer composite on steel comprising a layer on the steel of electrodeposited nickel 0.1 mil thick, a layer thereon of electrodeposited cobalt 0.1 mil thick, another layer of nickel 0.1 mil thick, a further layer of cobalt 0.1 mil thick, and an outer layer of nickel 1 mil thick, with a decorative coating of chromium 10-micro-inches thick is a satisfactory multi-layer composite in accordance with the invention.

In preparing the composite electrodeposited coatings in accordance with the invention, it is of the utmost importance that sound adhesion of each layer to each other layer be obtained.

In order to demonstrate the improved results achieved in carrying out the concepts of the present invention, an extensive testing program was conducted to establish the resistance of composite electrodeposited coatings within the invention and to compare the resistance to atmospheric corrosion of these composites with other composites outside the scope of the present invention and with control tests of conventional nickel-chromium electrodeposited coatings. In all cases a stain resistant chromium coating about 10 to 20 micro-inches thick was applied as the outer layer. Except where otherwise specified, the nickel layers employed were of the conventional Watts type or gray nickel. Data obtained as a result of this testing program is tabulated hereinafter in Tables I to VII. Testing was carried out both in an industrial atmosphere at Bayonne, New Jersey, and in a marine atmosphere at Kure Beach, North Carolina. The test specimens for the most part were electrodeposited upon panels of polished SAE 1010 steel in the form of $\frac{1}{8}$ " x 4" x 6" plates. One of the sets of test specimens comprised foils which were made by electrodepositing coatings to be tested on a highly polished cobalt-chromium alloy (such as is sold under the trademark "Stellite") starting sheet from which electrodeposited foils could easily be stripped. Conventional cleaning and plating methods well known to those skilled in the art were employed in the preparation of the test panels and foils. Thus, the steel panels were prepared for plating according to the following procedure.

(1) Polish the panels with grit belts, finishing with a 320-grit belt.

(2) Vapor degrease.

(3) Pumice scrub and hot water rinse.

(4) Cathodically clean in a solution of sodium carbonate containing 60 grams per liter Na_2CO_3 for 25 minutes at 160° F. and 25 amperes per square foot.

(5) Anodically clean the panels in the sodium carbonate solution for 5 minutes at 20 amperes per square foot.

(6) Dip in a solution containing 50% hydrochloric acid by volume for 30 seconds at 105°-115° F.

After exposure of the plated steel panels in the atmospheres and for the times indicated in the following tables, the panels were examined to compare the corrosion resistance of the coatings deposited thereon with each other and with the nickel-chromium control panels of the conventional type. The examination comprised a visual inspection wherein the panels were given a merit rating designating the relative order and the appearance of each panel, with the panel exhibiting the best appearance being designated by the numeral "1." In addition, the panels were rated according to the method recommended by the American Society for Testing Materials Committee B8, Subcommittee II, described in the Proceedings of the A.S.T.M., vol. 49 (1949), at pages 220 et seq. This method involves examination of the test panels to determine the corrosion-affected area and comparing the panels with standards so that a rating number up to 10 could be assigned thereto.

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The following comparison of percentage corrosion-affected area and rating numbers was employed in evaluating the panels described in Tables I to VII hereinafter:

Rating number :	Corrosion-affected area, percent
10	0
9	0.00-0.10
8	0.10-0.25
7	0.25-0.50
6	0.50-1.0
5	1.0-2.5
4	2.5-5.0
3	5-10
2	10-25
1	25-50
0	50-100

The results obtained in the testing program, as set forth in Tables I to VII, are as follows:

TABLE I

Tests of electrodeposits on steel exposed for 18 months in an industrial atmosphere. This set included composite electrodeposited nickel coatings of the sandwich type containing intermediate layers of cobalt, a cobalt-tungsten alloy containing about 15% tungsten, silver, palladium, lead, tin, copper, zinc, iron, a nickel-iron alloy containing about 16% iron, and a conventional nickel-chromium composite control panel (panel 9). All the coatings were deposited to a thickness of 1 mil to afford a comparison. It was found that, after exposure, the composites containing intermediate layers of cobalt, tin, palladium, cobalt-tungsten alloy and silver were markedly superior in all respects as compared to the conventional nickel-chromium deposit. On the other hand, the composites containing intermediate layers of zinc, iron-nickel alloy, copper and iron were inferior to the conventional nickel-chromium deposit.

TABLE II

Tests on electrodeposited foils exposed for 12 months in an industrial atmosphere. This set contained composite foils prepared to the same specifications as the composite coatings set forth in Table I. The foils were prepared upon a polished cobalt-chromium alloy starting sheet which was prepared for plating by vapor degreasing, pumice scrubbing, rinsing, cathodic cleaning at 50 amperes per square foot for 2 minutes at 160° F. in a solution containing 60 grams per liter of sodium carbonate, and rinsing. After plating, the foils were stripped from the starting sheet. After exposure, the foils were inspected by placing them against a strong light in a dark-room. A No. 2 photoflood bulb was used in a photographic printing box and the foil was masked to facilitate detecting and counting of the perforations. Examination of the foils after exposure established that the composites containing cobalt, cobalt-tungsten alloy, silver, tin and palladium were substantially more resistant to perforation as a result of corrosion than was the conventional nickel-chromium foil of the same thickness. It was observed that the foils containing intermediate layers of zinc, lead, iron-nickel alloy, copper and iron were badly perforated.

TABLE III

Steel panels having composite electrodeposited coatings exposed for 12 months to a marine atmosphere. This set included 1 mil thick composite electrodeposited coatings of the sandwich type including 0.1 mil thick intermediate layers of a cobalt-tungsten alloy containing about 15% tungsten, cobalt, tin, lead, palladium, silver and copper. Panels containing intermediate 0.3 mil thick layers of tin (panel 28) and of lead (panel 31) were also included. A panel having the conventional nickel-chromium electrodeposited coating of the same 1 mil thickness was also included (panel 35). Examination of these panels showed that all of the composite coatings within the invention were superior in corrosion

resistance to the conventional nickel-chromium electrodeposit.

TABLE IV

Tests in duplicate of coated steel panels for 12 months in an industrial atmosphere. This set included sandwich-type composite electrodeposited coatings containing intermediate layers of cobalt, tin and silver. All of the layers were deposited to a thickness of 1 mil and the thickness of the intermediate layer was varied between 0.01 and 0.1 mil. Control specimens of conventional nickel-chromium deposits having a thickness of 1 mil (panel 49) and 2 mils (panel 50) were included. A 1.5 mil composite coating containing an intermediate 0.1 mil layer of cobalt (panel 40) was also included. Inspection of the panels after exposure demonstrated that the composite coatings containing the intermediate layer of cobalt rated high on the visual inspection but the composites containing the thinner cobalt intermediate layers tended to be low on the A.S.T.M. rating since these composites tended to develop blisters. The composites containing the thicker (0.05 and 0.1 mil) cobalt intermediate layers were rated as good as, or better than, the conventional nickel-chromium control panels, even those having twice the nickel thickness. It was noted that the composites containing an intermediate layer of tin were prone to develop white stain spots, especially as the thickness of the tin intermediate layer was increased. The composite coatings containing an intermediate layer of silver 0.05 and 0.1 mil thick, respectively, demonstrated an improvement in performance as compared to the conventional nickel-chromium control panels having the same thickness.

TABLE V

Tests of coated steel panels for 12 months in a marine atmosphere. This set included 1 mil thick sandwich-type composite electrodeposited coatings containing intermediate layers of cobalt and tin varying in thickness from 0.01 mil to 0.1 mil. A 1.5 mil composite coating containing an intermediate layer of cobalt 0.1 mil thick (panel 55) was also included. Control steel panels having conventional nickel-chromium coatings 1 mil (panel 60) and 2 mils (panel 61) thick were also included. When the panels were examined after exposure it was found that all the composite coatings containing cobalt rated well on the visual examination and demonstrated an improved ability to prevent rusting of the underlying steel as compared to the conventional nickel-chromium control panels. Panel 55, the 1.5 mil thick composite coating, was rated best on the basis of appearance and protective value even as against panel 61, the conventional 2 mil thick coating. The blistering tendency of the composites containing the cobalt intermediate layer caused them to be rated low according to the A.S.T.M. system. The composite coatings containing the tin intermediate layers as thin as 0.025 mil demonstrated an improved protective effect as compared to the conventional nickel-chromium control panels.

TABLES VI AND VII

Tests in both the industrial (11 months) and the marine (10 months) atmosphere comparing, respectively, the corrosion resistance of sandwich-type composites on steel made, respectively, with bright nickel and with the standard Watts nickel. In the tests described in Table VI, cobalt in the thickness range from 0.01 mil to 0.1 mil was used as the intermediate layer in the sandwich-type deposits. In the tests described in Table VII, a cobalt intermediate layer 0.1 mil thick was included and in the tests described in both Tables VI and VII, a cobalt-nickel alloy intermediate layer 0.1 mil thick was included. The cobalt-nickel alloy contained about 50% nickel and in the test described in Table VI it was deposited in a bright condition while in the test described in Table VII it was deposited in the usual duller gray condition. Control steel

panels having a thickness of 1, 2 and 3 mils of bright nickel and of Watts nickel, respectively, and with the usual chromium outer coating, were employed in each series of tests.

The results of the tests indicated that bright nickel is generally as resistant to corrosion as Watts-type nickel. It was again observed that the sandwich-type protective and decorative deposits contemplated in accordance with the present invention, and containing cobalt or a cobalt-nickel alloy as the intermediate layer, displayed greatly improved corrosion resistance, both in the industrial and the marine atmosphere, as compared to a conventional type deposit having the same thickness.

All of the panels were examined in the as-exposed condition since this condition represents the appearance of the panels as they would be in use. Many of the panels were also cleaned and examined again. Cleaning improved the appearance of the panels but it was noted that, on re-exposure for a relatively short time, the conventional nickel-chromium control panels exhibited a much greater amount of rust staining than was the case with the composite coatings containing an intermediate layer embedded in the nickel as contemplated in accordance with the invention.

Table I

RESULTS OF EXPOSURE OF COMPOSITE ELECTRODEPOSITS ON STEEL TO BAYONNE ATMOSPHERE

Set No.—1
Panels—Not cleaned
Exposure—18 months

Final nickel layer buffed and chromium plated with 15 micro-inches of chromium

Panel No.	Order of depositing layers	Thickness, mils	Visual rating	ASTM rating
1.....	Ni-Co-Ni.....	.4-1-5	1	9.9
2.....	Ni-Sn-Ni ¹4-1-5	2	5.6
3.....	Ni-Sn-Ni.....	.4-1-5	3	4.8
4.....	Ni-Pd-Ni.....	.4-1-5	4	4.7
5.....	Ni-CoW-Ni.....	.4-1-5	5	8.7
6.....	Ni-Ag-Ni.....	.4-1-5	6	3.7
7.....	Ni-Pb-Ni.....	.4-1-5	7	3.5
8.....	Ni-Zn-Ni ²4-1-5	8	2.3
9.....	Nickel.....	.4-1-5	9	3.8
10.....	Ni-FeNi-Ni.....	.4-1-5	10	2.9
11.....	Ni-Cu-Ni.....	.4-1-5	11	0.9
12.....	Ni-Fe-Ni.....	.4-1-5	12	0

¹ Tin layer buffed.

² Heat treated after plating (2 hours at 300° F.).

Table II

CORROSION OF COMPOSITE ELECTRODEPOSITED FOILS IN BAYONNE ATMOSPHERE

Exposure—12 months
Foil taped on glass plates for exposure
Foil size—2" x 4.5"

Final nickel layer buffed and chromium plated with 0.00020 inch chromium

Panel No.	Order of depositing layers	Thickness, mils	Perforations ³	
			1	2
13.....	Ni-Co-Ni.....	.4-1-5	0	0
14.....	Ni-Sn-Ni ¹4-1-5	2	11
15.....	Ni-Sn-Ni.....	.4-1-5	4	6
16.....	Ni-Pd-Ni.....	.4-1-5	4	1
17.....	Ni-CoW-Ni.....	.4-1-5	0	0
18.....	Ni-Ag-Ni.....	.4-1-5	11	50
19.....	Ni-Pb-Ni.....	.4-1-5	630	1,440
20.....	Ni-Zn-Ni ²4-1-5	360	1,125
21.....	Nickel.....	.4-1-5	3,330	3,330
22.....	Ni-FeNi-Ni.....	.4-1-5	13,500	9,000
23.....	Ni-Cu-Ni.....	.4-1-5	1,746	250
24.....	Ni-Fe-Ni.....	.4-1-5	540	1,440

¹ Tin layer buffed.

² Heat treated after plating (2 hours at 300° F.).

³ Total perforations except where indicated.

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Table III

RESULTS OF EXPOSURE OF COMPOSITE ELECTRODE POSITS ON STEEL TO KURE BEACH ATMOSPHERE

Set No.—3
Panels—Not cleaned
Exposure—12 months
Panel size—4" x 8"
Steel—SAE 1010

Final nickel layer buffed and plated with 20 micro-inches of chromium

Panel No.	Order of depositing layers	Thickness, mils	Visual rating ¹	ASTM rating
25	Ni-Co-Ni	.4-1-5	1	5.1
26	Ni-Co-Ni	.4-1-5	2	6
27	Ni-Sn-Ni ²	.4-1-5	3	8.9
28	Ni-Sn-Ni	.2-3-5	4	10
29	Ni-Sn-Ni	.4-1-5	5	6.8
30	Ni-Pb-Ni	.4-1-5	6	3.9
31	Ni-Pb-Ni	.2-3-5	7	5.05
32	Ni-Pd-Ni	.4-1-5	8	2.7
33	Ni-Ag-Ni	.4-1-5	9	2.4
34	Ni-Cu-Ni	.4-1-5	10	2.1
35	Nickel	1	11	2

¹ Visual rating in order of merit with No. 1 best.

² Tin layer buffed.

Table IV

RESULTS OF EXPOSURE OF COMPOSITE ELECTRODE POSITS ON STEEL BY BAYONNE ATMOSPHERE

Set No.—4A and B
Panels—Not cleaned
Exposure—12 months

Final nickel layer buffed and plated with 10-12 micro-inches of chromium

Panel No.	Order of depositing layers	Thickness, mils	Visual rating ¹		ASTM rating	
			Set A	Set B	Set A	Set B
36	Ni-Co-Ni	.49-01-5	11	10	0	0
37	Ni-Co-Ni	.475-.025-5	9	4	0	3.8
38	Ni-Co-Ni	.45-.05-5	4	3	3.8	3.8
39	Ni-Co-Ni	.4-1-5	5	5	4.9	5.0
40	Ni-Co-Ni	.7-1-7	1	1	5.7	3.8
41	Ni-Sn-Ni	.49-01-5	10	11	3.1	3.1
42	Ni-Sn-Ni	.475-.025-5	3	9	5.9	3.6
43	Ni-Sn-Ni	.45-.05-5	2	2	5.8	5.8
44	Ni-Sn-Ni	.4-1-5	8	6	5.8	6.8
45	Ni-Ag-Ni	.49-01-5	15	14	1.9	2.2
46	Ni-Ag-Ni	.475-.025-5	14	15	1.9	2.2
47	Ni-Ag-Ni	.45-.05-5	12	12	3.1	2.8
48	Ni-Ag-Ni	.4-1-5	7	8	2.9	4.8
49	Nickel	1.0	13	13	2.7	2.2
50	Nickel	2.0	6	7	2.8	4.8

¹ Visual rating in order of merit, No. 1 being the best.

Table V

RESULTS OF EXPOSURE OF COMPOSITE NICKEL COATINGS ON STEEL TO KURE BEACH ATMOSPHERE

Set No.—6
Panels—Not cleaned
Exposure—12 months

Final nickel layer buffed and plated with 10-12 micro-inches of chromium

Panel No.	Order of depositing layers	Thickness, mils	Visual rating ¹	ASTM rating
51	Ni-Co-Ni	.49-01-5	4	3.9
52	Ni-Co-Ni	.475-.025-5	6	3.9
53	Ni-Co-Ni	.45-.05-5	3	4.2
54	Ni-Co-Ni	.4-1-5	5	5.1
55	Ni-Co-Ni	.7-1-7	1	6
56	Ni-Sn-Ni	.49-01-5	11	3
57	Ni-Sn-Ni	.475-.025-5	7	7.8
58	Ni-Sn-Ni	.45-.05-5	8	9
59	Ni-Sn-Ni	.4-1-5	9	9
60	Nickel	1.0	10	6.4
61	do	2.0	2	8.9

¹ Visual rating in order of merit, No. 1 being best.

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Table VI

COMPOSITE COATED STEEL PANELS MADE USING BRIGHT NICKEL

Final layer 10 micro-inches of chromium

Panel No.	Order of depositing layers	Thickness, mils	Bayonne (11 months), ASTM rating	Kure Beach (10 months), ASTM rating
62	Ni-Co-Ni	.4-1-5	9	4
63	Ni-Co-Ni	.45-.05-5	8	4.5
64	Ni-Co-Ni	.475-.025-5	9	4.5
65	Ni-Co-Ni	.49-01-5	9	8.5
66	Ni-Co-Ni-Ni	.4-1-5	8	4
67	Nickel	1.0	5	0
68	do	2.0	9	7
69	do	3.0	9	8

Table VII

COMPOSITE COATED STEEL PANELS MADE USING WATTS-TYPE NICKEL

Final nickel layer buffed and plated with 10 micro-inches chromium

Panel No.	Order of depositing layers	Thickness, mils	Bayonne (11 months), ASTM rating	Kure Beach (10 months), ASTM rating
70	Ni-Co-Ni-Ni	.4-1-5	8	7
71	Nickel	1.0	1	2
72	do	2.0	8	7.5
73	do	3.0	9	9.5

35 The electroplating baths and conditions of plating employed in producing the test panels described in Tables I to VII are as follows.

Watts-type nickel bath:

Plating composition—

NiSO ₄ ·7H ₂ O	300 g.p.l.
NiCl ₂ ·6H ₂ O	45 g.p.l.
H ₃ BO ₃	37.5 g.p.l.

Wetting agent (sodium salt of

lauryl sulfonic acid) 0.2 g.p.l.

Plating conditions—

Temperature	140° F.
pH	2.
Current density	50 a.s.f.

50 Bright nickel (Table VI):

Plating bath—

NiSO ₄ ·7H ₂ O	90 g.p.l.
NiCl ₂ ·6H ₂ O	206 g.p.l.
H ₃ BO ₃	37.5 g.p.l.

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Brightening agent (a mixture of saccharin, benzene sulfonamide and paratoluene sulfonamide) 6 g.p.l.

Luster-producing agent containing pyridinium and quinolinium compounds 1.25 ml./l.

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Wetting agent (a mixture of agents exemplified by a sodium salt of lauryl sulfoacetate and a sodium salt of monolauryl ether of ethylene glycol monosulfate) 5 ml./l.

Plating conditions—

Temperature	140° F.
pH	3.5.
Current density	50 a.s.f.

Residual corrected stress in deposit 7500 to 9500 p.s.i. (compressive).

Chromium:	
Plating bath—	
CrO ₃	250 g.p.l.
SO ₄	2.5 g.p.l.
Plating conditions—	
Temperature	113° F.
Current density	144 a.s.f.
Cobalt:	
Plating composition—	
CoSO ₄ ·6H ₂ O	450 g.p.l.
CoCl ₂ ·6H ₂ O	40 g.p.l.
Na ₂ BO ₃	40 g.p.l.
Plating conditions—	
Temperature	130° F.
pH	4.2.
Current density	25 a.s.f.
Anodes	Electrolytic cobalt.

Before the outer nickel layer was deposited on the cobalt layer, the latter was given a cold water rinse.

Cobalt-tungsten alloy:	
Plating composition—	
CoCl ₂ ·6H ₂ O	102 g.p.l.
Na ₂ WO ₄ ·2H ₂ O	45 g.p.l.
NaKC ₄ H ₄ O ₆ ·4H ₂ O	400 g.p.l.
NH ₄ Cl	50 g.p.l.
Plating conditions—	
Temperature	195° F.
pH	8.5-9.
Current density	10 a.s.f.
Anodes	Electrolytic cobalt.
Agitation	Mechanical stirrer.

Before the outer nickel layer was deposited on the cobalt-tungsten alloy layer, the latter was given a cold water rinse.

Cobalt-nickel alloy plating:	
Plating bath for dull plate—	
NiSO ₄ ·7H ₂ O	185 g.p.l.
NiCl ₂ ·6H ₂ O	44 g.p.l.
CoSO ₄ ·7H ₂ O	143 g.p.l.
H ₃ BO ₃	37.5 g.p.l.
Wetting agent sodium salt of lauryl sulfonic acid)	0.2 g.p.l.
Plating conditions—	
Temperature	140° F.
pH	2.0.
Current density	50 a.s.f.
Anode	Electrolytic nickel.
Deposit appearance	Dark matte.
Analysis of deposit	53.3% cobalt.

Plating bath for bright plate—	
Same composition as for dull plate but added—	
Brightening agent (a mixture of saccharin, benzene sulfonamide and paratoluene sulfonamide)	6 g.p.l.
Luster-producing agent containing pyridinium and quinolinium compounds	1.25 ml./l.
Wetting agent (a mixture of agents exemplified by a sodium salt of lauryl sulfoacetate and a sodium salt of monolauryl ether of ethylene glycol mono-sulfate)	5 ml./l.

Plating conditions—	
Temperature	140° F.
pH	4.5.
Current density	50 a.s.f.
Anode	Electrolytic nickel.
Deposit bright and analyzed 44.83% cobalt.	
Tin:	
Plating composition—	
SnSO ₄	75 g.p.l.
H ₂ SO ₄ (free)	100 g.p.l.
Cresol sulfonic acid	100 g.p.l.
Glue	1 g.p.l.
Plating conditions—	
Temperature	76° F.
Current density	11 a.s.f.
Anodes	Banka tin.
Before the outer nickel layer was deposited on the tin layer, the latter was given a cold water rinse.	
A silver strike was first applied	
Silver:	
Silver strike solution—	
AgCN	5 g.p.l.
Ag	4 g.p.l.
NaCN	75 g.p.l.
Silver strike conditions—	
Temperature	76° F.
Current density	20 a.s.f.
Anodes	Silver.
Time	30 seconds.
Plating composition—	
AgCN	30.3 g.p.l.
Ag	24.6 g.p.l.
KCN	54.8 g.p.l.
K ₂ CO ₃	45 g.p.l.
Plating conditions—	
Temperature	76° F.
Current density	10 a.s.f.
Anodes	Silver.
Before the outer nickel layer was deposited on the layer of silver, the latter was subjected to a cold water rinse.	
Palladium:	
Plating solution—	
Catholyte—	
[Pd(NH ₃) ₄]Cl ₂	40 g.p.l.
NH ₄ OH	35 cc./l.
NH ₄ Cl	10 g.p.l.
Anolyte—	
(NH ₄) ₂ CO ₃	10 g.p.l.
(NH ₄) ₂ SO ₄	20 g.p.l.
NH ₄ OH	50 cc./l.
Plating conditions—	
Temperature	70° F.
pH	9-10.
Current density	7 a.s.f.
Anodes	Platinum sheets.
Diaphragm	Porous Alundum cup.
Before the outer nickel layer was deposited on the layer of palladium, the latter was given a cold water rinse.	
Lead:	
Plating composition ¹ —	
Lead	32 oz./gal.
Lead fluoborate	59 oz./gal.
Boric acid	3.8 oz./gal.
Hydrofluoric acid (free)	5.4 oz./gal.
Plating conditions—	
Temperature	76° F.
Current density	16.5 a.s.f.
Anodes	Chemical lead.
¹ Composition diluted in half with distilled water and 0.1 g.p.l. of glue added.	
Before the outer nickel layer was deposited on the layer	

of lead, the latter was subjected to the following pre-treatment: (1) water rinsed, (2) anodically treated in alkaline solution for 15 seconds at 6 volts and at a temperature of 76° F. The solution contained 50 g.p.l. of NaOAc.

The present invention is particularly applicable to providing composite electrodeposited coatings on structural metals which are susceptible to atmospheric attack when exposed by themselves. Such foundation metals are copper, zinc, aluminum, brass, etc., and alloys such as steel, e.g., carbon steels and low alloy steels containing phases associated with alpha iron, etc. The composite electrodeposits of the invention are suitable for use in both industrial and marine atmospheres.

Although the phenomena underlying the improved results which are obtained in carrying out the present invention are very complicated and are not fully understood, it is believed that the improvements flowing from the present invention are related to the use as the intermediate layer of the special composite coating a metal having a definite galvanic relationship to nickel. Thus, metals such as zinc, iron and iron-nickel alloys are too strongly anodic to nickel and are unsatisfactory for purposes of the present invention. Copper also is unsatisfactory for purposes of the present invention, although the electrochemical explanation therefor is obscure. Thus, copper appears to act cathodically to nickel at some times and anodic at other times.

The beneficial effects brought about by the invention are not explainable on the simple basis of interrupting the continuity of the nickel coating, although this factor is involved. The available data indicate that the kind of metal used in the intermediate layer and the thickness of the intermediate layer are of primary importance in carrying out the invention to produce protective and decorative electrodeposited coatings having a thickness of about 1 mil, e.g., at least about 0.25 mil to 3 or 4 mils. The data also indicate that the metals cobalt, alloys thereof with tungsten and nickel, lead, tin, silver and palladium meet the requirements for producing improved results in composite electrodeposited decorative and protective coatings in accordance with the invention.

The preferred composite or "sandwich" electrodeposited coatings described hereinbefore are satisfactory for the usual commercial applications such as automotive bumpers and trim where a protective and/or decorative coating resistant to atmospheric corrosive effects is required. Other applications include trim and outer shells for electrical appliances and the like, metal furniture, etc., where a bright, attractive metal finish which is durable in service is required.

Metal coatings, e.g., nickel coatings, for use in accordance with the invention advantageously are produced by electrodeposition. However, it is to be understood that chemically deposited nickel coatings and cobalt coatings such as those described in the Brenner et al U.S. Patents Nos. 2,532,283 and 2,532,284, coatings produced by high vacuum vaporizing and by thermal decomposition of metal carbonyls, such as nickel carbonyl, may also be employed to produce metal layers in accordance with the invention.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. As a new article of manufacture, a metal article having firmly bonded to the surface thereof a protective and decorative composite metal coating, said coating consisting of a foundation layer of nickel about 0.1 to about 2 mils thick deposited on said metal surface, an electro-

deposited metal layer of cobalt with up to 20% tungsten and up to 90% nickel about 0.01 mil to about 0.3 mil thick applied to said nickel layer, a layer of nickel about 0.5 to 2 mils thick applied to said metal layer, and an outer decorative layer of electrodeposited chromium, said composite coating being characterized by an improved decorative and protective effect as compared to a coating having a single nickel layer of the same thickness.

2. As a new article of manufacture, a metal article having firmly bonded to the surface thereof a protective and decorative composite metal coating, said coating consisting of a foundation layer of nickel about 0.1 to about 2 mils thick deposited on said metal surface, an electrodeposited cobalt layer about 0.01 to about 0.1 mil thick applied to said nickel layer, a layer of nickel about 0.5 to 2 mils thick applied to said cobalt layer, and an outer decorative layer of electrodeposited chromium, said composite coating being characterized by an improved decorative and protective effect as compared to a coating having a single nickel layer of the same thickness.

3. As a new article of manufacture, a metal article having firmly bonded to the surface thereof a protective and decorative composite metal coating, said coating consisting of a foundation layer of nickel about 0.1 to about 2 mils thick deposited on said metal surface, a layer of electrodeposited dissimilar metal about 0.01 mil to about 0.3 mil thick from the group consisting of tin, lead, silver, palladium, cobalt and alloys of cobalt with up to 20% tungsten and up to 90% nickel applied to said nickel layer, a layer of nickel about 0.5 to 2 mils thick applied to said dissimilar metal layer, and an outer decorative layer of electrodeposited chromium, said composite coating being at least about 0.25 mil thick and being characterized by an improved decorative and protective effect in the deposited condition as compared to a coating having a single nickel layer of the same thickness.

4. As a new article of manufacture, a metal article having firmly bonded to the surface thereof a protective and decorative composite metal coating at least about 1 mil and up to about 4 mils thick, said coating consisting of a plurality of electrodeposited nickel layers wherein the outermost nickel layer is about 0.1 to 2 mils thick and at least one intermediate layer of electrodeposited dissimilar metal from the group consisting of tin about 0.05 to about 0.3 mil thick, lead about 0.1 to about 0.3 mil thick, silver about 0.05 to about 0.2 mil thick, palladium about 0.05 to about 0.2 mil thick, cobalt about 0.01 to about 0.1 mil thick, an alloy of cobalt with up to 20% tungsten about 0.05 to about 0.2 mil thick and an alloy of cobalt with up to 90% nickel about 0.1 to about 0.3 mil thick adherently contacting two of said nickel layers, said composite coating being characterized by an improved protective and decorative effect in the deposited condition as compared to a coating having a single nickel layer of the same thickness.

5. In the method for applying a protective and decorative composite metal coating upon a metal article, the improvement which consists of depositing a nickel layer about 0.1 to 2 mils thick upon a metal article, electrodepositing a dissimilar metal layer from the group consisting of tin about 0.05 to about 0.3 mil thick, lead about 0.1 to about 0.3 mil thick, silver about 0.05 to about 0.2 mil thick, palladium about 0.05 to about 0.2 mil thick, cobalt about 0.01 to about 0.1 mil thick, alloys of cobalt with up to about 20% tungsten about 0.05 to about 0.2 mil thick and alloys of cobalt with up to 90% nickel about 0.1 to about 0.3 mil thick upon said nickel layer and depositing a nickel layer about 0.5 to about 2 mils thick upon said dissimilar metal layer to provide a coated metal article having a composite protective and decorative coating characterized by an improved protective and decorative effect as compared to a similar metal article having thereon a single nickel layer of the same thickness.

6. In the method for applying a protective and decorative composite metal coating upon a metal article, the

improvement which consists of depositing a nickel layer about 0.1 to about 2 mils thick upon said article, electrodepositing upon said nickel layer a layer of dissimilar metal about 0.01 to about 0.3 mil thick from the group consisting of tin, lead, silver, palladium, cobalt and alloys of cobalt with up to 20% tungsten and up to 90% nickel, depositing a nickel layer about 0.5 to about 2 mils thick upon said dissimilar metal layer and depositing an outer chromium layer about 10 to 20 micro-inches thick upon the composite coating to provide a coated metal article having a composite protective and decorative coating characterized by an improved decorative and protective effect as compared to a similar coated article having a single nickel layer of the same total nickel thickness.

7. In the method for applying a decorative and protective composite metal coating upon a metal article, the improvement which consists of depositing a nickel layer about 0.1 mil to about 2 mils thick upon said article, electrodepositing upon said nickel layer an intermediate layer about 0.01 to about 0.3 mil thick of cobalt with up to 20% tungsten and up to 90% nickel, depositing on said intermediate layer a nickel layer about 0.5 to about 2 mils thick, depositing an outer chromium layer to provide a decorative and protective composite coating characterized by an improved decorative and protective effect in the deposited condition as compared to a coating having a single nickel layer of the same total nickel thickness.

8. In the method for applying a protective and decorative composite metal coating upon a metal article, the improvement which consists of depositing a nickel layer about 0.1 to 2 mils thick upon a metal article, electrodepositing a cobalt layer about 0.01 to about 0.1 mil thick upon said nickel layer, depositing a nickel layer about 0.5 to about 2 mils thick upon said cobalt layer and depositing an outer chromium layer about 10 to 20 micro-inches thick to provide a coated metal article having a composite protective and decorative coating characterized by an improved effect as compared to a similar metal ar-

article having thereon a single nickel layer of the same total thickness.

9. As a new article of manufacture, a metal article having firmly bonded to the surface thereof a composite metal coating at least about 1 mil and up to about 4 mils thick, said coating consisting of a plurality of electrodeposited nickel layers wherein the outermost nickel layer is about 0.1 to 2 mils thick, and at least one electrodeposited intermediate layer about 0.05 to about 0.2 mil thick of a cobalt-tungsten alloy containing about 10% to 20% tungsten and the balance essentially cobalt adherently contacting two of said nickel layers, said composite coating being characterized by an improved protective effect in the deposited condition as compared to a coating having a single nickel layer of the same total thickness.

10. As a new article of manufacture, a metal article having firmly bonded to the surface thereof a composite metal coating at least about 1 mil and up to about 4 mils thick, said coating consisting of a plurality of electrodeposited nickel layers wherein the outermost nickel layer is about 0.1 to 2 mils thick, and at least one electrodeposited intermediate layer about 0.1 mil to about 0.3 mil thick of a cobalt-nickel alloy containing about 50% to 90% nickel with the balance essentially cobalt adherently contacting two of said nickel layers, said composite coating being characterized by an improved protective effect in the deposited condition as compared to a coating having a single nickel layer of the same total thickness.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,009,238

November 21, 1961

Waclaw A. Wesley et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 10, for "10-micro-inches" read -- 10 micro-inches --; lines 21 and 22, for "atmosphereic" read -- atmospheric --; column 7, line 11, for "speciments" read -- specimens --; line 29, for "sliver" read -- silver --; line 57, for "protactive" read -- protective --; column 11, line 50, insert an open parenthesis before "sodium"; line 59, for "53.3% co." read -- 53.3% co- --; line 68, for "pyrodinium" read -- pyridinium --.

Signed and sealed this 1st day of May 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents