FIG. 1.

Corrosion Pit

Cr Plate (0.005 - 0.2 mil)
Ni Plate A (0.15 - 1.5 mil - 0.03 - 0.08 %)
Intermediate Ni Plate B (0.1 mil - 0.1 %)
Ni Plate C (0.15 - 1.5 mil - 0.000 - 0.005 %)
Base Metals Susceptible to Atmospheric Corrosion
(Fe, Cu, Ni, Brass, Zn, Mg, etc.)

Fig. 2.

Corrosion Pit

Cr Plate
Ni Plate A (0.02 - 0.08 %)
Intermediate Ni Plate B (0.1 %)
Ni Plate C (0.000 - 0.005 %)
Base Metal

Fig. 3.

Corrosion Pit

Cr Plate
Ni Plate A
Intermediate Ni Plate B
Ni Plate C
Base Metal

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This invention relates to an improved composite electrolyte on a metal base comprising three types of nickel electrolytes which are adjacent or contiguous to each other, and to the method of preparing this composite coating. Such a composite coating provides greatly improved outdoor corrosion protection to underlying base metals which are susceptible to atmospheric corrosion such as steel, copper and its alloys, zinc and its alloys, aluminum and its alloys, magnesium and its alloys, etc. The basic idea of the invention is to produce a three-layered nickel coating of about 0.005 to 0.2 mill thickness. In general the upper layer of nickel should contain about 0.005% to about 0.3% sulfur and must contain more sulfur than the lower layer of nickel underneath the intermediate layer. The lower nickel layer should contain from zero to a maximum of 0.03% sulfur and have a thickness of about 0.15 to 1.5 mils, and this thickness would include any nickel or cobalt or nickel alloy strike plate such as nickel-cobalt, nickel-iron or nickel-cobalt-iron. The intermediate nickel layer should contain more than about 0.05% sulfur and must contain more sulfur than the top nickel layer. In general it should contain from about 0.05% to about 0.3% sulfur. The thickness of the intermediate layer should be from about 0.005 to about 0.2 mil. The thickness of the lower layer should contain about 0.005% to about 0.15% sulfur and have a thickness of about 0.15 to 1.5 mils. When the upper nickel layer has only 0.02% or 0.03% sulfur then the intermediate layer may have as low as 0.05% sulfur, but when the upper nickel layer contains 0.04% to 0.07% sulfur then the intermediate nickel layer should contain at least 0.05%. In general it is preferred that the intermediate nickel layer contain about 0.02% to about 0.1% more sulfur than the upper nickel when the upper layer is a bright nickel containing 0.02 to 0.08% sulfur, and the lower nickel is a semi-bright sulfur-free (less than about 0.005% sulfur) nickel.

Under such conditions this essentially three layered nickel deposit with an overlying thin bright chromium plate provides considerably improved outdoor corrosion protection to the basis metal especially in a marine or saline atmosphere (where salt is used to de-ice streets in winter) than does an equal total thickness of nickel of either the lower layer nickel or the upper layer nickel or a double layer of these two nickel, with the same final thin chromium plate. This marked increase in corrosion protection is clearly shown in the now well established accelerated corrosion tests, the CASS and CorrodKote tests, which tests are described in "Plating," vol. 44, p. 763, 1957, where the improvements obtained in corrosion protection of for example steel or copper plated zinc die castings than when other intermediate layers were used such as cobalt or tin. With cobalt as the intermediate layer, blisters resulted when the corrosion pit reached the cobalt layer and proceeded laterally at a very rapid rate thus lifting the top nickel deposit around the corrosion pit to form an objectionably large blister. With the use of an intermediate layer of tin, the adhesion between the two nickel layers was greatly decreased. Other intermediate coatings such as zinc or copper have already been proved to be detrimental, with the zinc causing excessive blistering and with copper causing staining and also decreased corrosion resistance.

FIGURES 1-3 are diagrams which illustrate the mechanism by which the tri-nickel plate of this invention diverts the corrosion from the basis metal. These diagrams show the progression of a corrosion pit in a preferred example of a bright chromium plated composite of the three-layered nickel coating when exposed to saline or acidic saline atmospheres or to the CASS or CorrodKote corrosion tests. In FIG. 1, the usual type of hemispherical corrosion pit starting from a pore (p) in the uppermost bright chromium plate is shown penetrating down into the upper bright nickel plate. In FIG. 2, the corrosion pit has become a flat bottom pit practically stopping at the lower nickel layer of low sulfur content, and going laterally in the upper and intermediate nickel layers. Also a certain degree of preferential lateral progression is proceeding in the intermediate nickel layer B which has a higher sulfur content than the upper nickel layer A and an even more appreciably higher sulfur content than the lower nickel layer C. In FIG. 3, the corrosion pit has widened further without penetrating appreciably into the lower nickel layer C. This is the important consequence of the progression of corrosion with this tri-nickel plate under continued severe exposure conditions. That is, unsightly rust spots do not readily occur when the base metal is steel, nor while corrosion blisters when the base metal is copper or brass plated zinc alloy die castings, or when the base metal is aluminum or magnesium or a pre-alloy thereof. The important fact is that both nickel layers A and B continue to corrode, with intermediate layer B corroding somewhat faster than A, but not in complete preference to A, and thus the maximum protection to nickel layer C is obtained, which in turn protects the more vulnerable basis metal.

The three-layered nickel composite may be made with dull Watts nickel as the lower layer, and bright nickel or even a semi-bright nickel or dull nickel as the upper layer providing the upper nickel layer as, as already specified, higher sulfur content than the bottom layer. The methods of obtaining the higher sulfur content will be described hereinafter. Improved corrosion protection is obtained even in the absence of a final chromium plate. A preferred form of this invention includes the three-layered nickel plate in which the upper nickel is a bright nickel finish with a final overlying bright chromium plate of about 0.005 mil to 0.2 mil thick, and in this form is excellently suited for use on the exterior hardware and trim of automobiles and boats. For these applications, for example, bumpers of automobiles, door handles, housing for lights, etc., the basis metal, such as steel, copper, brass, aluminum or zinc die castings after first plating with copper, brass or chromium, or nickel strikes can then be plated with the three-layered nickel composite as follows: A semi-bright sulfur-free nickel plate in a thickness of about 0.7 to 1.5 mils is first applied and then covered with an intermediate plate of about 0.005 to 0.1 mil nickel having a sulfur content of about 0.08 to about 0.18%, which is then overlaid with a bright nickel plate of about 0.5 to 1 mil thickness from a bright nickel bath that produces about 0.02 to 0.07% sulfur in the deposit, and this upper nickel layer is then covered with a final thin bright chromium plate (or even a dual micro-cracked chromium plate) of about 0.005 to 0.2 mil thickness. In general the upper layer of nickel should...
be thinner than the lower layer (the preferred ratio is from 50:50 to 80:20 for obtaining the highest ductility of the composite as needed, for example on bumpers) and the intermediate layer should be the thinnest of the three plates. If ductility is not of great importance, then the lower layer may be thinner than the upper layer, for example a 46:50 ratio, and still obtain excellent corrosion protection of the base metal. For less severe exposure, the lower and upper layers may be only 0.15 mils thick, and still obtain improved corrosion protection.

Small percentages of other impurities besides sulfur may be present in the plates, for example, cadmium, tellurium, zinc, cadmium and iron, and very appreciable quantities of cobalt, up to 50% cobalt, may be present in the intermediate and upper layers of nickel. The lower plate should, however, be as pure nickel as possible.

Thus the lower nickel plate should be from a Watts-type nickel, as shown in Example 1, or a fluoroborate, high chloride, or sulfamate nickel plating bath, or a sulfur-free semi-bright nickel plating bath, as shown in Example 2. The intermediate nickel plate can be from these same types of baths or even an alkaline nickel bath, or a high content sodium, ammonium, lithium or magnesium type nickel plating bath, and should preferably have dissolved in the bath, sodium benzene sulfonate, or sodium p-toluene sulfonate in a concentration of about 0.1 to 1 gram/liter. Other compounds with a sulfur atom of valence less than plus six can be used to give a sulfur content to the intermediate nickel plate of about 0.03 to about 0.3% preferably about 0.08 to about 0.2%. For example, the following sulfur containing compounds in concentrations of about 0.004 to about 0.1 gram/liter can be employed: Sodium thiosulfate, sodium bisulfite or sulfite, sodium hyposulfite or hydrosulfite, sodium formaldehyde sulfonate, although sodium benzene sulfinate, sodium toluene sulfinate, sodium naphthalene sulfonates, sodium chloro- or bromo- or iodobenzene sulfonate are the best to use. In lieu of the sodium salts, the potassium, lithium, zinc, magnesium, etc., salts may be used. Copper or lead salts should not be used because copper and lead ions are known to be harmful impurities, even in traces, in nickel baths. Besides the above-mentioned inorganic and organic sulfur compounds containing a sulfur atom with less than plus six valence, other types can also be used, including sodium thiacetate, phenyl sulfonate, methyl sulfonate, mercapto benzene acid, mercaptobenzene sulfonic acid, mercaptosuccinic acid, mercaptoacetic acid, mercaptosuccinic acid, mercaptoacetic acid, mercaptobenzene sulfonic acid, thiourea, iso-thiourea, thiohydantoin, and especially their alkane sulfonic derivatives such as iso-thioureas-S-propionate sulfonic acid. With this latter list of compounds, it is best to use concentrations which range from 0.005 to about 0.05 gram/liter, though when sulfonic groups are also present in the molecule, even 0.5 to 1 gram/liter concentrations may be used. For example, with thiourea only 0.005 to 0.04 gram/liter should be used as this is one of the most critical materials to use since an excess produces very brittle, poorly adherent plate, whereas the alkane sulfonic derivatives of the thiourea form are not very critical and can be used in concentrations as high as 1 gram/liter. The sulfonates, however, such as sodium benzene sulfonate or toluene sulfonate are the least critical with variations in concentration and the best of all to use and can be employed as already mentioned in concentrations of 0.1 to 1 gram/liter and even higher, and even though bright plate is obtained, the adhesion and ductility are excellent.

In conjunction with the above-mentioned sulfur compounds there may also be present in the bath for plating the intermediate layer, organic sulfon-comounds such as sulfonic acids, sulfonamides, sulfonimidazoles, sulfonbenzyl fluorides, sulfones. If just the organic sulfon-compounds such as o-benzyl sulfamide, p-toluene sulfonamide, naphthalene sulfonic acid (mono-, di-, and tri-), benzene sulfonic acid (mono-, di-, and tri-) etc. are present in the nickel bath used for plating the intermediate layer, then the maximum sulfur content obtained for the intermediate nickel layer is about 0.06 or 0.07%. This is true if a wetting agent such as sodium octyl or lauryl sulfate is also present in the bath. For example, with 1.5 grams/liter nickel bath having dibutyrosulfonate present in a Watts bath, the sulfur content of the nickel plate is about 0.064%. With 8 grams/liter of naphthalene 1,5 disulfonic acid present in a Watts bath, the sulfur content is about 0.044%, and with 1 gram/liter of p-toluene sulfonamide, it is just about 0.025%. With 1.5 grams/liter of sodium benzene sulfonate, the sulfur content is about 0.17%. With 1 to 10 grams/liter of sodium thiosulfate present, the sulfur content is about 0.8% or about 2.3% as nickel sulfide. This is too much sulfur, and the plate is very brittle, and the lateral corrosion of the intermediate plate is too rapid. It is preferred that the sulfur content of the intermediate plate should range from about 0.05% to about 0.3%, with the optimum range at about 0.06% to about 0.2% sulfur. In general, for the intermediate plate a Watts bath at a pH of about 2.5 to 4.5 with one of the best materials, sodium benzene sulfonate or sodium p-toluene sulfonate present in a concentration of 0.3 to 1 gram/liter is about the best and simplest baths to use for plating the intermediate layer of nickel, and actually only a 0.005 to about 0.05 mil thick plate is needed in this case. With sodium thiosulfate instead of the sulfonates, a low concentration of 0.01 to 0.03 gram/liter in the Watts bath must be maintained in the intermediate nickel plating bath to give comparable results, that is, sulfur contents in this case of about 0.05 to about 0.1%. The drop-out tank or tanks following a semi-bright nickel tank may be used for the intermediate layer plating by merely adding about 0.1 to 0.3 gram/liter of sodium benzene sulfonate or 0.01 to 0.03 gram/liter of sodium thiosulfate and maintaining this concentration during continued plating, and using only about one-half to about three minutes plating time at 30 to 40 amps./sq. ft.

The upper nickel may be from a bath similar to the ones used for plating the intermediate layer except lower concentrations of the sulfur containing compounds would be used. For decorative plate, the top nickel should be from a bright nickel plating bath that employs one of the organic sulfo-oxygen compounds illustrated in Table II of U.S. 2,513,280 (July 4, 1950) and Table II of U.S. 2,800,440 (July 23, 1957) and preferably used together with the use of a pH regulator to control the pH of the bath and brilliance. The unsaturated compounds such as those carrying olefinic type bonds or acetylenic bonds without sulfonic groups in the 1 or 2 position to the unsaturated group do not in general cause a very marked increase in the sulfur content of the bright nickel plate, whereas amines such as pyridine, isouquinoline, polyamines, etc., do cause a very appreciable increase in sulfur content of the bright plate from the same baths using the same sulfo-oxygen organic compounds present in the same concentrations. Thus, in the latter case, the bright nickel baths with amines and sulfo-oxygen organic compounds present, yield nickel plate about 0.06 to about 0.14% sulfur, but when olefinic or acetylenic compounds not containing amine groups are present with the same sulfo-oxygen organic compounds, then the sulfur in the plate is usually around 0.03 to 0.06%. With the latter type of bright nickel, the intermediate plate need have only about 0.06% to about 0.1% sulfur to obtain excellent corrosion protection results.

Wetting agents may be present in the baths to prevent pitting, or air agitation may be used. Besides boric acid, other buffers may be used such as formic, citric, acetic, fluoboric, etc. The temperature of the baths may be from room to at least 180° F. and the pH values range from at least 1 to 6 for the acidic baths. The following examples illustrate plating baths which can be used for
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plating the three layered nickel plate of this invention on steel, aluminum, zinc, magnesium, brass and other commercial base metals which are susceptible to atmospheric corrosion.

Example I

(Tri-nickel plate)

Lower plate:

NiSO₄·6H₂O -------------- grams/liter --- 200–400
NiCl₂·6H₂O -------------- do -- 30–100
H₂BO₃ -------------- do -- 30–45

Temperature ------------------ °C -- 30–70
pH ------------------ 1.5–5.5

Plate thickness 1 to about 1.5 mils.

Intermediate plate: Lower plate bath modified to include sodium thiosulfate concentration of 0.01 to 0.03 gram/liter, temperature 30°–60° C., pH 2.5, thickness of plate 0.005 to 0.2 mil.

Upper plate: Same bath as for lower plate except that 2 grams/liter of one or more of the following are dissolved in the bath: p-toluene sulfonamide, o-benzoyl sulfamide, benzene sulfonamide, naphthalene sulfonic acids, benzene sulfonic acids; thickness of plate 0.5 to 1.5 mils.

Example II

(Tri-nickel plate)

Lower plate:

NiSO₄·6H₂O -------------- grams/liter --- 200–400
NiCl₂·6H₂O -------------- do -- 30–60
H₂BO₃ -------------- do -- 30–45

0.05 to 0.2 gram/liter of one or more of the following: broman hydrate, chlorate hydrate, formolhydrate, 8-methoxy coumarin, coumarin, 3-chlorocoumarin. pH 3.0 to 5.5; temperature 30–65° C.

Plate thickness 0.15 to 1.5 mils.

Intermediate plate: Same bath as for lower plate or Watts bath of pH 2.5 to 4.2 with 0.1 to 0.3 gram/liter of sodium benzene sulfonate or sodium thiosulfate in a concentration of 0.02 gram/liter; thickness of plate 0.005 to 0.1 mil.

Upper plate:

NiSO₄·6H₂O -------------- grams/liter --- 50–300
NiCl₂·6H₂O -------------- do -- 200–30
H₂BO₃ -------------- do -- 30–45

1 to 3 grams per liter of one or more of the following: o-benzoyl sulfamide, p-toluene sulfonamide, benzene sulfonamide, naphthalene sulfonic acids, 2-butyne 1,4-disulfonic acid, allyl sulfonic acid together with 0.1 to 0.3 gram/liter of 2-butyne 1,4-dioxoythanesulfonic acid. Thickness of plate 0.15 to 1.5 mils. A final bright chromium plate of 0.005 to 0.2 mil thickness.

Example III

(Tri-nickel plate)

Lower plate: Same as upper plate in Example II.

Intermediate plate: Same bath as for lower plate (or a Watts bath) with 0.1 to 1 gram/liter of sodium p-toluene sulfonate or benzene sulfinate (Na, K, Li, Mg or Zn salt); thickness of plate, 0.005 to 0.2 mil.

Upper plate: Same inorganic bath composition as given for upper plate in Example II and same organic sulfon-composition, but containing 0.003 to 0.01 gram/liter of N-allyl quinaldinium bromide; thickness of plate, 0.15 to 1.5 mils; a final bright chromium plate of 0.005 to 0.2 mil thickness.

Example IV

(Tri-nickel plate)

Lower plate: Watts nickel bath with 0.02 to 0.1 gram per liter of sodium bisulfite with 0.005 to 0.3 gram/liter of sodium p-chlorobenzene sulfinate, or sodium p-toluene sulfinate, or sodium benzene sulfinate. Thickness of plate 0.005 to 0.2 mil.

Upper plate: Same upper plate as in Example III.

The most durable tri-nickel plate compositions are those illustrated in Examples I, II and IV. Examples II, III and IV give very excellent results on copper plated steel and copper plated zinc die castings. Example I is primarily for non-decorative use where protection of the basis metal against marine or saline type exposure is practically the entire purpose. It could also be chromium plated. Example II illustrates the most ductile tri-nickel plate combination for decorative use in severe outdoor exposure, and is very well suited for plating automobile bumpers.

What is claimed is:

1. A firmly bonded laminated corrosion-protective composite coating on a metal base susceptible to atmospheric corrosion comprising as its essential layers three adjacent bonded layers of electroplates, the lower layer of which consists essentially of nickel electroplate having a thickness of about 0.15 mil to about 1.5 mils and an average sulfur content less than about 0.03%, the intermediate layer of which consists essentially of an electroplate selected from the group consisting of nickel electroplate and nickel-cobalt alloy electroplate containing at least about 50% nickel, said intermediate layer having a thickness of about 0.005 mil to about 0.2 mil and an average sulfur content of about 0.05% to about 0.3%, and the upper layer of which contains essentially an electroplate selected from the group consisting of nickel electroplate and nickel-cobalt alloy electroplate containing at least about 50% nickel, said upper layer having a thickness of about 0.15 mil to about 1.5 mils and an average sulfur content of about 0.02% to about 0.15%, said upper nickel plate containing a lower percentage of sulfur than said intermediate nickel layer, and a higher percentage of sulfur than said lower layer.

2. A firmly bonded laminated corrosion-protective composite coating on a metal base of the group consisting of iron, steel, copper and its alloys, zinc and its alloys, aluminum and its alloys, and magnesium and its alloys, comprising a three-layered nickel electrodeposit, the lower layer of which is a nickel electroplate having a thickness of about 0.15 mil to 1.5 mils and an average sulfur content less than about 0.03%, the intermediate layer of which is nickel electroplate having a thickness of about 0.005 mil to about 0.2 mil and an average sulfur content of about 0.05% to about 0.3%, and the upper layer of which is nickel electroplate having a thickness of about 0.2 to about 1.5 mils and an average sulfur content of about 0.02% to about 0.15%, said upper nickel plate containing a lower percentage of sulfur than said intermediate nickel layer, and a higher percentage of sulfur than said lower layer.

3. A firmly bonded laminated corrosion-protective composite coating on a metal base susceptible to atmospheric corrosion comprising essentially three adjacent bonded layers of electroplates, the lower layer of which consists essentially of nickel electroplate having a thickness in the range of about 0.15 mil to about 1.5 mils and an average sulfur content less than about 0.03%, the intermediate layer of which consists essentially of an electroplate selected from the group consisting of nickel electroplate and a nickel-cobalt alloy electroplate containing less than about 30% cobalt having a thickness of about 0.005 mil to about 0.2 mil and an average sulfur content of about 0.05% to about 0.3%, and the upper layer of which consists essentially of an electroplate selected from
the group consisting of nickel electroplate and nickel-cobalt alloy electroplate containing less than about 50% cobalt having a thickness of about 0.15 mil to about 1.5 mils and an average sulfur content of about 0.02% to about 0.15%, said upper nickel plate containing a lower percentage of sulfur than said intermediate electroplate and a higher percentage of sulfur than said lower electroplate.

4. A coating in accordance with claim 1 wherein said lower layer of nickel is a semi-bright nickel electroplate which contains less than about 0.005% sulfur, said intermediate nickel layer is an electroplate which contains 0.06% to about 0.2% sulfur, and said upper nickel layer is a bright nickel electroplate which contains 0.02 to about 0.06% sulfur, said upper nickel plate containing a lower percentage of sulfur than said intermediate plate.

5. A coating in accordance with claim 1 wherein said upper nickel layer is electroplated with a chromium deposit of 0.005 to 0.2 mil thickness.

6. A coating in accordance with claim 2 wherein said upper nickel layer is electroplated with a chromium electrodeposit of 0.005 to 0.2 mil thickness.

7. A coating in accordance with claim 3 wherein said upper bright nickel layer is electroplated with a bright chromium deposit of 0.005 to 0.2 mil thickness.

8. A coating in accordance with claim 2 wherein said metal base is steel.

9. A method for electroplating from aqueous solutions a corrosion-protective composite nickel coating comprising as its essential layers three adjacent layers of electroplated on a metal surface susceptible to atmospheric corrosion which comprises the steps of electroplating on said surface an adherent layer consisting essentially of nickel having a thickness of about 0.15 mil to 1.5 mils and an average sulfur content of less than about 0.03%, electroplating on said lower layer a small or intermediate layer consisting essentially of an electroplate selected from the group consisting of nickel electroplate and nickel-cobalt alloy electroplate containing at least about 50% nickel, said intermediate layer having a thickness of about 0.005 to about 0.2 mil and an average sulfur content of about 0.05% to about 0.3%, electroplating on said intermediate layer a nickel-cobalt upper layer containing essentially of an electroplate selected from the group consisting of nickel electroplate and nickel-cobalt electroplate containing at least about 50% nickel, said upper layer having a thickness of about 0.2 to about 1.5 mils and an average sulfur content of about 0.2 to 0.15%, said upper nickel layer containing a lower percentage of sulfur than said intermediate nickel layer, and a higher percentage of sulfur than said lower layer, each of said layers being electroplated in at least one electroplating step.

10. A method for electroplating from aqueous solutions a corrosion-protective composite three layered nickel coating on an industrial metal base of the group consisting of iron, steel, copper and its alloys, zinc and its alloys, aluminum and its alloys, and magnesium and its alloys, comprising the steps of electroplating on said surface an adherent lower layer of nickel having a thickness of about 0.15 mil to 1.5 mils and an average sulfur content less than about 0.03%, electroplating on said lower layer of nickel an intermediate layer of nickel having a thickness of about 0.005 to about 0.2 mil and an average sulfur content of about 0.05% to 0.3%, electroplating on said intermediate nickel layer an upper nickel plate having a thickness of 0.15 to 1.5 mils and an average sulfur content of about 0.02% to about 0.15%, said upper nickel plate containing a lower percentage of sulfur than said intermediate nickel layer, and a higher percentage of sulfur than said lower layer.

11. A method in accordance with claim 9 wherein said lower layer of nickel is plated from an aqueous acidic semi-bright sulfur-free nickel plating bath, said intermediate nickel layer is plated from an aqueous acidic nickel bath containing from 0.004 to about 0.1 gram per liter of a bath soluble sulfur compound selected from the group consisting of thioureas, sulfites, bisulfites, and hypo-sulfites, and said upper nickel layer is plated from a bright nickel plating bath containing at least one organic sulfon-com-pound.

12. A method in accordance with claim 9 wherein said lower layer of nickel is plated from an aqueous acidic semi-bright sulfur-free nickel plating bath, said intermediate nickel layer is plated from an aqueous acidic nickel bath containing from about 0.01 to about 1 gram per liter of a compound selected from the group consisting of benzene sulfonic acid and substituted benzene sulfonic acids, and said upper nickel layer is electroplated from a bright nickel plating bath containing at least one organic sulfon-com-pound.

13. A method in accordance with claim 11 wherein said upper bright nickel layer is electroplated with a bright chromium deposit of 0.005 to 0.2 mil thickness.

14. A method in accordance with claim 12 wherein said upper bright nickel layer is electroplated with a bright chromium deposit of 0.005 to 0.2 mil thickness.

15. A laminated corrosion protective composite coating on a metal base susceptible to atmospheric corrosion comprising as its essential layers three adjacent bonded layers of electroplates, the lower layer thereof consisting essentially of nickel electroplate having a thickness of about 0.15 mil to about 1.5 mils and an average sulphur content less than about 0.005%, the intermediate layer of said three layers consisting essentially of an electroplate selected from the group consisting of nickel electroplate and nickel-cobalt alloy electroplate containing at least about 50% nickel, said intermediate layer having a thickness of about 0.005 mil to about 0.2 mil and an average sulphur content of about 0.04% to 0.18%, and the upper layer of said three layers consisting essentially of an electroplate selected from the group consisting of nickel electroplate and nickel-cobalt alloy electroplate containing at least about 50% nickel, said upper layer having a thickness of about 0.15 mil to about 1.5 mils and an average sulphur content of about 0.02% to 0.08%, said upper nickel plate containing a lower percentage of sulphur than said intermediate nickel plate, and a higher percentage of sulphur than said lower nickel plate.

16. A laminated coating on a metal base in accordance with claim 15 wherein said upper nickel plate is electroplated with a chromium electrodeposit of 0.005 to 0.2 mil thickness.

17. A method for electroplating from aqueous solutions a corrosion protective composite coating on a metal surface susceptible to atmospheric corrosion which comprises the steps of (1) electroplating on said surface in at least one electroplating step an adherent layer consisting essentially of nickel having a thickness of about 0.15 mil to about 1.5 mils and an average sulphur content of less than about 0.03%, to thus form an adherent lower layer, (2) electroplating directly on said lower layer in at least one electroplating step an adherent intermediate layer consisting essentially of an electroplate selected from the group consisting of nickel electroplate and nickel-cobalt alloy electroplate containing at least about 50% nickel, said intermediate layer having a thickness of about 0.005 to about 0.2 mil and an average sulphur content of about 0.05 to about 0.3%, (3) electroplating directly on said intermediate nickel layer an adherent upper layer in at least one electroplating step consisting essentially of an electroplate selected from the group consisting of nickel electroplate and nickel-cobalt alloy electroplate containing at least about 50% nickel, said upper layer having a thickness of about 0.2 to about 1.5 mils and an average sulphur content of about 0.02% to 0.15%, said upper nickel plate containing a lower percentage of sulphur than said lower nickel layer, said intermediate layer being plated from an aqueous acidic nickel bath containing
9 from about 0.004 to about 1 gram per liter of a bath soluble sulphur compound.

18. A method in accordance with claim 17 wherein said intermediate nickel layer is plated from an aqueous acidic nickel bath containing from about 0.004 to about 0.1 gram per liter of a bath soluble sulphur compound selected from the group consisting of bath soluble thiosulphates, sulphites, bisulphites and hyposulphites.

19. A method in accordance with claim 17 wherein said intermediate nickel layer is plated from an aqueous acidic nickel bath containing about 0.01 to about 1 gram/liter of a compound selected from the group consisting of benzene sulfinic acid and substituted benzene sulfinic acids.

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