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ELECTROPLATING A DUCTILE ZINC-NICKEL ALLOY ONTO STRIP STEEL

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ABSTRACT OF THE DISCLOSURE

A method of electroplating a nickel-zinc alloy on a steel strip is described, in which the plating bath is maintained within a selected pH range, through use of a preselected ratio of nickel to zinc in the bath, and a preselected plating current density, whereby an electroplated coating is formed having a nickel content of from 9.5 to 12.5%, which coating has a low internal stress, and increased resistance to corrosion.

In Roehl Pat. No. 3,420,754, there is described a method of electroplating a ductile zinc-nickel alloy onto steel strip, in which the strip is caused to traverse an aqueous plating bath having a pH of from 2.5 to 3.5, in which nickel chloride and zinc chloride have been dissolved in sufficient amounts for each gallon of the bath to have a zinc content of from 8 to 10 ounces and a nickel content of from 4 to 5 ounces, and in which the strip is made a cathode as it passes through the bath, and an electroplating current density of 50 to 100 amperes per square foot of cathode surface of the strip is maintained, whereby a zinc-nickel alloy coating is electrodeposited on the steel strip, the alloy consisting of from 6.5 to 9.5% nickel with the remainder zinc. The bath is maintained at a temperature of from 115° to 125° F.

The aforesaid coating is characterized by the fact that it has an expansive internal stress of about −500 to −1400 p.s.i., and has substantially greater corrosion resistance than zinc.

In the interest of increasing the resistance of such coatings to corrosion, it is desirable to increase the nickel content of the coating to a range above 9.5%, but reference to the graph of FIG. 1 of the aforesaid Roehl patent indicates that the contractile internal stress of the coating rises very rapidly with such increase in nickel content, and since such rise in contractile internal stress is a measure of decreasing ductility of the coating, ways and means have been sought by us to counteract this decrease in ductility.

We have discovered, through a series of tests, that by

increasing the pH of the plating bath, and making certain changes in the ratio of the nickel to the zinc in the bath, that the percentage of nickel in the electrodeposited coating may be increased to a range of 9.5 to 12.5%, while effecting a substantial lowering of the internal stress of the deposit, as well as a substantial increase in the corrosion resistance of the coating.

In particular, we have found that in increasing the pH of the plating bath from 3.5 to 4.0, while increasing the nickel-zinc metal ratio in the bath only slightly, i.e., from 0.56:1 to 0.60:1, the internal or deposit stress is reduced from a contractile stress of +2700 p.s.i. to +30 p.s.i., and that by increasing the pH of the plating bath to 4.5, while increasing the nickel-zinc metal ratio in the bath to 0.63:1, the internal or deposit stress is further reduced to an expansive stress of −1200 p.s.i.

At the same time, the corrosion resistance or salt spray life, in hours, of the flat coating is increased from 122 hours to 160 hours and 156 hours respectively, the salt spray life of the bent edge of the coating (at a bend of 90°) is increased from 133 hours to 156 hours and 172 hours respectively, and the salt spray life of the bent edge of the coating (at a bend of 180°) is increased from 98 hours to 133 hours and 145 hours respectively.

The results of the foregoing and other tests are tabulated below for comparison purposes:

EFFECT OF pH ON DEPOSIT STRESS AND CORROSION RESISTANCE OF NICKEL-ZINC ALLOY COATINGS ON STEEL STRIP

pH of bath	4.5	4.0	3.5	3.0	2.5
Average deposit stress, p.s.i.	−1,200	+30	+2,700	+3,200	+4,500
Salt spray life, hours:					
Flat coating	156	160	122	145	110
Coating bent 90°	172	156	133	133	122
Coating bent 180°	145	133	98	110	98
Bath composition:					
Ni metal, oz./gal.	4.9	5.1	4.5	4.6	4.4
Zn metal, oz./gal.	7.8	8.5	8.0	7.8	7.6
Ni-Zn metal ratio	0.63	0.60	0.56	0.59	0.58
Acetic acid, percent of bath volume	2.5	2.0	2.0	2.7	2.4
Wetting agent, percent of bath volume	0.20	0.19	0.20	0.20	0.20
Operating conditions:					
Bath temperature, ° F.	130	130	130	130	130
Cathode current density, amps per sq. ft. of cathode surface	50	50	50	50	50
Coating thickness, inches	.00010	.00012	.00011	.00011	.00011
Percent nickel in coating	10.3	9.9	10.7	10.0	9.9

In the foregoing tests, the zinc in the bath is provided in the form of zinc chloride ($ZnCl_2$), and the nickel in the form of nickel chloride ($NiCl_2 \cdot 6H_2O$).

The wetting agent is used to lower the surface tension of the bath to eliminate pitting, if encountered, and to improve the uniformity of deposit appearance. The identity of the wetting agents chosen is not important, although they must, of course, be compatible with the bath and cause no deleterious effects. Some of the wetting agents used in commercial nickel plating have been found to be satisfactory, as, for example, sulfated or sulfonated lauryl alcohol, one of the commonest so used. Others which produce less foam may be preferred, but the selection of such wetting agents most suitable for specific conditions is well within the knowledge of those skilled in the art of electroplating, there being a wide variety available from purveyors of materials for nickel plating processes.

The subjects of internal residual stress, expansive internal stress and contractile internal stress, and deposit stress are discussed in the aforesaid Roehl patent, to which reference may be made for an understanding thereof.

In general, we find that in our method of electroplating steel strip, the pH value of the bath should be maintained between 4.0 and 4.5, the bath temperature at 125–135° F., the current density at 40–100 a.s.f., and the percentage of nickel in the deposit within the range of 9.5 to 12.5%, with 11% as the optimum. Chanpes in the nickel content of the deposit, within this range are effected primarily by changing the nickel-zinc metal ratio in the bath. An increase in the pH value of the bath beyond 4.5 is undesirable, due to the fact that this results in an increase in the expansive stress produced in the deposit.

While, in theory, maintenance of a zero stress is most desirable, it is to be noted that although an increase in the pH value of the bath to 4.5 increases the expansive stress of the deposit to —1200, this is compensated for by the resulting increase in salt spray life of the bent coatings.

The following example illustrates a preferred embodiment of the invention:

Bath composition	Optimum	Limits
Zn as metal, oz./gal	8	7-9
Ni as metal, oz./gal	4.5	4-5
$ZnCl_2$, oz./gal	16.7	14.6-18.8
$NiCl_2 \cdot 6H_2O$, oz./gal	18.2	16.2-20.3
Acetic acid, percent of bath volume	2.2	2-2.5
pH	4.25	4.0-4.5
Operating conditions:		
Cathode current density, amp per sq. ft	50	40-100
Temperature, ° F	130	125-135
Deposit composition:		
Zn, percent	89	90.5-87.5
Ni, percent	11	9.5-12.5

Having thus described our invention, we claim:

1. The method of plating steel strip with a zinc-nickel alloy which comprises: causing the strip to traverse an aqueous plating bath having a pH of from 4.0 to 4.5, in which nickel chloride and zinc chloride have been dissolved in sufficient amounts for each gallon of the bath to have a zinc content of from 7 to 9 ounces and a nickel content of from 4 to 5 ounces; making said strip a cathode as it passes through said bath and maintaining an electroplating current density of from 40 to 100 amperes per square foot of cathode surface of the strip, whereby a zinc-nickel alloy coating is electrodeposited on the steel strip, said zinc-nickel alloy consisting of from 9.5 to

12.5% nickel with the remainder zinc, said coating having an internal stress of from +30 to —1200, and which coating also has substantially greater corrosion resistance than a coating produced under like conditions, but having a pH value of the bath of less than 4.

2. The method, as defined in claim **1**, in which the plating bath is maintained at a temperature of from 125° to 135° F.

3. A method of plating a metallic article with a zinc-nickel alloy which comprises: coating the article in an aqueous plating bath having a pH of from 4.0 to 4.5, in which nickel chloride and zinc chloride have been dissolved in sufficient amounts for each gallon of the bath to have a zinc content of from 7 to 9 ounces and a nickel content of from 4 to 5 ounces; making the article a cathode in the bath and maintaining an electroplating current density of from 40 to 100 amperes per square foot of cathode surface of the article, whereby a zinc-nickel alloy coating is electrodeposited on the article, said zinc-nickel alloy consisting of from 9.5 to 12.5% nickel with the remainder zinc, and which coating has substantially greater corrosion resistance than a coating produced under like condition, but having a pH value of the bath of less than 4.

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