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Electrodeposition of Zinc-Nickel Alloys Coatings

(Presented at the Government-Industries Workshop on Alternatives for Cadmium Electroplating in Metal Finishing held October 4-6, 1977 in Gaithersburg, MD)

J. W. Dini, H. R. Johnson

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ELECTRODEPOSITION OF ZINC-NICKEL ALLOYS COATINGS

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ABSTRACT

One possible substitute for cadmium in some applications is a zinc-nickel alloy deposit. Previous work by others showed that electrodeposited zinc-nickel coatings containing about 85% zinc and 15% nickel provided noticeably better corrosion resistance than pure zinc. Present work which supports this finding also shows that the corrosion resistance of the alloy deposit compares favorably with cadmium.

ACKNOWLEDGMENTS

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Introduction

Thermally prepared coatings of Zn-Ni have been obtained by the interdiffusion of separately deposited nickel and zinc coatings and used as a protective coating for steel under the trade name Corronizing.[1] The commercial use of the diffusion coating indicates that electrodeposited Zn-Ni coatings also should have applications, if a convenient method of deposition could be developed. One of these applications could be a substitute for cadmium.

The literature on the topic of Zn-Ni plating up to 1960 was covered by Brenner[2] in his treatise on alloy deposition. Since 1960, very little has appeared on this subject. Hammond and Bowman[3,4] were granted patents in 1961 and 1962. Kudryautsev[5] reported on deposition from cyanide and ammoniacal solutions in 1964. Domnikov[6] reviewed some Russian work in 1965, Roehl[7] was granted a patent in 1969, and Roehl and Dillon[8] a patent in 1971. These latter two patents were the starting point for the work described in this paper. Roehl[7] reported that in salt spray tests, 92% Zn-8% Ni alloy coating was three to four times as corrosion resistant as electrodeposited zinc or hot-dipped zinc (Figure 1). Based on the results reported in the literature and the fact that zinc-nickel coatings have shown promise at Sandia Laboratories, Livermore, in protecting uranium alloys from corrosion, it was deemed worthwhile to investigate zinc-nickel alloy plating in further depth. The present study was divided into two parts. The first portion consisted of determining the optimum operating conditions for the electroplating process. The factors evaluated were the influence of current density and temperature on deposit appearance, composition, stress, and efficiency. The second portion of the study evaluated the proposed zinc-nickel coating in a salt fog environment. To provide comparison data, unalloyed zinc and cadmium coatings were also evaluated in the same environment. A salt fog environment was selected for this study because previous investigations had demonstrated the superiority of cadmium over unalloyed zinc in this test.

Selection of Operating Conditions

General

The work reported herein was done with 10-litre solutions of the composition listed in Table I. The solution is basically Roehl's[7] with some changes. He used the chloride salts of zinc and nickel whereas we used zinc sulfate and nickel sulfamate. The reason for this change is that one potential application for Zn-Ni coatings is corrosion protection for uranium and its alloys, and these materials are notoriously attacked by chlorides.

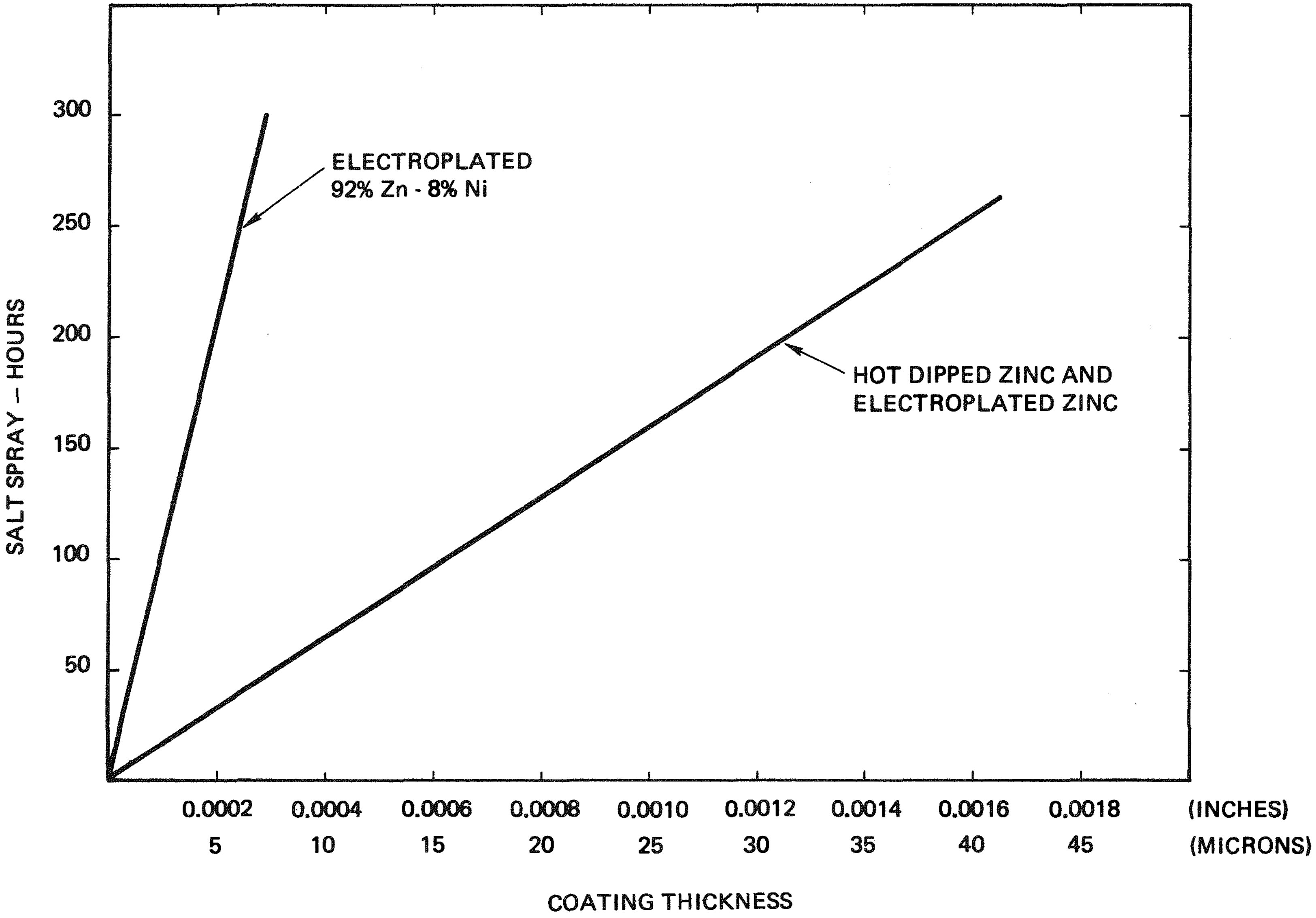


Figure 1. Salt Spray Test Comparison of Hot Dipped Zinc, Electroplated Zinc, and Electroplated 92% Zn-8% Ni Coatings on Strip Steel (from Roehl, Ref. 7)

TABLE I

ZINC-NICKEL SOLUTION FORMULATION

Zinc Sulfate ($ZnSO_4 \cdot 7H_2O$)	266 g/l
Zinc	60 g/l
Nickel Sulfamate*	190 ml/l
Nickel	34 g/l
Sodium Lauryl Sulfate	0.375 g/l
Surface Tension	35-40 dynes/cm
pH	5.0

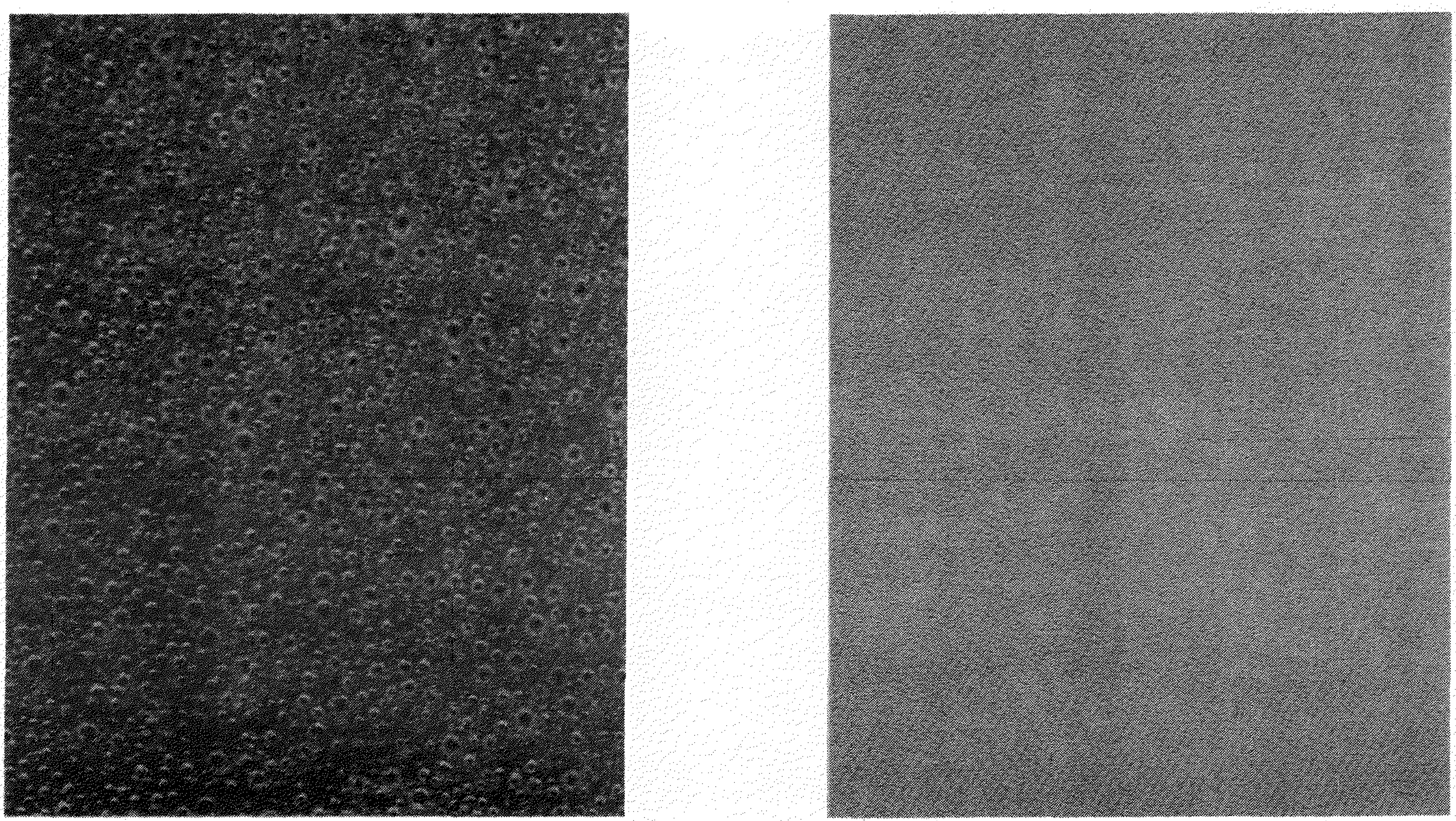
*SNR 24 sulfamate nickel concentrate, Allied-Kelite Products Div., the Richardson Co., Des Plaines, Ill.

A few cursory experiments revealed that nickel sulfate could be substituted for the nickel sulfamate. If this coating system were to be used in production, the sulfate would be less expensive than sulfamate. Roehl[7] recommended a small amount of acetic acid as a buffer to promote ease of pH control. We found this to be unnecessary, and furthermore discovered as a result of some Hull cell tests that acetic acid reduced the covering power of the solution. Zinc anodes were used for most of the work, but alloy anodes of the approximate composition Zn-10 Ni would probably be quite suitable.

A wetting agent (sodium lauryl sulfate) was used to lower the surface tension of the solution to eliminate pitting. The importance of this ingredient is shown in Figures 2a and 2b, which compare deposits produced in solutions with and without wetting agent. Heavy pitting was evident in the deposit obtained from the solution containing no wetting agent, whereas no pitting was evident when the wetting agent was present. An additional benefit of the wetting agent is that it improves the appearance of the deposit and has a grain refining effect.

Steel panels 6.4 x 10.2 cm (2.5 x 4 in.) were used as the plating substrates. Steel was selected because the red rust produced on unprotected surfaces in salt spray gives a good indication of the corrosion process occurring.

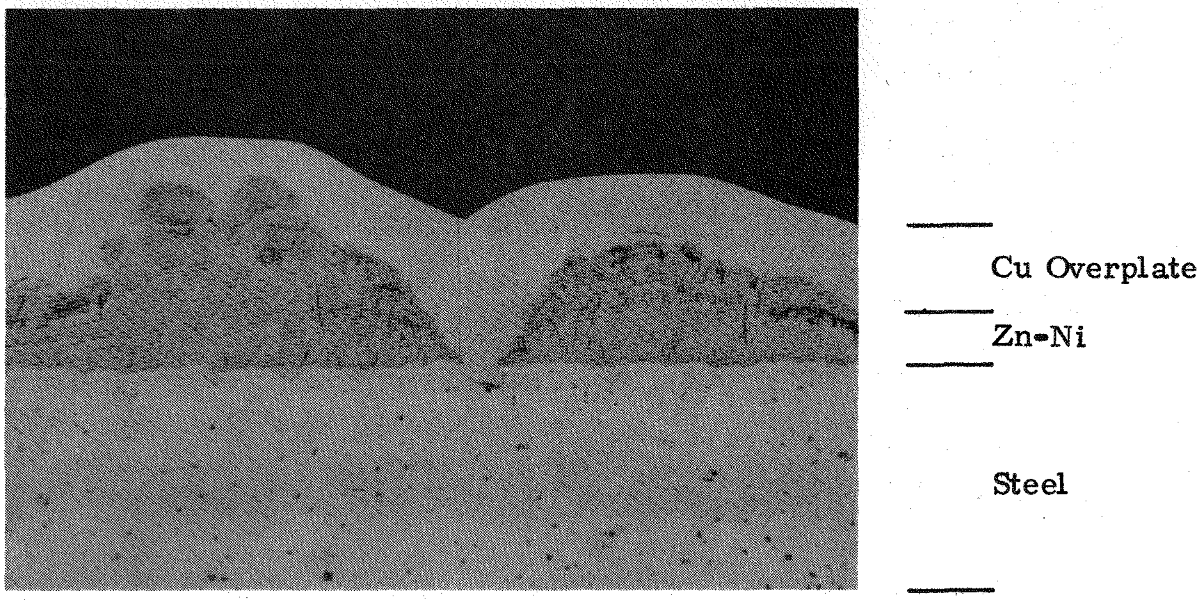
The parameters used to evaluate the operating conditions were: influence of current density and temperature on deposit appearance, composition, stress and efficiency.



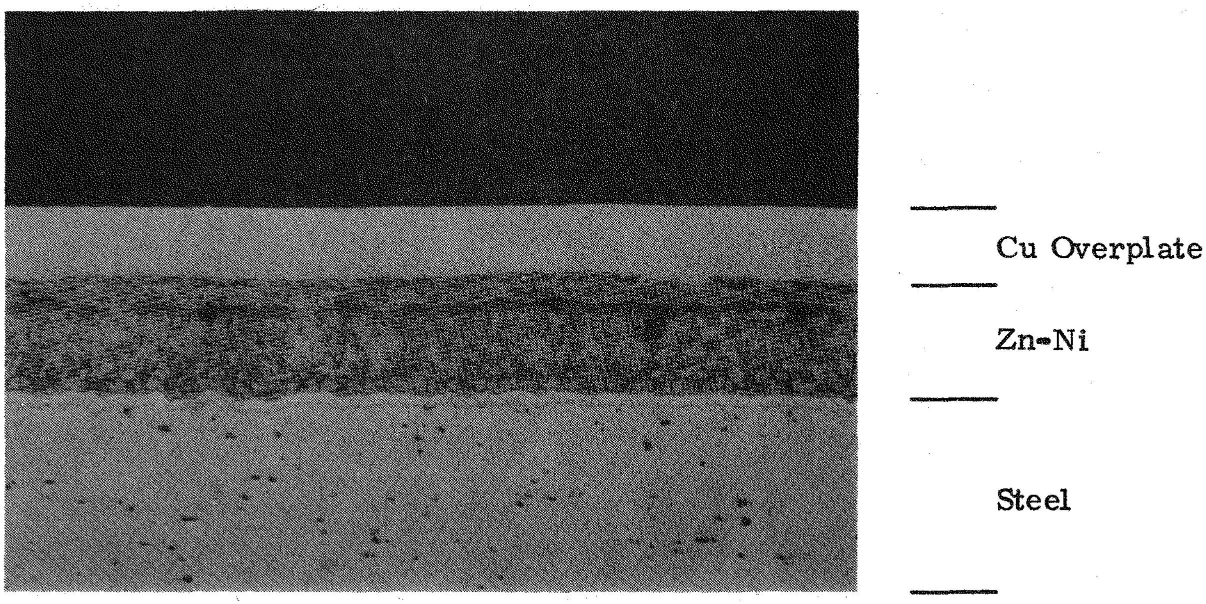
(a) Plated in Solution Containing No Wetting Agent

(b) Plated in Solution Containing Wetting Agent

Figure 2a. Surface Appearance of 100 μ (4 Mil) Thick Zn-Ni Alloy Deposits



(a) Plated in Solution Containing No Wetting Agent



(b) Plated in Solution Containing Wetting Agent

Figure 2b. Cross Sections of Zn-Ni Alloy Deposits

Influence of Current Density and Temperature

As illustrated in Figure 3, deposits with the highest nickel contents were obtained at the lowest current densities. Likewise, the higher the plating temperature, the higher the nickel content of the deposit. The appearance of the deposits produced at 27 and 50°C did not change much over the current density range of 54 to 538 A/m^2. However, a noticeable difference was obtained at 93°C. Figure 4 shows that deposits plated at 93°C were black at 54 A/m^2, grey at 538 A/m^2 and grey-black at 269 A/m^2. The black coloration is attributed to the higher amounts of nickel plated out at the lower current densities.

Repeated measurements revealed that efficiency* at 54 A/m^2 was greater than 100%, which is indicative of either material being occluded in the deposit or autocatalytic deposition; we choose to believe the former. There are indications that deposition at the lower current densities was accompanied by heavy oxides and hydroxides. Gas and carbon analysis of some deposits revealed noticeably higher impurity content at lower current densities. This is especially evident when comparing deposits produced at 54 and 538 A/m^2 (Table II). There was no weight change in the deposits

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*The efficiency measurements were based on the standard established by a copper coulometer connected in series with the Zn-Ni plating solution. The coulometer contained 200 g/l of copper sulfate, 100 ml/l (specific gravity 1.83) of sulfuric acid and 50 ml/l of absolute ethyl alcohol. To calculate the efficiency, the deposit composition was first determined by atomic absorption analysis, and then electrochemical equivalents of the alloy were calculated by the reciprocal method described by Lowenheim.[9]

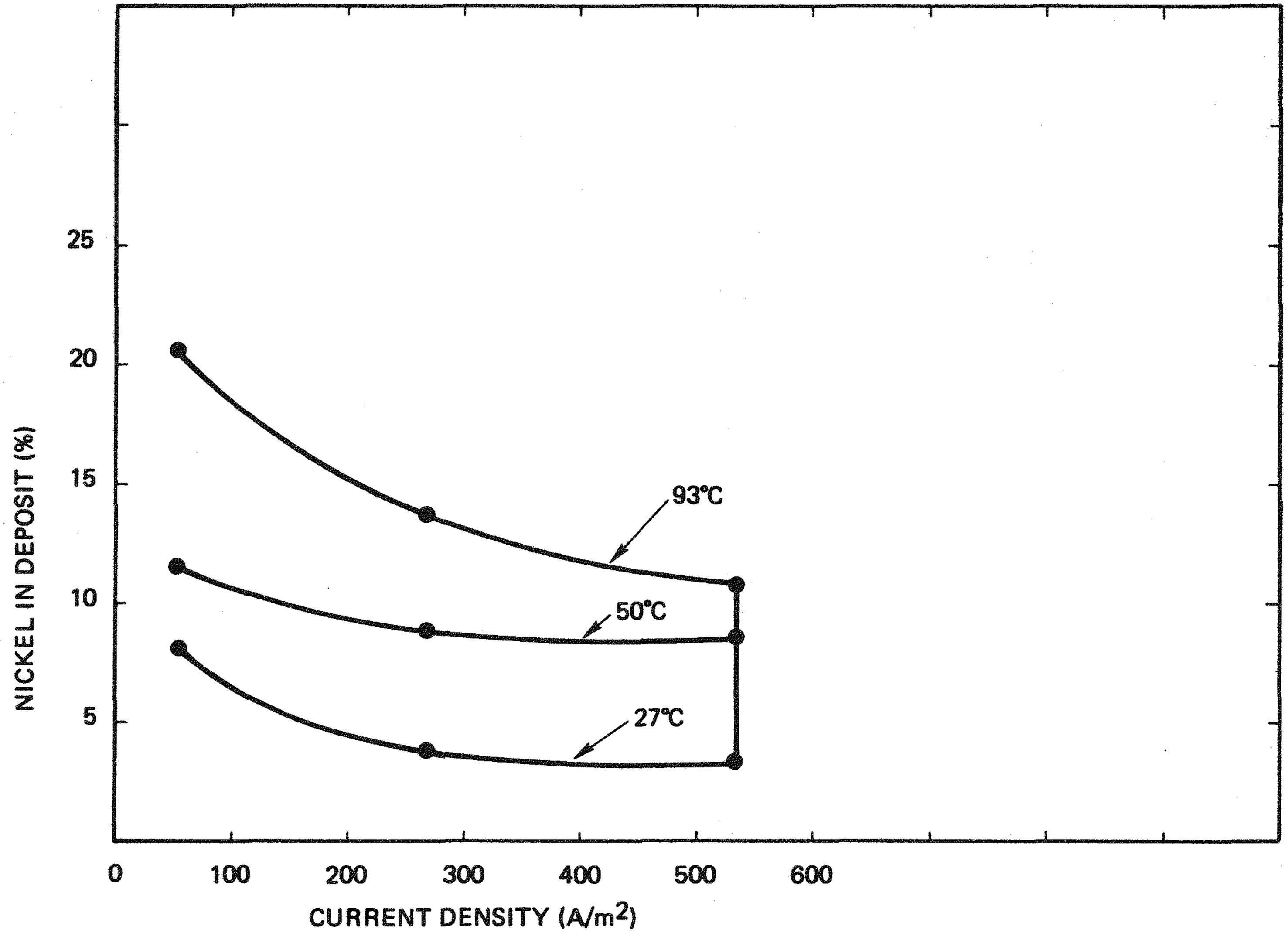
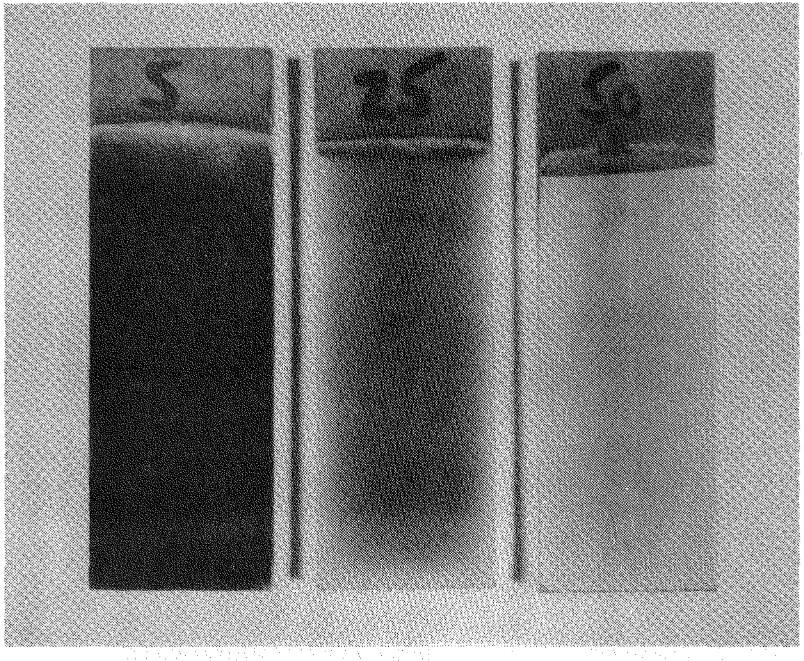


Figure 3. Influence of Current Density and Temperature on Composition



5 asf	25 asf	50 asf
54 A/m^2	269 A/m^2	538 A/m^2

Figure 4. Influence of Current Density on Deposit Appearance (Plating Temperature = 93°C)

TABLE II

GAS AND CARBON CONTENT OF ZINC-NICKEL DEPOSITS

Current Density		Carbon①	Hydrogen②	Oxygen②	Nitrogen②
A/m^2	A/ft^2	(ppm)	(ppm)	(ppm)	(ppm)
54	5	2500	170	1200	800
269	25	2200	115	170	105
538	50	1000	44	181	190

① Determined by combustion in oxygen, and then use of a residual gas analyzer.

② Determined by gas fusion.

after heating at 150°C for 24 hours, which ruled out trapped moisture. For the 54-A/m^2 samples, deposition above 60°C was accompanied by heavy gas evolution and efficiency increased with temperature (Figure 5). This phenomenon was not as obvious at 269 A/m^2 because at this current density efficiencies greater than 100% were not obtained until plating temperatures greater than 70°C were used. At 538 A/m^2, efficiency was 100% over the temperature range of 27 to 93°C (Figure 5).

X-Ray Diffraction

The Debye-Scherrer method was used to obtain X-ray information on some Zn-Ni deposits. The results of this analysis, along with the results from the computer program SEARCH[10] revealed a major line of zinc sulfate hydroxide hydrate, $ZnSO_4 \cdot 3Zn(OH)_2 \cdot 4H_2O$, some minor probable Zn lines, and some unidentified lines. In addition, the SEARCH program also indicated that NiO and $NaNiO_2$ could be present in the sample.

Stress

Stress in the deposit was measured with the rigid-strip technique described by Borchert.[11] Temperature was varied from 49 to 88°C and current density from 27 to 269 A/m^2. The data, included in Table III, show that the stress was quite low, less than 35 MN/m^2 (5000 psi) and influenced very little by variations in current density or temperature.

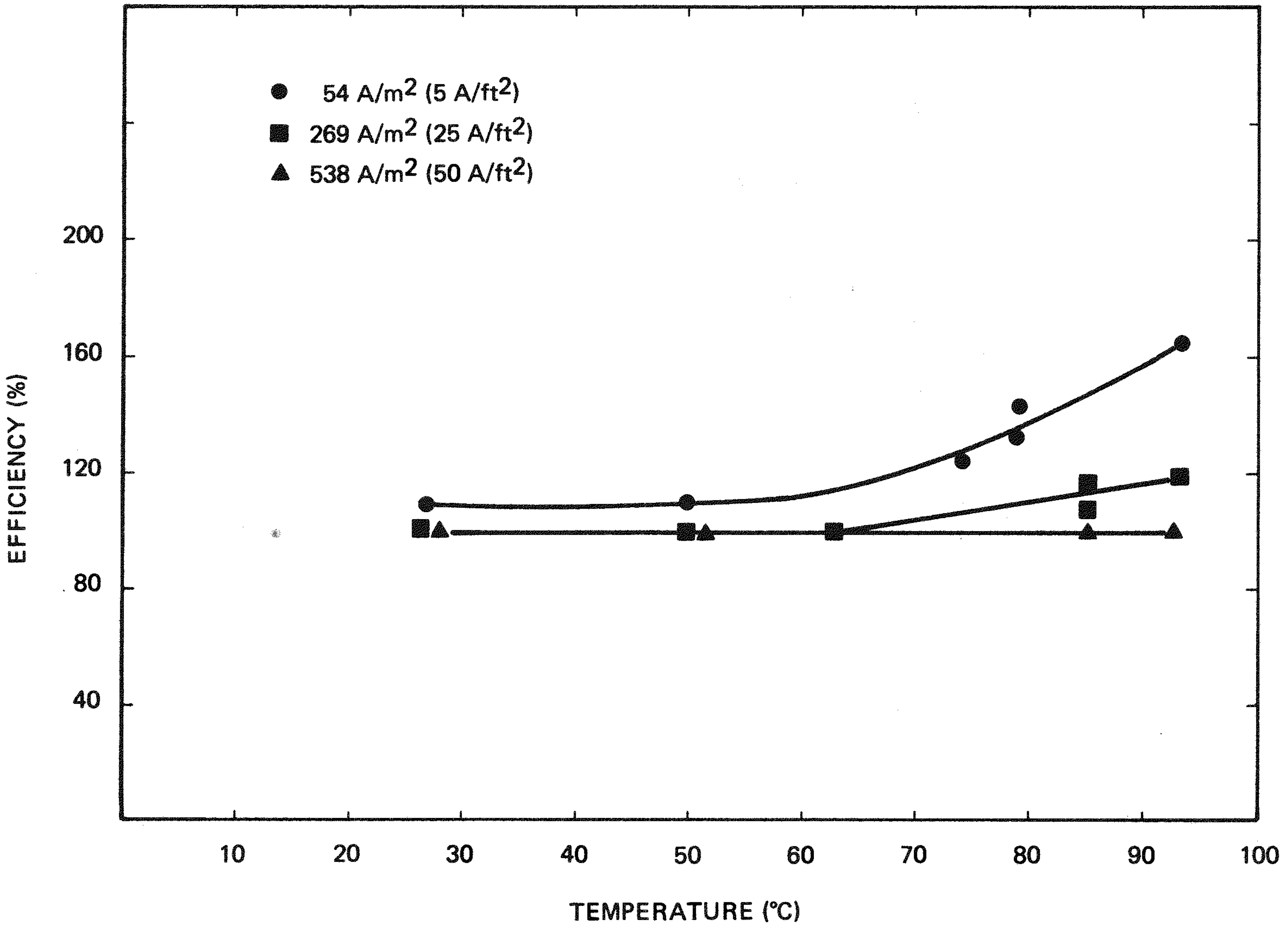


Figure 5. Influence of Temperature and Current Density on Efficiency

TABLE III

INFLUENCE OF TEMPERATURE AND CURRENT DENSITY ON STRESS

Current Density		Temperature		Stress①	
A/m^2	A/ft^2	C°	F°	MN/m^2	psi
27	2.5	88	190	24.1	3500
270	2.5	49	120	35.2	5100
270	2.5	88	190	33.4	4850

① Measured by the rigid strip method, Reference 11.

Salt Fog Tests

Samples and Plating Solutions

For the salt fog tests, steel panels were plated with 2.5, 7.5, 12.5, and 25 μm (0.1, 0.3, 0.5, and 1.0 mil) of cadmium, zinc, and zinc-nickel alloy. The cadmium was plated in a cyanide solution and the zinc in an acid chloride solution according to formulations and operating conditions listed in Table IV. Some of the panels from each set were chromated prior to salt fog testing. Some comment should be made on the chromating of zinc-nickel deposits. A number of proprietary immersion processes were tried with no success, inasmuch as either no apparent chromate film was formed or if one was formed it was non-uniform and/or non-adherent. Use of electrical current in Macro Drab No. 6* which is a proprietary process for zinc and cadmium, did provide a uniform adherent film similar in appearance to the films typically seen on zinc. Parts were cathodically treated in this solution at 9 volts for 1 minute at 32°C.

All samples were placed in plastic holders that inclined them 15 degrees from the vertical. They were exposed up to 500 hours in a cabinet with a 5 percent salt fog environment at 35°C (95°F), per ASTM B117-49T.

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*Mac Dermid, Inc., Waterbury, Conn.

TABLE IV

FORMULATION AND OPERATING CONDITIONS FOR CADMIUM AND ZINC PLATING AND CHROMATING SOLUTIONS

Cadmium		Zinc	
Plating Solution	g/l	Plating Solution	g/l
Cadmium	22.5	Zinc (as zinc chloride)	46
Sodium Cyanide	124	Ammonium Chloride	190
Caustic Soda	19.5	Maz Brightener 8480**	As Recommended by Supplier
Udylyte Bry-Cad #53 Brightener*	As Recommended by Supplier	Maz Brightener 8482**	"
Current Density	161 A/m^2 (15 ASF)	Current Density	259 A/m^2 (25 ASF)
Temperature	27°C	Temperature	27°C
Chromating Solution		Chromating Solution	
Sodium Dichromate	200 g/l	Macro Drab No. 6**	
Sulfuric Acid	6 ml/l		
pH	1.0		
Temperature	25°C	Temperature	27°C
Time	15 s	Time	30 s

*The Udylyte Corp., Detroit Mich.

**Mac Dermid, Inc., Westbury, Conn.

Results

Unchromated Panels

The salt spray results are summarized in Tables V and VI and presented pictorially in Figures 6-11. The panels with no chromate clearly showed the inferiority of unalloyed zinc when compared with cadmium or zinc-nickel alloy coatings in salt spray. Heavy white corrosion products commonly referred to as "white rust"* were obtained very quickly on the pure zinc-coated panels, and rusting started much quicker than on the cadmium or zinc-nickel coated panels. Corrosion was so heavy on the pure zinc panels that none of these were left in salt spray for more than 192 hours, whereas all but the thinnest cadmium and zinc-nickel coatings were exposed for 500 hours. The zinc-nickel coatings exhibited a moderate amount of white corrosion products, considerably less than the pure zinc coatings but more than the cadmium coatings. Figure 6 compares the white rust on unchromated panels after 24 hours. The red rusting on the zinc-nickel deposits was about equivalent to that observed on the cadmium panels. The zinc-nickel coating deposited at 54 A/m^2 was slightly more corrosion resistant to red rusting than the panel plated at 269 A/m^2.

Chromated Panels

The chromated zinc-nickel panels plated at 32°C were not as corrosion resistant during 500 hours of salt spray as those plated at 60°C. This is probably because less nickel is included in the alloy when deposition takes place at lower temperatures (see Figure 3). For the samples plated at 60°C,

---

*These corrosion products are mixtures of zinc hydroxide and zinc carbonate.

TABLE V

SALT SPRAY CORROSION RESULTS FOR CADMIUM (CYANIDE) AND ZINC (ACID) DEPOSITS[A]

Cadmium							Zinc				
Thickness		Chromate Treatment	Hours in Test				Chromate Treatment	Hours in Test			
Mils	Microns		48	192	360	500		24	72	168	192
0.1	2.5	None	Red Rust [C]				None	Red Rust [D]			
0.3	7.5	None	No Corrosion	Red Rust	Red Rust	Red Rust	None	Heavy White Rust	Red Rust [E]		
0.5	12.5	None	No Corrosion	No Corrosion	Red Rust	Red Rust	None	Heavy White Rust	Heavy White Rust	Red Rust [F]	
1.0	25.0	None	No Corrosion	No Corrosion	White Edge Corrosion	White Edge Corrosion	None	Heavy White Rust	Heavy White Rust	Heavy White Rust	Red Rust [G]
			48	192	336	500		240	360		500
0.1	2.5	Yes [B]	No Corrosion	Red Rust	Red Rust	Red Rust	Yes [B]	Slight White Corrosion	Red Rust		Red Rust
0.3	7.5	Yes [B]	No Corrosion	No Corrosion	White Edge Corrosion	White Edge Corrosion	Yes [B]	Slight White Corrosion	Slight White Corrosion		Slight Red Rust
0.5	12.5	Yes [B]	No Corrosion	No Corrosion	No Corrosion	White Edge Corrosion	Yes [B]	Slight White Corrosion	Slight White Corrosion		White Corrosion
1.0	25.0	Yes [B]	No Corrosion	No Corrosion	No Corrosion	No Corrosion	Yes [B]	Slight White Corrosion	Slight White Corrosion		White Corrosion

[A] See Table IV for solution composition and operating conditions.

[B] See Table IV for chromating details.

[C] Tested for only 72 hours.

[D] Tested for only 24 hours.

[E] Tested for only 144 hours.

[F] Tested for only 168 hours.

[G] Tested for only 192 hours.

TABLE VI

SALT SPRAY CORROSION RESULTS FOR ZINC-NICKEL DEPOSITS[A]

Plating Current Density		54 A/m^2					269 A/m^2						269 A/m^2	
Plating Temp.		60°C					60°C						32°C	
Thickness		Chromate Treatment	Hours in Test				Chromate Treatment	Hours in Test					Chromate Treatment	Hours in Test
Mils	Microns		24	48	360	500		24	48	240	336	500		
0.1	2.5	None	Light White Rust	Red Rust [C]			None	Light White Rust	Red Rust	Red Rust	Red Rust	Red Rust		
0.3	7.5	None	Light White Rust	Light White Rust	Red Rust	Red Rust	None	Light White Rust	White Rust	Red Rust	Red Rust	Red Rust		
0.5	12.5	None	Light White Rust	Light White Rust	Light White Rust	Red Rust	None	Light White Rust	White Rust	White Rust	Red Rust	Red Rust		
1.0	25.0	None	Light White Rust	Light White Rust	Light White Rust	Light White Rust	None	Light White Rust	White Rust	White Rust	White Rust	Red Rust		

Mils	Microns	Chromate Treatment	24	360	500	Chromate Treatment	24	48	240	500	Chromate Treatment	24	144	384	500
0.1	2.5	Yes [B]	No Corrosion	Red Rust	Red Rust	Yes [B]	No Corrosion	No Corrosion	White Staining	White Staining	Yes [B]	Light White Rust	Red Rust	Red Rust	Red Rust
0.3	7.5	Yes [B]	No Corrosion	White Staining	White Staining	Yes [B]	No Corrosion	No Corrosion	White Staining	White Staining	Yes [B]	Light White Rust	White Corrosion	Red Rust	Red Rust
0.5	12.5	Yes [B]	No Corrosion	White Staining	White Staining	Yes [B]	No Corrosion	No Corrosion	White Staining	White Staining	Yes [B]	Light White Rust	White Corrosion	White Corrosion	White Corrosion
1.0	25.0	Yes [B]	No Corrosion	White Staining	White Staining	Yes [B]	No Corrosion	No Corrosion	White Staining	White Staining	Yes [B]	Light White Rust	White Corrosion	White Corrosion	White Corrosion

[A] See Table IV for solution composition.

[B] Cathodic at 9 volts for 1 minute at 32°C in Macro-Drab No. 6, Mac Dermid Inc., Waterbury, Conn.

[C] Tested for only 72 hours.

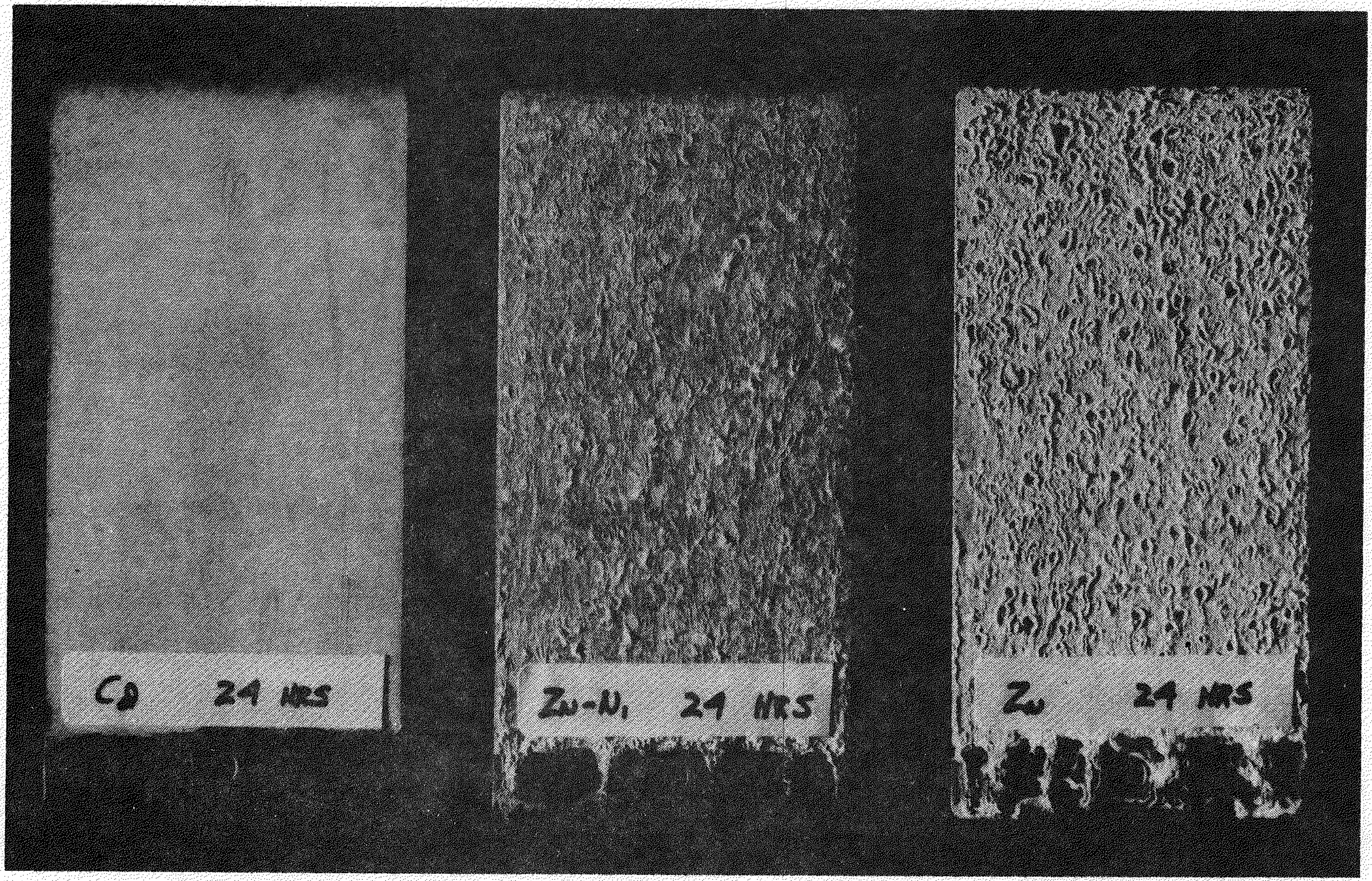
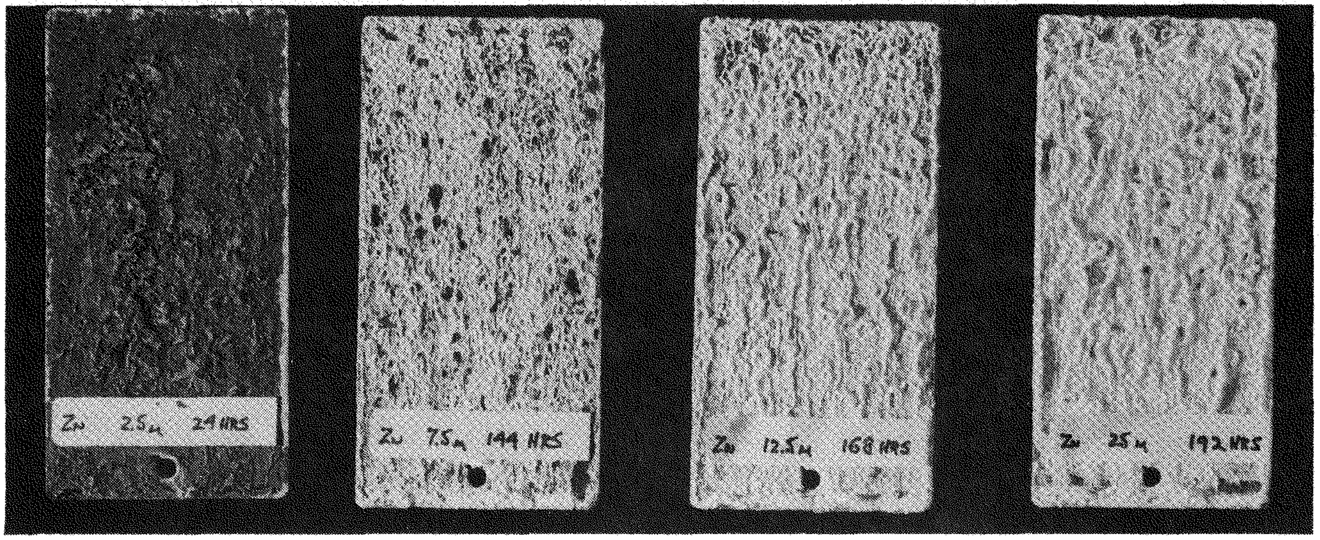
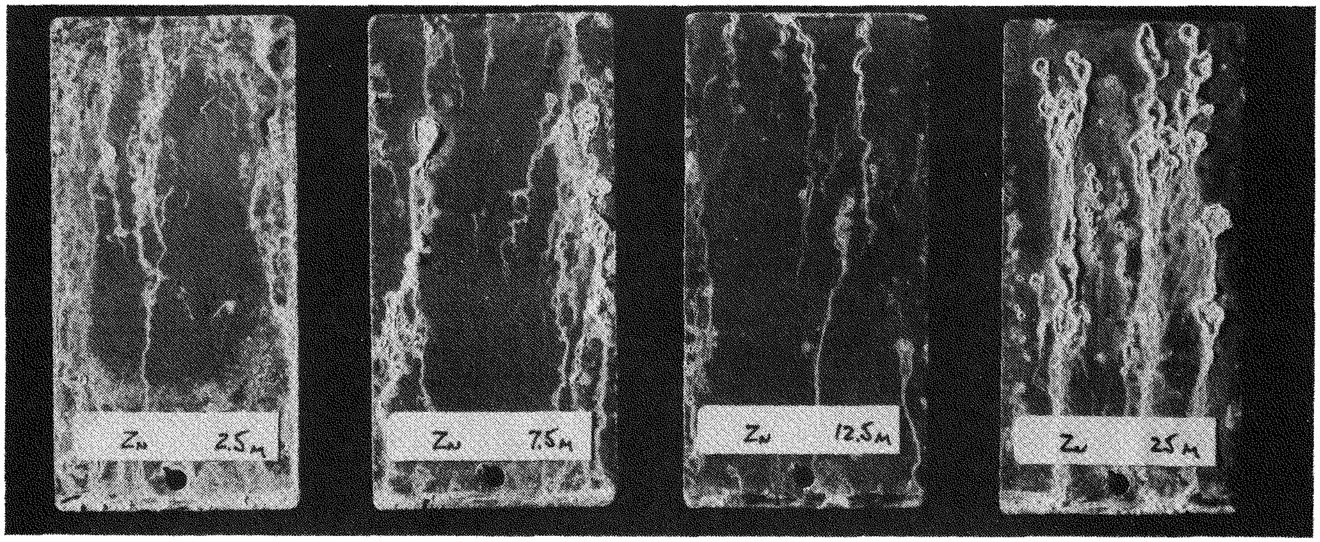


Figure 6. Unchromated Panels After 24 Hours in Salt Spray

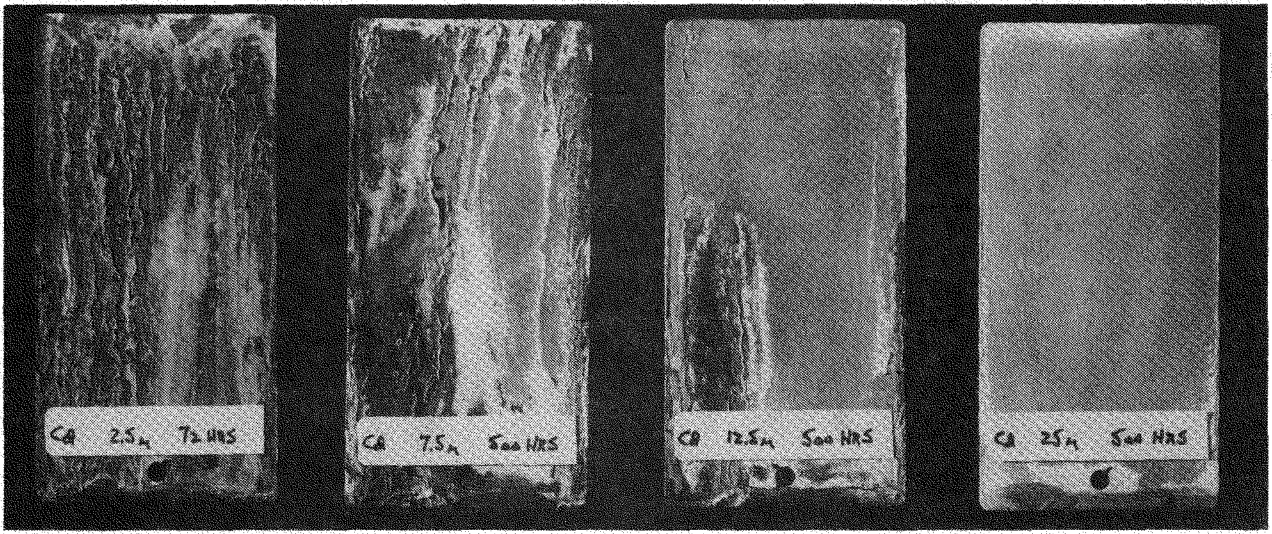


No Chromate Treatment (salt fog exposure time as indicated on panels)

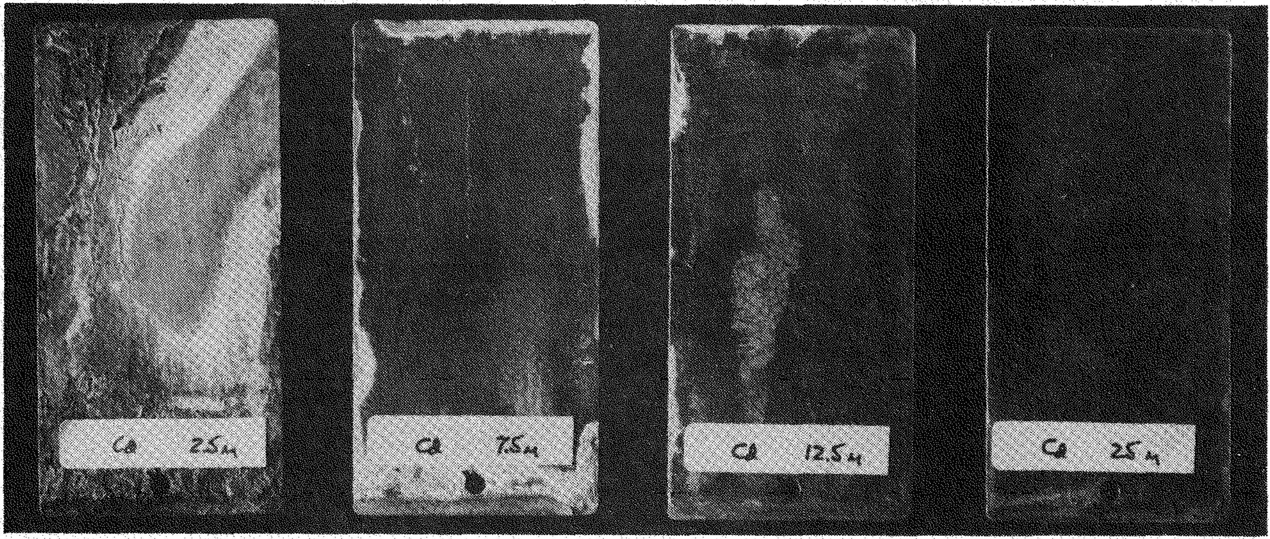


Chromate Treatment (500 hours salt fog exposure)

Figure 7. Samples Plated in Acid Zinc Solution

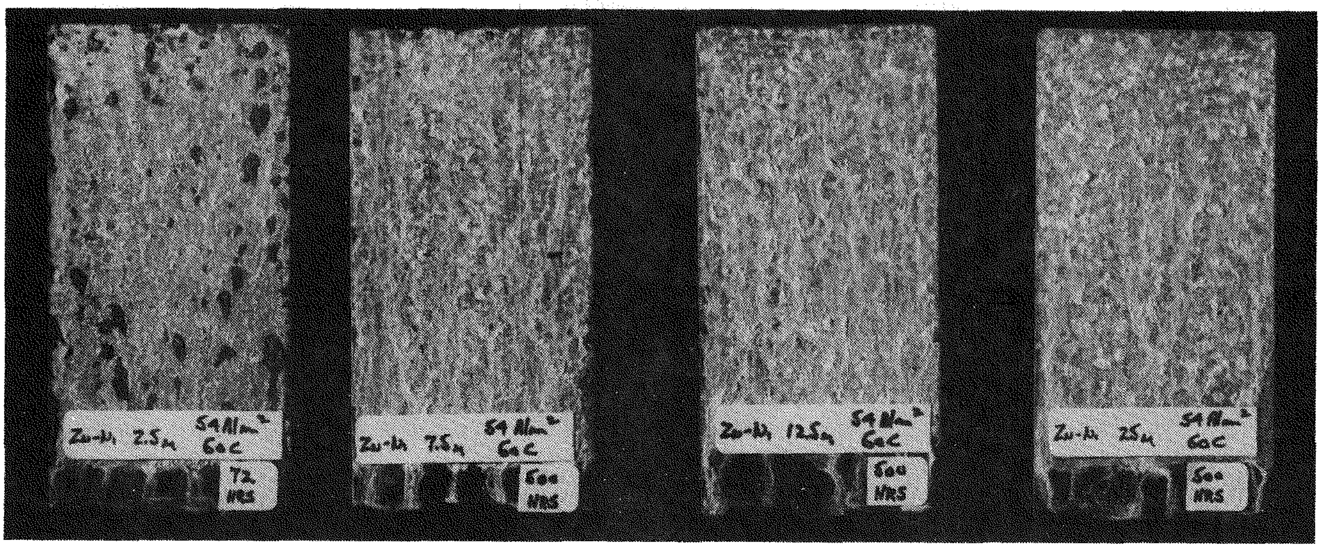


No Chromate Treatment (salt fog exposure time as indicated on panels)

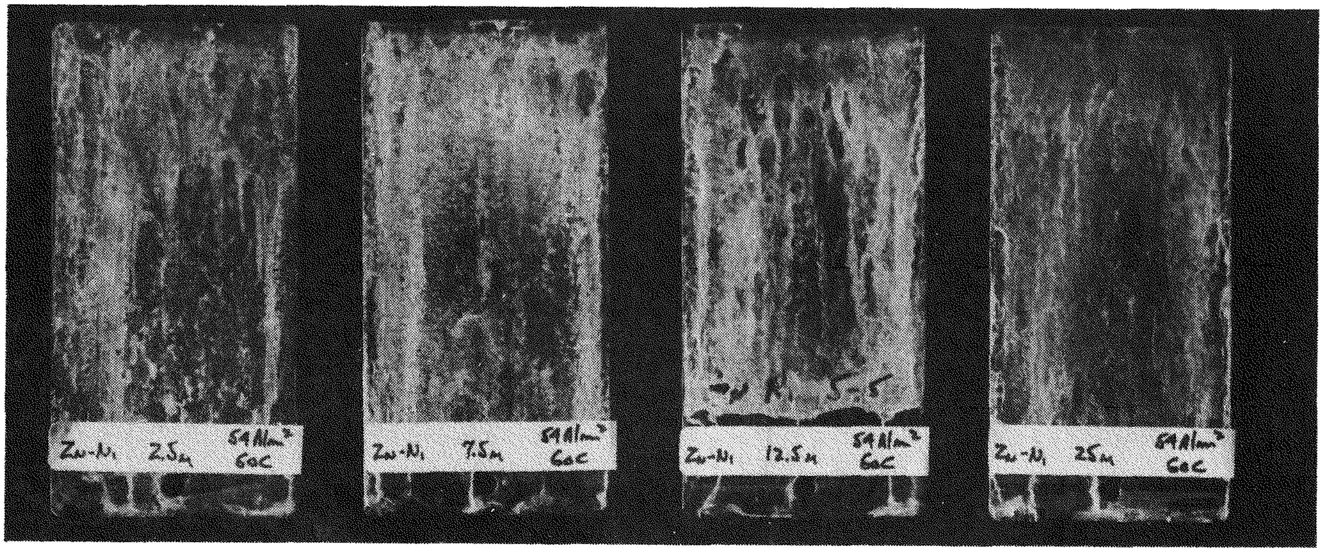


Chromate Treatment (500 hours salt fog exposure)

Figure 8. Samples Plated in Cyanide Cadmium Solution

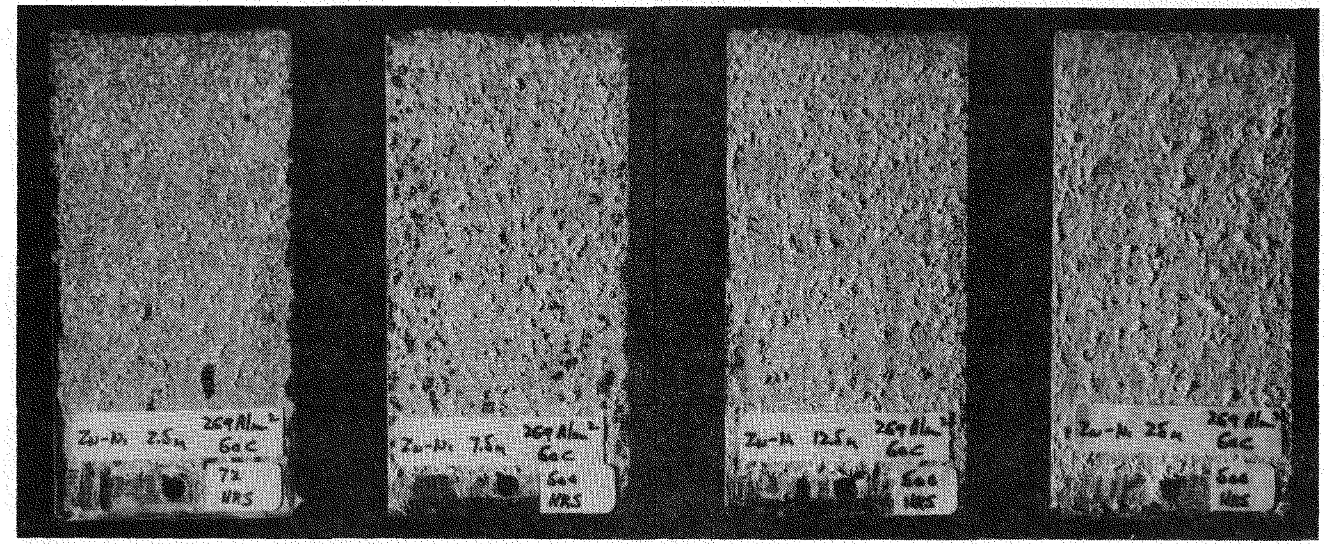


No Chromate Treatment (salt fog exposure time as indicated on panels)

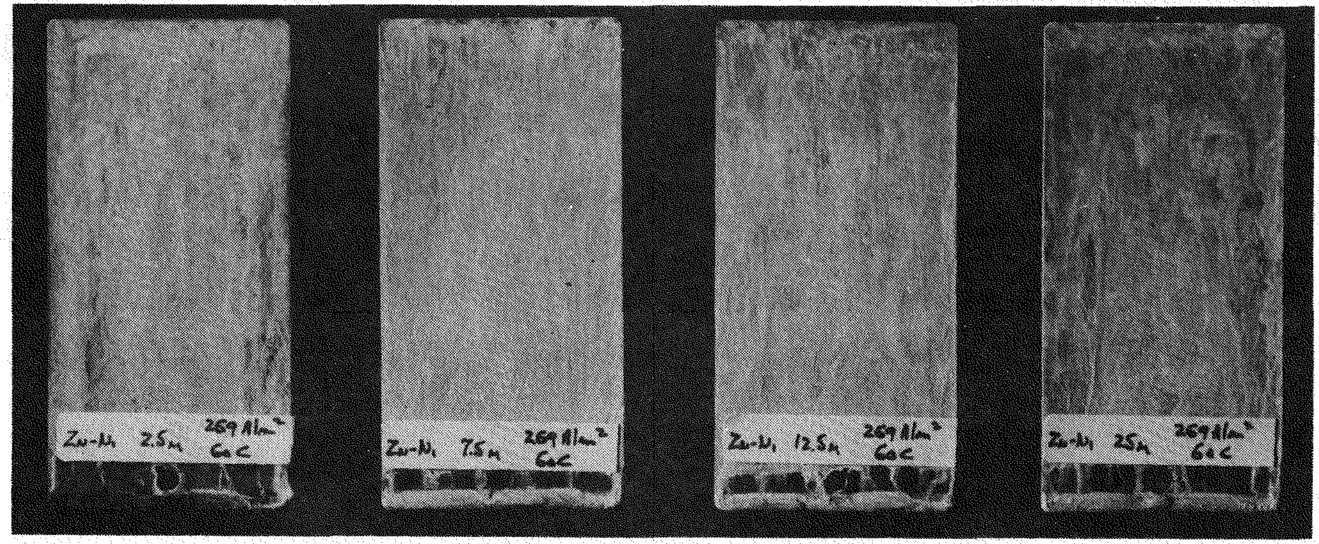


Chromate Treatment (500 hours salt fog exposure)

Figure 9. Samples Plated With Zinc-Nickel (54 A/m^2, 60°C)



No Chromate Treatment (salt fog exposure time as indicated on panels)



Chromate Treatment (500 hours salt fog exposure)

Figure 10. Samples Plated With Zinc-Nickel (269 A/m^2, 60°C)

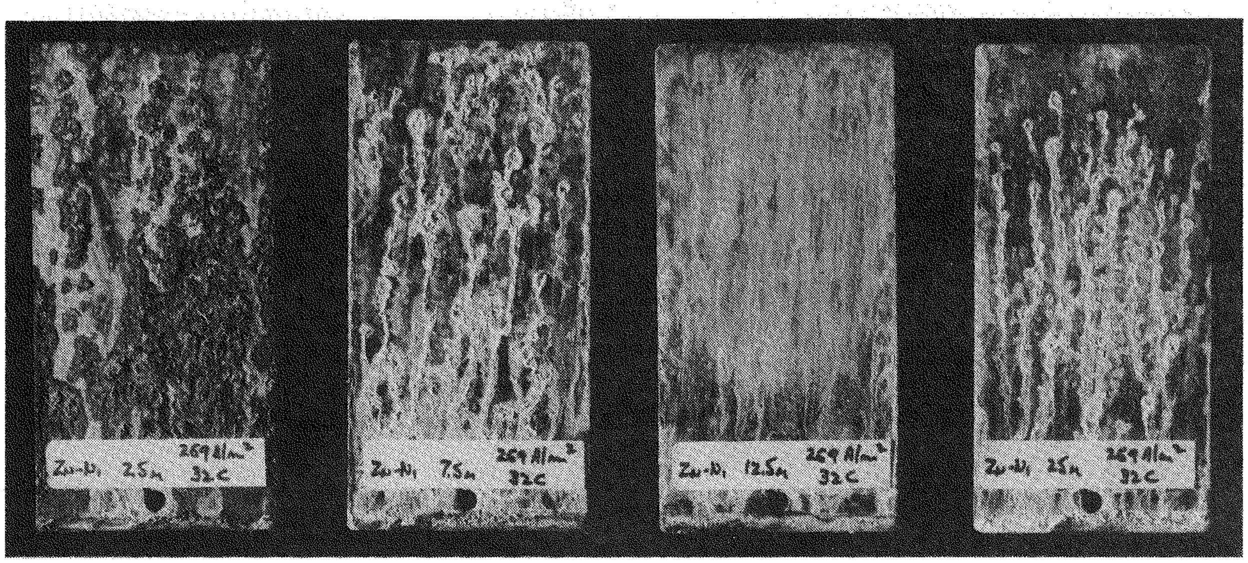


Figure 11. Samples Plated With Zinc-Nickel (269 A/m^2, 32°C) After 500 Hours Salt Fog Exposure (all were given a chromate treatment)

some rust was evident on the panel with 2.5 μm of coating plated at 54 A/m^2; no rust was evident on the companion panels plated at 269 A/m^2.

The zinc-nickel panels plated at 60°C were more corrosion resistant than the acid zinc deposit. Zinc-nickel coatings plated at a current density of 269 A/m^2 exhibited no rusting for the duration of the test, whereas acid zinc coatings and the zinc-nickel coatings plated at 54 A/m^2 did show some rusting. A coating of 2.5 μm of acid zinc started to rust at 360 hours, and at 500 hours the 7.5-μm thick coating of this deposit also started showing red rust. The zinc-nickel deposit plated at 54 A/m^2 showed red rust on the 2.5-μm thick coating at 360 hours but no red rust on the remainder of the panels after 500 hours.

Comparison of zinc-nickel samples with cadmium plated samples showed that the zinc-nickel deposits plated at 60°C performed better than the cadmium panels, especially for a deposit thickness of 2.5 μm. Zinc-nickel deposits plated at 32°C, however, were slightly inferior to the cadmium plated panels. After 500 hours of exposure, heavy red rust was evident on the 2.5-μm thick cadmium panel; no rust appeared on the zinc-nickel coating plated at 269 A/m^2, and only a small amount of rust was evident on the zinc-nickel panel plated at 54 A/m^2.

Summary

Zinc-nickel alloy coatings appear to be a potentially viable substitute for cadmium coatings. Salt fog exposure tests showed that zinc-nickel coatings performed at least as well as cadmium in protecting steel from corrosion. Data on operation of the solution is presented, including the influence of current density and temperature on deposit composition and stress.

Although this effort has demonstrated that Zn-Ni coatings are a potentially viable system for protecting steel from corroding, much work remains to be done to economize the process. Further work is needed on the composition and operating conditions of the solution. Nickel sulfate can be substituted for the nickel sulfamate used in this work but compositional ranges of both the nickel and zinc salts are presently unknown. The solution can probably be operated with much less nickel and still produce satisfactory deposits, but this would have to be proved. Additional effort should also be expended to define the most economical current density and temperature. Also, it is very important to evaluate the potentiality of barrel plating Zn-Ni, since much of the cadmium is plated in this fashion. Further work would also be needed to determine the anode system (pure zinc with occasional additions of nickel, or zinc-nickel alloy anodes) most economical for this solution. Lastly, and perhaps most important, a brightener system would have to be developed if this deposit is ever to really compete with cadmium. Most of the applications for cadmium call for a bright deposit and to try to replace these with a dull zinc-nickel deposit could be an insurmountable task. A bright zinc-nickel deposit would be much easier for users of plated products to accept as a substitute for cadmium.

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