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ELECTRODEPOSITION OF A MICRO-CRACKED CORROSION RESISTANT NICKEL-CHROMIUM PLATE

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8 Claims

ABSTRACT OF THE DISCLOSURE

A method of electroplating, comprising depositing on a basis metal at least three successive layers including, an underlying nickel electroplate, an overlying nickel strike electroplate, and a top bright chromium layer. A critical feature of the invention is that the nickel bath from which the overlying nickel strike is electrodeposited must be a high-chloride bath, and must contain at least one amino acid selected from the group consisting of amino carboxylic acids, amino sulfonic acids, and amino phosphonic acids. The nickel strike causes the overlaying thin chromium plate to develop a porous and finely micro-cracked structural pattern. The nickel strike bath may additionally contain insoluble fine powders which are deposited with the nickel strike and occluded therein.

This invention relates to the improvement of the corrosion protection afforded to underlying commercial basis metals such as steel, brass, copper, zinc die cast, magnesium, etc., by electrodepositing thereon certain composite decorative electroplates of nickel and chromium. More particularly, it relates to the use of certain composite nickel electroplates having a fine "nickel strike" layer as a critical part of the nickel composite, followed by a final chromium plate to impart maximum corrosion protection to the underlying metal.

As early as 1958 it was known that the use of a thin nickel plate of a columnar or partial columnar structure on top of bright nickel plate followed by the usual chromium plate of about 0.01 mil thickness made possible enhanced corrosion results as measured by The Standard Corrodokote test, see H. Brown, et al., "Corrosion Studies With Nickel-Chromium Plate," Plating, vol. 45, p. 149 (1958). For a description of the Corrodokote test see Pinner, "Accelerated Corrosion Tests," Plating, vol. 44, p. 763 (1957). Without the thin flash of nickel plate of columnar or partial columnar structure, the same underneath bright nickel plate with the same final chromium plate fails the Corrodokote test. As stated in the Brown et al. reference, the flash plate could be dull nickel, semi-bright nickel or a low pH nickel strike up to a thickness that does not unduly dull the underneath bright nickel plate. In practice, the difficulty with this particular system of composite nickel plate is the tendency for dulling of the high current density areas of complex shaped parts before the low current density areas are sufficiently covered to provide the desired corrosion protection. On simpler shaped objects, this is less of a problem.

A later paper (Proceedings of the American Electroplaters' Society, vol. 50 (1963), p. 169) disclosed that if very fine particles such as barium sulfate, silica, zirconium silicate, etc., are dispersed in semi-bright nickel baths, there is extensive co-deposition of these fine, discrete particles along with the nickel plate. Upon electrodeposition of a final thin chromium plate over this surface, a very fine porosity pattern is developed in the thin chromium plate which makes possible enhanced cor-

2

rosion protection. That is, a very fine, dense porosity pattern or a "micro-cracked" pattern in the final chromium plate leads to much improved corrosion protection as compared to a medium dispersion of pores in the final chromium. This at first anomalous appearing result was explained in the 1958 Brown et al. article.

One of the problems with the co-deposition of the very fine bath-insoluble non-metallic particles is that there is much less co-deposition of particles from an acidic, high-chloride bath (containing over about 150 grams/liter of nickel chloride) than from Watts baths (high nickel sulfate content). Unfortunately, it is from the acidic, high-chloride nickel baths that the best adhesion can be obtained to an underlying nickel plate under adverse conditions, such as long transfer time, trace bi-polar effects and highly passive nickel surfaces.

It is an object of this invention to provide a method of depositing a composite electroplate on basis metals to impart superior corrosion protection thereto. Another object is to provide decoratively, electroplated articles having enhanced corrosion resistance. Still another object is to provide a nickel strike plate which does not unduly dull an underlying bright nickel electrodeposit and which causes the overlying thin chromium plate to develop a porous and finely micro-cracked structural pattern.

The foregoing and other objects are accomplished by the use of the method of this invention which broadly comprises electrodepositing as the essential layers:

- (1) an underlying nickel plate
- (2) an intermediate thin nickel strike layer deposited from an acidic, high-chloride nickel bath containing dissolved therein an effective amount of at least one amino acid, and
- (3) a top, bright chromium layer.

As will be described hereinafter, with a preferred embodiment of this invention, corrosion resistance of the basis metals is further enhanced by the dispersion of certain bath-insoluble powders in the high-chloride nickel strike bath.

In the practice of the instant invention, it is essential that a thin nickel strike be electrodeposited on an underlying nickel electroplate, which underlying nickel plate may itself be deposited either on the basis metal, or on one or more intermediate layers of electroplates of nickel, copper, yellow brass, white brass, etc. In general, the underlying nickel plate may be deposited from any conventional semi-bright or bright nickel plating bath. Of course, if bright, decorative electroplates are desired, the directly underlying plate should be bright nickel. While the invention will hereinafter be described in terms of utilizing a bright nickel underlying plate, it is understood that enhanced corrosion resistance can also be obtained if such underlying nickel plate is deposited from a semi-bright plating bath.

In general, the underlying nickel plate beneath the nickel strike plate should be at least about 0.3 and preferably 0.8 to 1 mil thick if it is the sole underlying plate. If a copper or brass plate of at least 0.2 or 0.3 mil thickness is present underneath the bright nickel plate, excellent corrosion results can be obtained with a nickel plate of about 0.6 mil thick. If a double, or duplex nickel plate consisting of at least 50% semi-bright relatively "sulfur-free" nickel, followed by bright nickel plate containing a substantially higher sulfur content is used, then a total thickness of even 0.5 mil nickel underneath the thin nickel strike gives excellent corrosion protection results. Even further corrosion improvement can be obtained if the underlying nickel plate is tri-layered wherein a thin layer of nickel plate of higher sulfur content than the bright nickel plate is sandwiched between the bottom

semi-bright and top bright nickel layers. For best corrosion protection, especially in severe industrial atmosphere, it is preferred that the total nickel plate be about one mil in thickness plated on top of 0.5 to 1.0 mil of a copper electroplate. Using much more than 3 mils total nickel plate would in general be wasteful for most decorative uses even in the most severe marine or industrial atmospheres.

After the underlying nickel plate as described above has been deposited on the basis metal, there is electrodeposited thereon, a thin nickel strike having a thickness of from about 0.005 to about 0.4 mil from a high-chloride bath. This latter step constitutes a critical step in the practice of the present invention. The high-chloride baths of this invention contain as an essential constituent an amino acid as will hereinafter be defined. Other agents well-known to the art may be present in such baths including other nickel salts, buffers, wetting agents, etc. As used herein, the term "high-chloride bath" denotes a plating bath containing from about 150 to 500 grams/liter of nickel chloride calculated as $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and having a pH of less than about 6. These baths may be operated at temperatures of from about 50 to 160° F. The amino acids of the invention added to such baths throughout this pH and temperature range enhance the corrosion properties of the final composite plate by improving the micro-crack pattern of the top chromium plate. However, we have found that at the higher pH levels of about 2 and temperatures above 110° F., in those cases where the underlying nickel plate is a bright nickel, there is a tendency toward haze formation. In these situations, it is preferred to use the amino acids in combination with the well-known secondary brighteners such as chloral hydrate, formaldehyde, coumarin, etc. and/or primary brighteners such as aryl sulfonic acids or sulfonamides or sulfonimides such as sulfobenzaldehydes, benzene or naphthalene sulfonic acids, benzene sulfonamides or sulfonimides such as o-benzoylsulfonimide, or the aliphatic unsaturated sulfonic acids, vinyl or allyl sulfonic acids, vinyl or ethynyl benzene sulfonic acids to obtain a full bright plate.

With a preferred embodiment of the invention, decorative, bright electroplates are obtained by utilizing a bright nickel as the underlying nickel plate and a nickel strike is deposited thereon from a bath of this invention preferably at a pH of below 2 and operated at a temperature of from about 50° to 110° F. Under these conditions, using the amino acids, there is obtained a bright nickel strike of excellent adhesion on top of the underlying bright nickel without dulling or hazing at the end of 3 to about 10 minutes of plating time at 40–50 amperes/sq. ft. especially if good solution agitation is used. A top chromium plate is then deposited thereon and a full bright composite plate having superior corrosion properties is obtained.

While any of the nickel strike baths of this invention may have any of the conventional brighteners included therein, it is preferred that the use of sulfur containing materials be restricted so that the intermediate nickel strike plate has a sulfur concentration lower than that of the underlying bright nickel plate. If the sulfide sulfur content of the nickel strike plate is higher than the underneath nickel layer, the strike plate would corrode preferentially under saline conditions such as salted winter streets causing unsightly surface pits. Moreover, if high concentrations of cobalt salts are also present in the nickel strike baths containing aryl sulfonic, sulfonamide, or sulfonimide brighteners, the tendency to form surface pits is greatly increased in both marine and industrial atmospheres. Further, considering that the percentage of sulfur deposited from baths containing sulfon-compounds increases with a decreasing pH, it is best to restrict or eliminate the presence of these sulfon compounds in baths operated at a pH level of below 2.

Since greatest utility for the present invention is found

in the decorative field, the intermediate nickel strike must not be too thick as to dull the underlying bright nickel plate. If a conventional plain nickel bath were used to deposit the strike, the underlying bright nickel plate would become hazy after a plating time of one or two minutes at an average current density of 40–50 amps/sq. ft. However, using the amino acid addition agents of this invention, a strike plate of up to 10 minutes or over to obtain a plate thickness of up to 0.4 mil thickness can be utilized without dulling, especially if the bath is operated at temperatures below about 110° F. Utilizing a strike plate of greater thickness than that defined above does not result in a further enhancement of corrosion protection, but may cause dulling unless the conventional brighteners are added thereto. However, it is preferred to utilize strike plate having a thickness within the foregoing limits and deposited from a bath containing an amino acid but free from conventional secondary brighteners. The presence of such brighteners (the non-sulfur containing secondary brighteners) has a tendency to reduce adhesion and makes the bath more difficult to operate.

A critical requirement in the practice of the present invention is that the high-chloride bath from which the nickel strike is electrodeposited must contain an amino acid selected from the group consisting of amino-carboxylic acids, amino-sulfonic acids and amino-phosphonic acids, wherein the number of acid groups are equal to or greater than the number of amino groups in said amino acid molecule. These acids may be aliphatic, cyclo-aliphatic, heterocyclic or aromatic and may contain other functional groups such as hydroxyl, nitro, cyano, halogen, etc. The foregoing groups have only minimum effect on the effectiveness of the amino acids, and for purposes of this invention, it is only necessary that the amino acid have at least one amino group and one acid group which may be carboxylic, sulfonic or phosphonic, and that the number of acid groups is equal to or greater than the number of amino groups. The acids may contain multiple amino groups and/or acid groups which acid groups may be the same or different. Since nitro groups are easily reduced to amino groups in an acidic plating bath, as used herein, the term amino group will be understood to encompass nitro groups. Further, it is understood that the term amino, as used herein, shall include groups such as



as are found in heterocyclics such as pyridine, quinoline, etc.

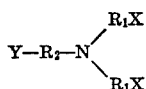
The concentration of the amino acid is, in general, not sharply critical, though each acid has its optimum range, and in case of the aliphatic amino acids such as ethylenediaminetetraacetic acid and nitrilotriacetic acid, amounts up to saturation concentration can be used. We have found that from about 0.2 to 50 grams/liter is a preferred amount for most applications using the aliphatic amino acids, whereas with heterocyclic amino acids such as nicotinic acid, optimum results are obtained with as little as 0.1 to 2 grams/liter.

Specific examples of some of the usable amino acids include picolinic acid, proline, pyridine dicarboxylic acids, picolene dicarboxylic acids, pyridine tricarboxylic acids, the amides of these acids, N-aceto pyridinium chloride, N-sulfopropene pyridinium sulfone, N-sulfoethane pyridinium chloride or bromide, anthranilic acid, sulfanilic acid, p-amino benzoic acid, sulfonylamide, aminonaphthoic acids, etc. These aryl and heterocyclic amino acids require only small concentrations around 0.1 to 2 grams/liter for optimum results, and especially beneficial are the carboxylic derivatives of pyridine and picolines such as nicotinic acid. It is to be understood that the sulfonamide group is slightly acidic and is here considered as an acidic group.

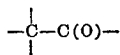
One group of amino acids usable in the high-chloride, nickel strike bath of this invention are amino acids containing at least one acid group and wherein the number

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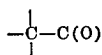
of acid groups is equal to or greater than the number of amino groups having the following formula:



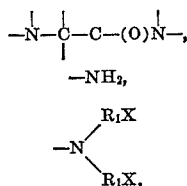
wherein R_1 in each instance is the same or different and is hydrogen, or alkyl or alkylene groups containing from one to about eight carbon atoms; when R_1 is alkylene, X in each instance is the same or different and is $-OH$, $-COOH$, $-SO_2OH$, $-P(O)(OH)_2$; R_2 is hydrogen,



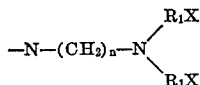
or an alkyl, cyclo-alkyl, alkylene, aryl, arylen, alkanol or cyclo-alkylene group containing up to about eight carbon atoms; when R_2 is alkylene, cyclo-alkylene, arylen or



then Y is H ,

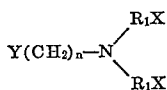


or



wherein X and R_1 are as previously defined, and n is an integer from 1 to 6.

Another preferred group of amino acids, as constituents of the high-chloride nickel strike plating baths of this invention, are amino acids containing at least one acid group wherein the number of acid groups is equal to or greater than the number of amino groups having the following formula:



wherein R_1 in each instance is the same or different and is hydrogen or an alkylene group containing from one to about six carbon atoms, when R_1 is alkylene the attached X is $-COOH$; Y is NH_2 , $-COOH$, $-OH$ or



wherein R_1 and X are as just defined, and n is an integer from 1 to 6.

Examples of the amino acids usable in the nickel strike baths of the present invention include nitrilotriacetic acid (ammoniatricetic acid), N-hydroxyethyliminodiacetic acid, N-dihydroxyethyl-glycine, glutamic acid, glycine, glycyglycine, glycyglycyglycine, asparatic acid, 1, 2-diaminocyclohexanetetraacetic acid, alanine, taurine, N-methyltaurine, amino ethane phosphonic acid, asparagine and aminino-ethane sulfonamide. Amino acids which are highly preferred are ethylenediaminetetraacetic acid (EDTA), N,N' - ethylenediaminediacetic acid (EDDA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), N,N' - dihydroxyethylenediaminediacetic acid (HEDDA) diethylenetriaminepentaacetic acid (DTPA), picolinic acid and nicotinic acid.

The final essential step in the practice of the present method is the electrodeposition of a chromium layer on

6

top of the thin nickel strike layer as defined above. Any chrome bath known to the industry may be used for this purpose. Thus the conventional chromium plating baths containing 150-350 grams/liter of CrO_3 and containing only the sulfate ion as catalyst may be used. One preferred type of chromium plating bath is one with a chromic acid content of about 200-250 grams/liter and with CrO_3 to SO_4 ratio of about 150-170 to one, and having dissolved therein a fluosilicate ion content of about 0.4 gram/liter calculated as fluoride ion. The thickness of chromium plate is not critical and may vary within the range used by the industry as from about 0.005 to 0.050 mil thickness.

By the use of the present method including the use of the specified amino acids in the nickel strike bath, a very significant improvement in the corrosion protection afforded to basis metal is obtained. The presence of the amino acid in the nickel chloride strike bath enhances the corrosion protection of the basis metal by indirectly causing a more uniform porosity in the final thin chromium plate, especially in the medium and lower current density areas. Just how the amino acid makes this marked improvement possible is not clear, but they do cause increased micro-stress in the nickel strike plate which is communicated to the overlying chromium plate without loss of adhesion. Further, the presence of the amino acids in the strike baths causes an increase in the amount of co-deposition of the fine, insoluble powders (as described hereinafter) that may be present in the high-chloride baths. It does not appear that sequestration of ions, as is the classical role of such amino acids as EDTA, is involved. For example, citric acid, a well-known sequestering agent is ineffective for the purpose of this invention.

With a preferred embodiment of this invention, certain bath insoluble organic and inorganic materials in the form of fine powders are dispersed in the high-chloride nickel strike bath. These particles are co-deposited with the thin nickel strike and are occluded in the final nickel electroplate. Inclusion of these powders permits a more uniform porosity pattern in the final chromium plate, thereby resulting in maximum corrosion protection. Examples of the inorganic bath insoluble powders are described in our Patents 3,152,971, 3,152,972 and 3,152,973 assigned to the same assignee hereof. As used in the baths of the present invention, these co-deposited powders may have a particle size of up to about 10 microns and preferably less than about 5 microns in diameter and can be included in baths in a concentration of from about 0.2 to 500 grams/liter, preferably from 10 to about 50 grams/liter. The inorganic particles as described in the foregoing patents include, insoluble sulfates, carbonates, phosphates and oxalates of barium, strontium and calcium; silicates of aluminum, magnesium, boron, zirconium, calcium, barium and strontium and mixed silicates thereof; carbides of silicon, boron, and titanium; oxides of silicon, manganese, titanium, zirconium, aluminum, cerium, iron chromium; fluorides of calcium, strontium and barium etc.

The bath insoluble organic resin particles which are also useable in the nickel strike baths of this invention are described in our co-pending application Ser. No. 421,623 filed Dec. 28, 1964, now Patent No. 3,356,467 and include the group of resins consisting of saran, nylon, polyolefins, polyphenyleneoxide, acrylonitrile-butadiene-styrene polymers, acetal polymers, polyvinylchloride polymers, and mixtures thereof.

Much better corrosion protection is obtained when the fine bath insoluble powders are used in a high-chloride strike bath containing an amino acid as compared to Watts (high sulfate) nickel strike baths or the high-chloride bath without the amino acid. For example, outdoor corrosion tests were carried out on identical test panels wherein three duplicate sets of panels had a composite plate thereon of 0.8 mil of an underlying bright

nickel followed by an intermediate thin nickel strike, and a top layer of about 0.01 mil of chromium plate. The plating procedure for these panels was the same except that the composition of the nickel strike bath was varied. The nickel strike bath compositions from which the strike was deposited on panels A, B and C were as follows:

- (A) High-chloride bath containing 15 grams/liter of ethylenediaminetetraacetic acid (EDTA) and 50 grams/liter of fine silica powder of 0.01 to 0.05 micron particle size.
 (B) High-chloride bath containing silica powder as in (A), but without EDTA
 (C) High-sulfate Watts bath containing 50 grams/liter of fine silica powder as in (A) but without EDTA.

Also included in the test was a fourth panel, (D) which was plated with 0.8 mil of an underlying bright nickel followed by a top layer of about 0.01 mil of chromium as with panels A, B and C, but no intermediate nickel strike was used.

After eight months of marine exposure at Kure Beach, test panels A were markedly superior in both corrosion properties and general appearance to all other panels, especially as compared with panels B and D.

With other bath insoluble non-metallic powders of larger particle size than the above fine silica, as for example zirconium silicate of about 2 microns average diameter (0.05 to 5 micron particles), there is the added beneficial factor of more extensive co-deposition of these larger particles. This results in an increase in the micro-stress around the particles and an increase in micro-stress cracking in the final thin chromium layer. This latter result is most easily seen when the final chromium plate is from the so-called crack-free bright chromium plating baths, and less easily seen in the plates obtained from chromium plating baths that micro-stress crack of themselves, i.e., dilute hexavalent chromium plating baths using both sulfate and silicofluoride catalysts.

Below are listed representative examples of some preferred high-chloride nickel strike baths for plating on top of an underlying semi-bright or bright nickel plate. A final chromium layer of about 0.01 to 0.05 mil thickness is then plated on top of the nickel strike. In examples wherein bath insoluble powders are utilized, the powders may be dispersed in the high-chloride nickel strike bath by air agitation or mechanical solution agitation.

EXAMPLE I

	Grams/liter
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	150-500
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	0-50
H_3BO_3 -----	40
o-Benzoyl -----	1-4
Benzene sulfonamide -----	2-3
Allyl sulfonic acid -----	2-3
Silica powder (0.01 to 0.05 microns) -----	40-50
Ethylenediaminetetraacetate acid -----	10-20
Air agitation or mechanical agitation.	
Temperature=50° F. to 160° F.	
pH=2 to 6, preferably 3.5.	
Plating time—1-10 minutes.	

EXAMPLE II

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	150-500 grams/liter (preferred 300-450 g./l.).
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	50-0 grams/liter (preferred 25-50 g./l.).
H_3BO_3 -----	0-30 grams/liter.
HCl (conc.) -----	0-20 cc./l. preferably to give a pH of 0.2-2.0.
Ethylenediaminetetraacetic acid or its sodium salts.	10 g./l. to saturation concentration, preferably 15-30 g./l.
Temperature, 50-110° F. -----	Preferably 70-80° F.
Cathode current density -----	40-50 amps/sq. ft. average (higher C.D. with faster agitation).
Plating time -----	1-6 minutes.
Air agitation or mechanical solution agitation.	

EXAMPLE III

5-50 grams/liter of very fine silica powder (0.01-0.05 micron particle size) is dispersed in the nickel strike bath of Example II.

EXAMPLE IV

To the bath of Example II is added 0.2-30 grams/liter of fine zirconium silicate powder (0.05 to 5 micron particle size).

EXAMPLE V

1-150 grams/liter of very fine barium sulfate powder (0.1 to 2 micron particle size) is dispersed in the nickel strike bath of Example II.

EXAMPLE VI

The nickel plate strike is deposited from the bath of Example II, but 4-30 grams of hydroxyethylenediaminetriacetic acid is used in place of EDTA.

EXAMPLE VII

From 0.3 to 2 grams/liter of diethylenetriaminepentacetic acid is added to the nickel strike bath of Example VI.

EXAMPLE VIII

To the bath in Example II is added 1-30 grams/liter of fluoboric acid or nickel fluoborate or sodium or ammonium fluoborate or mixtures thereof. In place of fluoborate about 1-10 grams/liter of fluosilicic acid or the nickel, sodium or ammonium salt can be added. The fluoborate ions serve to decrease burning at very high current densities.

EXAMPLE IX

To the bath in Example II is added 0.2 grams/liter of polyethylene glycol of average molecular weight of 400 (as for example, Carbowax 400) or 0.01 to 0.2 g./l. of butyne diol, or the ethylene oxide adducts of butyne diol or allyl alcohol.

EXAMPLE X

	Grams/liter
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	300-400
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	50-0
H_3BO_3 -----	0-30
Nicotinic acid -----	0.1-1.5
pH=2.0-6.0 (preferably pH=1).	
Room temperature operation, 70-80° F.	
Air agitation or mechanical solution agitation.	
Cathodecurrent density 40-50 amps./sq. ft.	

The nicotinic acid used in Example X is especially useful at the higher pH values (2-6) of the high-chloride nickel strike baths in that it functions to produce an exceptionally bright plate. This is no doubt due to the fact that this compound functions also as an unsaturated secondary brightener because of the pyridine ring structure with its



group.

It is to be understood that the amino acids of this invention can be added as the acids or as the salts of the acids. Thus, when the acid is referred to as such herein, the term is also meant to include the acid in the form of its salts, such as the sodium, potassium, ammonium, lithium or nickel salts.

While it is not necessary to use buffers in the high-chloride nickel strike baths of this invention, it is preferred to use boric acid. Other buffers such as citrate, acetate, formate, etc., or mixture can be used. The presence of small concentrations of cations such as zinc, cadmium or thallium can be present in the strike baths, but concentrations of over about 0.3 g./l. of such materials may cause poor chromium coverage or poor adhesion in the low current density recesses. The presence of copper ions on the

other hand, are much more detrimental in causing poor adhesion and should be kept as low as possible, preferably below 0.01 g./l. in total. Also, lead is very harmful.

With high speed solution agitation, cathode current densities of at least 200 amps/sq. ft. can be used. The high solution agitation greatly reduces the tendency toward hazy plates from the strike baths when more than about 2 minutes plating (at 40-50 amps/sq. ft.) is used on top of the bright nickel plate. When very little agitation is employed, a wetting agent may be used such as n-octyl sulfonic acid, its sodium salt, sodium 2-ethyl hexyl sulfate or the sulfonate, etc. The saturated aliphatic sulfonic acids may be used liberally in the nickel strike baths because they do not contribute any appreciable sulfide sulfur to the nickel plate.

The plate deposited from the amino acid-containing high-chloride nickel strike bath on top of the underlying nickel is highly micro stressed and especially so when dispersed fine powders such as zirconium silicate or aluminum silicate are present in the bath and co-deposited in the plate. The final chromium layer deposited thereon develops pores and a micro-cracked pattern not only because it is itself, highly stressed, but also because of the added stress in the nickel strike layer.

There is no gross-cracking of the thicker chromium plate on the higher current density areas when plated on the nickel strike plates of this invention. Also, the degree of hydrogen embrittlement of the composite plates of this invention is markedly reduced as compared to conventional nickel-chromium plates. This is because of the high porosity due to pores and the micro-cracked pattern of the top chromium layer which allows hydrogen to escape rather than being sealed in by the usual relatively impervious chromium layer.

It is to be understood that in carrying out the method of this invention, the simplest procedure is to plate the final chromium plate directly on the nickel strike plate as previously described. Nevertheless, it is possible to electrodeposit over the nickel strike plate one or more additional thin flashes of nickel from a dull or semi-bright nickel plating bath with or without the amino acids without very appreciably masking the desirable properties of the critical nickel strike plate of this invention. This additional strike plate must not be too thick, and furthermore, should not contain appreciable amounts of sulfide sulfur. Thus, it is considered that such a procedure of a double or even a triple nickel strike plate is not a departure from the teaching of the present invention.

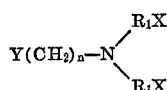
We claim:

1. A method of electrodepositing a composite corrosion protective electroplate on a basis metal susceptible to atmospheric corrosion which comprises the final steps of:

(a) electroplating over an underlying nickel plate an adherent nickel strike electroplate having a thickness of from about 0.005 to 0.4 mil, deposited from an acidic, high-chloride aqueous nickel bath having a pH less than about 2.0 and operated at a temperature of from about 50 to 110 degrees F., said bath containing dissolved therein as essential constituents from about 150 to 500 grams per liter of nickel chloride and at least 0.1 gram per liter of at least one amino acid selected from the group consisting of amino carboxylic acids, amino sulfonic acids and amino phosphonic acids, and

(b) electroplating on said overlying nickel strike layer a final layer of bright, adherent chromium plate.

2. A method in accordance with claim 1 wherein said amino acid is present in an amount of from 0.2 to 50 grams/liter and has one or more acid groups for every amino in the molecule and is of the formula:



wherein R_1 in each instance is the same or different and is hydrogen or an alkylene group containing from one to about six carbon atoms, wherein when R_1 is alkylene the attached X is $-\text{COOH}$; Y is $-\text{NH}_2$, $-\text{COOH}$, $-\text{OH}$ and



wherein R_1 and X are as just defined, and n is an integer of from 1 to 6 inclusive.

3. A method in accordance with claim 2 wherein said amino acid is ethylenediaminetetraacetic acid.

4. A method in accordance with claim 2 wherein said amino acid is hydroxyethylethylene diaminetriacetic acid.

5. A method in accordance with claim 2 wherein said amino acid is diethylenetriaminepentaacetic acid.

6. A method in accordance with claim 2 wherein said high-chloride nickel strike bath additionally contains from 0.2 to 100 grams/liter of a bath-insoluble powder of average particle size of less than about 5 microns and selected from the group consisting of barium sulfate, zirconium silicate, aluminum silicate and silica and mixtures thereof, and wherein said bath has a pH of less than 2.0 and is operated at temperatures in the range of 50-110° F.

7. The method in accordance with claim 1 wherein said amino acid is nicotinic acid and is present in an amount of from 0.1 to 2 grams/liter.

8. An article comprising a basis metal susceptible to atmospheric corrosion and an electroplate thereon, said electroplate comprising as its essential layers:

(a) an underlying nickel electroplate from about 0.3 to 3 mil thickness,

(b) an overlying adherent nickel strike electroplate of from about 0.005 to 0.4 mil thickness electro-deposited from an acidic, high-chloride aqueous nickel strike bath having a pH less than about 2.0 and operated at a temperature of from about 50-110 degrees F., said bath containing dissolved therein as essential substituents from about 150-500 grams per liter of nickel chloride and at least 0.1 gram per liter of at least one amino acid selected from the group consisting of amino carboxylic acids, amino sulfonic acids and amino phosphonic acids, said high-chloride nickel strike bath additionally containing from 0.2 to 50 grams per liter of bath insoluble powders of average particle size of less than about 5 microns and selected from the group consisting of barium sulfate, zirconium silicate, aluminum silicate, and silica, and mixtures thereof, and

(c) a top, adherent, bright chromium layer.

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