ELECTROPLATING A DUCTILE ZINC-NICKEL ALLOY ONTO STRIP STEEL

Filed March 12, 1965

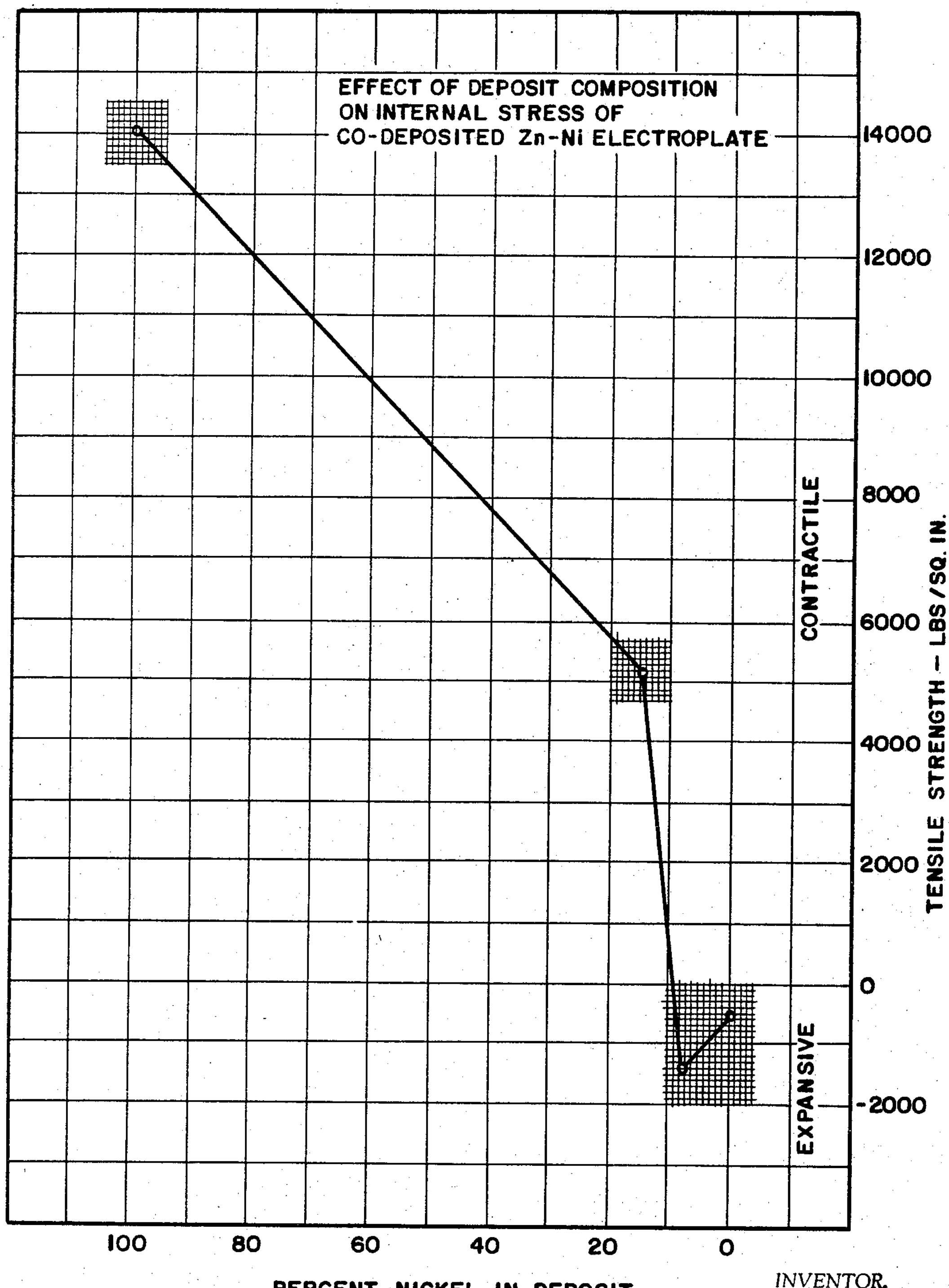

Fig. 1

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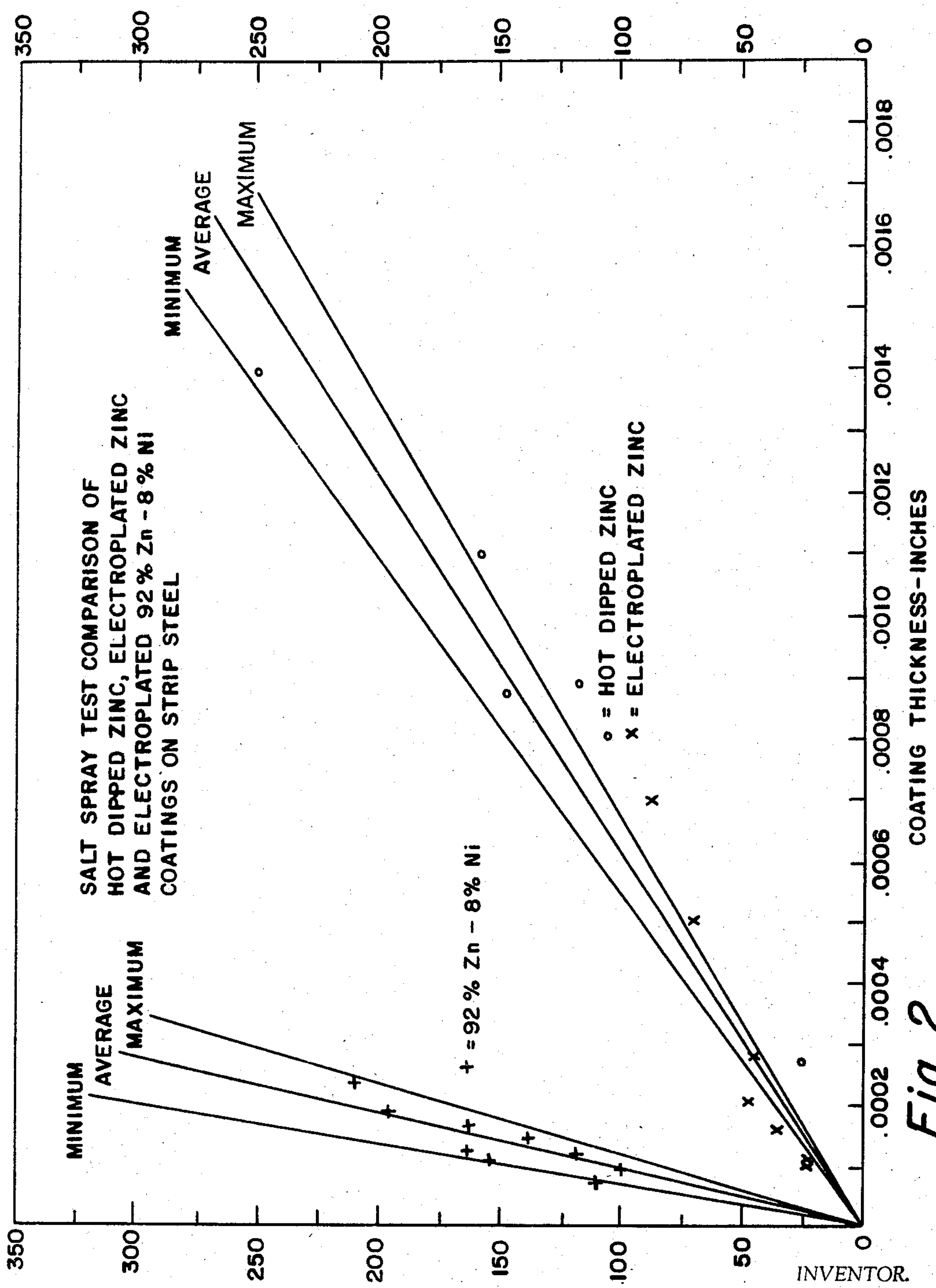

Fig. 2

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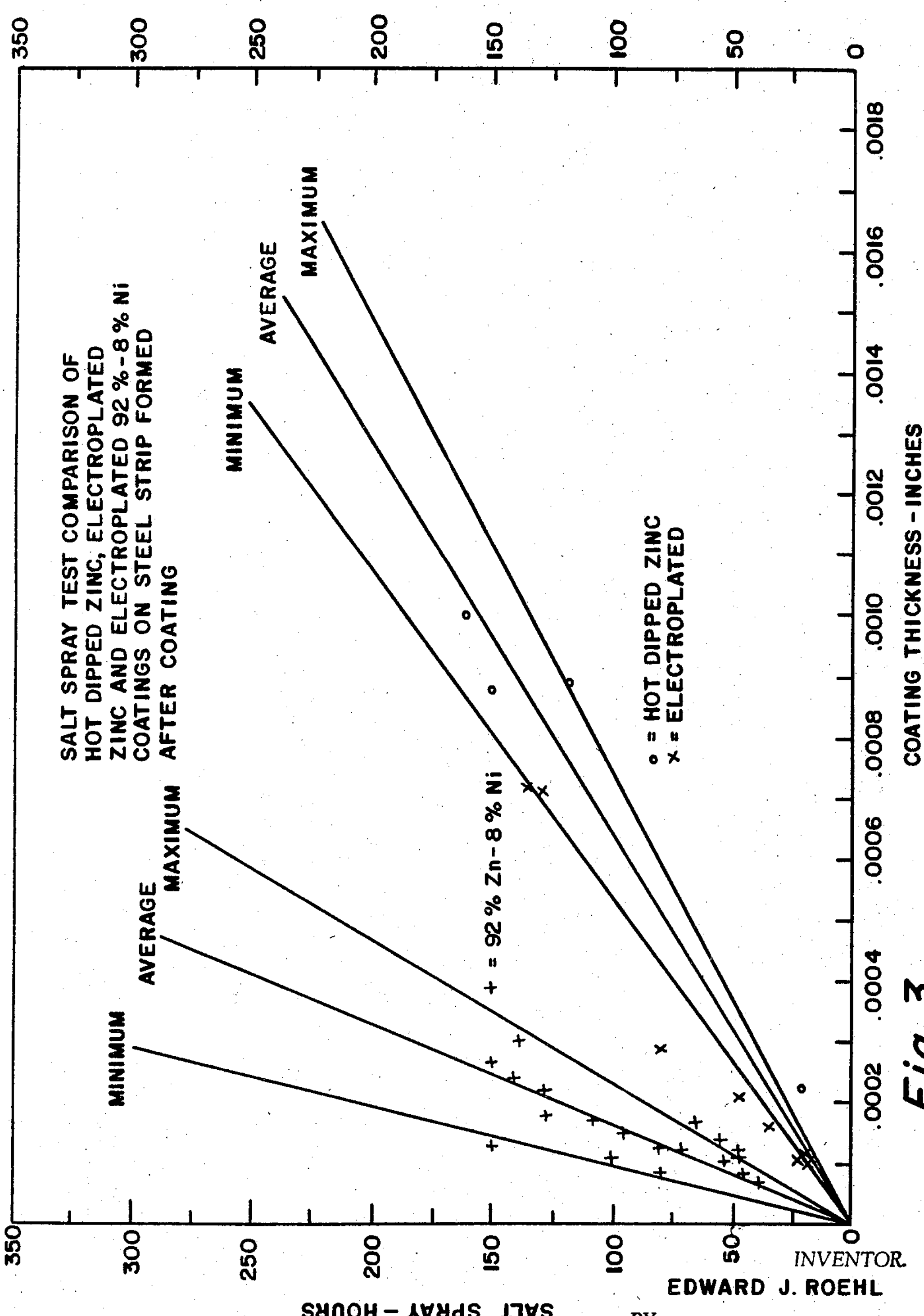

Fig. 3

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ELECTROPLATING A DUCTILE ZINC-NICKEL ALLOY ONTO STRIP STEEL

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U.S. Cl. 204—28 3 Claims

Int. Cl. C23b 5/04

ABSTRACT OF THE DISCLOSURE

The invention is concerned with the electrodeposition on steel strip of a zinc-nickel alloy plating containing nickel in a predetermined range of 6.5 to 9.5%, for the purpose of providing a coating having an expansive internal stress of about 500–1400 p.s.i., whereby a high ductility and low internal stress enables the plated strip to be subjected to cutting, bending, stamping or forming operations without cracking or breaking of the plating. At the same time, superior corrosion-resistant properties for the plating are obtained.

This invention relates generally to the electrodeposition of alloys from acid plating baths, but has reference more particularly to the electrodeposition of alloys or co-deposits of zinc and nickel, the composition of which is controlled within specific, fairly critical, limits or ranges for the purpose of obtaining new and desirable physical properties for specific, useful, commercial applications.

Zinc is one of the most widely used metallic coatings for steel surfaces to protect such surfaces from corrosion, the principal methods of applying such coatings being hot dipping and electroplating. The hot dipping method produces thick coatings of a thickness of 0.001 inch or more, which are alloyed to the surfaces of the steel. These intersurface alloys are brittle and not suitable for drawing and forming operations. Electroplating produces thinner coatings, of the order of a few ten-thousandths of an inch in thickness, with no alloy intersurface layer between the base metal coating, and hence can be formed and drawn satisfactorily.

Zinc has been electroplated on steel surfaces from acid plating baths for many years for the purpose of providing protection of the steel surface for commercial uses. Among commercial materials so protected is continuous steel strip which, after being plated, is fabricated into useful articles of manufacture by cutting, stamping, drawing and forming operations. In order to withstand the stresses of such operations without damage or injury to the zinc plating or interfering with its adhesion to the steel strip or sheet and the corrosion protection offered by the zinc, it is essential that the electroplated zinc coating possesses minimum internal stress and maximum ductility. Heretofore, these conditions or requirements have been best met by eliminating impurities from the plating bath, so as to deposit zinc of the highest purity.

It has also been proposed, as in U.S. Patent No. 2,419,231, to produce an electrodeposited coating of an alloy high in zinc and low in nickel, by the addition of nickel salts to an acid zinc plating bath, whereby a plated coating is provided, the resistance of which to corrosion is superior to that provided by pure zinc alone when

plated on steel surfaces. The patent is concerned primarily with alloys consisting of about 85% zinc and about 15% nickel, which alloys provide better corrosion resistance or protection than pure zinc but which coatings themselves are not as ductile as pure zinc, and hence are not as suitable as pure zinc for forming and drawing operations.

Efforts to use the invention of the aforesaid patent, especially for the plating of continuous steel strip, have met with almost insurmountable practical difficulties, for two reasons. The preferred range of alloy compositions in the aforesaid patent for maximum corrosion protection is 11–18% nickel, with the remainder zinc. In the first place, it is difficult to secure good adhesion of the plated alloys of this composition range, and this difficulty is recognized in the patent which recommends the use of a pre-plate or "strike" of pure nickel on the steel prior to alloy plating to insure good adhesion. Such pre-plates or "strikes" are expensive to apply commercially because two plating ssytems are required, thus adding materially to the cost of the product, so that this additional plating operation is to be avoided whenever possible. In the second place, a far more serious difficulty has been encountered due to the low ductility and high internal stress inherent in electroplated alloys of zinc and nickel within said preferred range of 11 to 18% nickel. When continuous steel strip, plated in accordance with the teachings of the aforesaid patent, is subjected to cutting, bending, stamping or forming operations in the manufacture of articles for which purpose it is made, the plating cracks or breaks or becomes separated from the steel base, because it is brittle and has relatively high internal stress. This defect destroys the corrosion-resistant properties of the electroplated alloy, and consequently the commercial value of the plated product.

I have found that by carefully controlling the plating bath composition and the operating conditions under which the high zinc—low nickel alloy is plated, I can produce alloys within a narrow and critical composition range outside the preferred range disclosed in the aforesaid patent, and which have a surprisingly lower internal stress and higher ductility, as well as satisfactory adhesion to the base metal, than does pure zinc itself, and, at the same time, possess corrosion-resisting properties superior to pure zinc characteristic of high zinc—low nickel alloys.

These improvements are best illustrated in FIG. 1 of the accompanying drawings, forming a part of this specification, which shows that electrodeposited alloys within a narrow range of 6.5–9.5% nickel, with the remainder zinc, and preferably within a range of 7–9% nickel, with the remainder zinc, have an expansive internal stress of about 500–1400 p.s.i., as compared with an expansive internal stress of about 500 p.s.i. for pure electroplated zinc, while electroplated nickel alloys containing over 9.5 nickel have a rapidly rising contractile internal stress, with corresponding loss of ductility, which accounts for the great difficulty encountered in working or forming products plated with them, as hereinbefore referred to. FIG. 1 further indicates that a preferred alloy or composition within the selected range, and which has a maximum expansive internal stress of about 1400 p.s.i., is one consisting of about 92% zinc and about 8% nickel.

Internal residual stress is stress present in a body that is free of external forces or thermal gradients. The subject of internal stress, in connection with electroplating, is discussed on pp. 386–388 of the second edition (1962) of A. Kenneth Graham's Electroplating Engineering Handbook, to which reference may be made.

The coated material made in accordance with my invention, having a coating of the composition described above, can be bent, stamped, drawn, formed, or otherwise worked into finished articles or products without cracking or damaging the coating in any manner.

In FIG. 2 of the accompanying drawings, the results of salt spray tests on flat specimens of coated strip steel, coated respectively with the aforesaid 92%–8% nickel alloy, pure electrolytic zinc, and hot-dipped zinc, are depicted graphically, and in FIG. 3 of the accompanying drawing, the results of the same salt spray tests, on similar specimens, after forming, are depicted graphically. In both cases, the 92% zinc–8% nickel alloy coating is seen to be from three to four times as corrosion-resistant as the electrolytic zinc and hot-dipped zinc coatings, and can therefore be used in thickness of only one-third to one-fourth those of pure zinc, for corresponding degrees of protection, thereby effecting considerable economies.

This discovery was most surprising and unexpected. The invention, therefore, simply stated, comprises plating or electrodepositing a highly corrosive-resistant alloy of zinc and nickel, of minimum internal stress and maximum ductility, on steel surfaces, said alloy having a carefully controlled composition within narrow critical limits achieved by careful control of the plating bath composition and operating conditions, thus producing a new and useful product at low cost.

In carrying out the invention, the important factor in plating bath composition and control is to maintain the ratio between the concentration of zinc metal in solution and the concentration of nickel metal in solution with respect to total metal concentration and operating conditions so that the composition of the alloy plated therefrom will be as close to 92% zinc and 8% nickel as possible, and preferably within the limits of 93–91% zinc and 7–9% nickel, but never less than 90.5% zinc or more than 9.5% nickel. I have found that this objective can best be accomplished by maintaining the zinc metal concentration in the bath at between 8 and 10 ounces per gallon, with the nickel metal concentration at between 4 and 5 ounces per gallon, and the ratio of zinc metal concentration to nickel metal concentration as close as 2:1 as possible.

The anionic composition of the plating bath is not critical, hence any water-soluble salts of zinc and nickel commonly used in plating baths and compatible therewith can be used alone or in any desirable combination, although I prefer to use a chloride bath because of its higher conductivity and therefore greater productivity. Other salts which may be used, however, include sulfates, sulfamates, fluoborates, and in some cases, acetates. I use small concentrations of acetates or acetic acid, for example, as a buffer to promote ease of pH control.

The following example illustrates a preferred embodiment of my invention:

	Optimum	Limits
Bath Composition:		
Zn as metal, oz./gal	9	8–10
Ni as metal, oz./gal	4.5	4–5
$ZnCl_2$, oz./gal	18.8	16.8–20.8
$NiCl_2 \cdot 6H_2O$, oz./gal	18.2	16.2–20.2
Acetic Acid, percent of bath volume	3	(1)
pH	3.0	2.5–3.5
Operating Conditions:		
Cathode Current Density, amperes per sq. ft	75	50–100
Temperature, ° F	120	115–125
Deposit Composition:		
Zn, percent	92	93–91
Ni, percent	8	7–9

1 Not critical.

As anodes, I prefer to use separate zinc and nickel anodes, although alloys consisting of approximately 92% zinc and 8% nickel can be used if desired. In using separate anodes, I maintain the ratio of approximately 92% of zinc surface to 8% of nickel surface and to manipulate this ratio as required to maintain the ratio of zinc metal concentration to nickel metal concentration in the bath as near 2:1 as possible and thus maintain the composition of the electrodeposited alloy within the desired limits of 93–91% zinc and 7–9% nickel, preferably 92% zinc–8% nickel.

Wetting agents which lower the surface tension of the bath may be added thereto if desired 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 nickel plating process.

Mild agitation of the bath, or relative movement between bath and cathode such as obtained by cathode movement or bath circulation is advantageous in maintaining uniform bath composition and therefore uniform deposit composition. The passage of continuous steel strip through the plating bath while it is being plated is entirely adequate and bath circulation through a pump and filter is desirable to maintain the bath clean as well as in motion.

Although the invention has been described particularly with reference to the electroplating of continuous steel strip, for which it is especially adapted, it is equally suitable for electroplating any steel surface for protection against corrosion, as for example, sheet steel, steel pipes, conduits, tubing, wire, and any object that can be protected by zinc electroplating.

It is understood that slight changes may be made in the method and in the alloys and compositions and products, as described, without departing from the spirit of the invention or the scope of the appended claims.

Having thus described my invention, I 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 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; making said strip a cathode as it passes through said bath and maintaining an electroplating current density of from 50 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 6.5 to 9.5% nickel with the remainder zinc, said coating having an expansive internal stress of about 500–1400 p.s.i. and which coating also has substantially greater corrosion resistance than zinc.

2. The method, as defined in claim **1**, in which said bath contains a surface tension lowering agent which is compatible with the bath.

3. The method, as defined in claim **1**, in which the plating bath is maintained at a temperature of from 115° to 125° F.

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U.S. Cl. X.R.

204—43; 29—196.5