

COPPER UNDERCOATS ON THE CORROSION RESISTANCE OF BRIGHT NICKEL-CHROMIUM AND OF NICKEL-IRON-CHROMIUM ELECTRODEPOSITS ON STEEL SUBSTRATES

SOBHA JAYAKRISHNAN, MALATHY PUSHPAVANAM, SR NATARAJAN and R SUBRAMANIAN

Central Electrochemical Research Institute, Karaikudi - 623 006

ABSTRACT

The present paper deals with the testing of the newly developed nickel-iron plating process with regard to the corrosion performance of coatings produced. Acetic acid salt spray method has been used as the test method. The results show that mild steel plated with nickel iron-chromium systems with iron contents up to 35 % are suitable for indoor applications though slightly inferior to nickel-chromium systems. Literature reports suggest that nickel-chromium systems for outdoor applications are to be modified by inducing microporosity in the chromium top layer and by giving suitable undercoats. The use of a microporous chromium topcoat in improving the performance of nickel and nickel iron coatings are tested. The effect of copper undercoats on the corrosion performance of nickel and nickel iron-chromium systems are compared and it is concluded that a copper undercoat is more beneficial for a nickel iron-chromium system than a nickel-chromium system.

Key words: Corrosion resistance, Ni-Cr, Ni-Fe-Cr, Electrodeposition, copper undercoat

INTRODUCTION

The current escalation in the cost of chemicals and anode materials has necessitated the development of processes designed either to reduce their quantities or to find viable substitutes. Research in the field of decorative chromium plating has led to the development of the nickel-iron process which can help replace a substantial portion of nickel. Reports on the use of nickel-iron alloys have been published from 1973 onwards [1-5]. The important technical question, however, is whether nickel-iron deposits are as corrosion resistant as the iron-free nickel deposits. Earlier the deposits were found suitable for moderately corrosive conditions associated with indoor service. But later reports [6,7] refer to modification of coating systems for severe service conditions by making use of multilayer coatings.

The objections generally raised against nickel-iron alloy deposits are: (i) the addition of iron increases the electrochemical activity of nickel and hence corrosion resistance should be lower and (ii) the corrosion products of iron are brown and more unsightly than the green nickel corrosion products and hence rust stains will be visible in nickel iron coating.

The objections can be annulled by (i) restricting the percentage of iron inclusion in such a way that the corrosion resistance is not drastically reduced and staining is not very heavy and (ii) by improving the coating system by use of multilayer coatings. The possibilities that can be thought of are: (a) to apply a copper undercoat so that pitting attack over the substrate is delayed (b) to use microporous chromium topcoats so that localised attacks at the discontinuities below the chromium layer are spread over a higher area thereby delaying pitting attack and (c) to use multilayer nickel-iron coatings with a nickel-iron alloy of a lower iron content at the top so that staining is reduced.

The authors undertook a comparative study of the corrosion resistance of nickel and nickel-iron alloy coating systems. Accelerated corrosion tests like CASS test [8] and Corrodokote test [9] were earlier carried out. The results of acetic acid salt spray test are discussed in the present paper.

EXPERIMENTAL

Experiments were planned to test the panels with different combinations of deposits in respect of their suitability for mild, moderate, severe and very severe service conditions by inspecting them respectively after 8, 24, 96 and 144 hours of exposure to acetic acid modified salt spray. Testing for periods extending to 240 hrs was carried out to assess the effect of (a) varying the iron percentage in the deposit (b) use of a thin nickel layer with fine inorganic particles embedded thereby inducing microporosity in the chromium topcoat and (c) use of a copper undercoat.

The first part of the work consisted in the preparation of plated panels. Mild steel specimens were plated to 15 μm or 25 μm thickness with nickel or nickel-iron and finally a thin layer of conventional or microporous chromium. In another series of experiments, the panels were subjected to copper plating before nickel or nickel-iron plating. Details of the panels prepared are given in Tables I-III.

Table I: Details of steel specimens prepared with varying iron contents of nickel-iron alloy deposits

Coating system	Percentage of iron in alloy	Thickness of coatings, μm		
		Nickel	Nickel-iron	Chromium
Ni 15b Cr r	—	15	—	0.25
Ni 25b Cr r	—	25	—	0.25
NiFe(1) 15b Cr r	15	—	15	0.25
NiFe(1) 25b Cr r	15	—	25	0.25
NiFe(2) 15b Cr r	20	—	15	0.25
NiFe(2) 25b Cr r	20	—	25	0.25
NiFe(3) 15b Cr r	25	—	15	0.25
NiFe(3) 25b Cr r	25	—	25	0.25
NiFe(4) 15b Cr r	30	—	15	0.25
NiFe(4) 25b Cr r	30	—	25	0.25
NiFe(5) 15b Cr r	35	—	15	0.25
NiFe(5) 25b Cr r	35	—	25	0.25

Table II: Specimens prepared with copper undercoats

Coating system	Thickness of coatings, μm		
	Copper	Nickel or Nickel-iron (25%)	Chromium
Cu5 Ni15b Cr r	5	15	0.25
Cu 5 Ni25b Cr r	5	25	0.25
Cu10 Ni15b Cr r	10	15	0.25
Cu 10 Ni25b Cr r	10	25	0.25
Cu5 NiFe15b Cr r	5	15	0.25
Cu 5 NiFe25b Cr r	5	25	0.25
Cu10 NiFe15b Cr r	10	15	0.25
Cu 10 NiFe25b Cr r	10	25	0.25

Table III: Specimens prepared with microporous chromium topcoats

Coating system	Thickness of coatings, μm			
	Copper	Nickel or Nickel-iron (25%)	Nickel*	Chromium
Ni 15b Cr mp	—	15	2.5	0.25
Ni 25b Cr mp	—	25	2.5	0.25
NiFe 15b Cr mp	—	15	2.5	0.25
NiFe 25b Cr mp	—	25	2.5	0.25
Cu5 Ni15b Cr mp	5	15	2.5	0.25
Cu5 Ni25b Cr mp	5	25	2.5	0.25
Cu5 NiFe15b Cr mp	5	15	2.5	0.25
Cu5 NiFe25b Cr mp	5	25	2.5	0.25
Cu10 Ni15b Cr mp	10	15	2.5	0.25
Cu10 Ni25b Cr mp	10	25	2.5	0.25
Cu10 NiFe15b Cr mp	10	15	2.5	0.25
Cu10 NiFe25b Cr mp	10	25	2.5	0.25

* Satin nickel with fine inorganic particles was applied before chromium plating for inducing microporosity in the chromium layer.

Compositions of the plating baths that were used are given in Table IV. The nickel and nickel-iron alloy plating solutions used are those reported by the authors earlier [10, 11]. Nickel-iron alloys of varying iron contents were produced by adjusting the bath composition and operating conditions [12]. Copper undercoats were applied from a conventional cyanide copper bath with proprietary brighteners. A nickel layer containing codeposited fine inert particles was deposited from a conventional nickel bath with a suspension of fine barium sulphate particles, so that the latter effectively induced microporosity in the chromium layer finally plated from a conventional chromic acid bath. Regular chromium deposits could be produced when the special nickel layer was not included.

Rates of deposition from the above baths were determined by depositing the metal on stainless steel specimens of 7.5 cm x 3 cm size. In the case of nickel-iron alloy coated specimens, the deposits were stripped in 1 : 1 nitric acid and analysed for iron.

Mild steel panels 7.5 cm x 3 cm were pretreated by conventional methods and plated suitably, for preparing each set of plated specimens for the corrosion test. The panels were masked at the edges leaving an effective area of 5.0 x 2.5 cm exposed in each case. They were degreased and cleaned

with a slurry of magnesium oxide before being subjected to the acetic acid salt spray test.

Table IV: Plating bath compositions and operating conditions used

Sl. No.	Solution	Composition	Conditions			
			pH	c.d. A/dm ²	Temperature °C	Mode of agitation
1.	Bright nickel	Nickel sulphate—250 g/l Nickel chloride 30 g/l Boric acid—40 g/l Brightener—as required	4.0	4	60	By means of air
2.	Bright nickel-iron	Nickel sulphate 75 g/l Nickel chloride 75 g/l Ferrous sulphate 15 g/l Boric acid 45 g/l Stabiliser 30 g/l Brightener—as required	3.2	4	60	—do—
3.	Bright copper	Copper cyanide 26 g/l Sodium cyanide 35 g/l Sodium carbonate 30 g/l Rochelle salt 45 g/l Brightener—as required	12.6	3	55	Mechanical
4.	Nickel seal	Nickel sulphate 250 g/l Nickel chloride 30 g/l Boric acid 40 g/l Barium sulphate 100 g/l	4.0	4	55	—do—
5.	Chromium	Chromic acid 250 g/l Sulphuric acid 2.5 g/l	—	15	50	—do—

The solution for the spray test was a 5% solution of AR NaCl in distilled water, the pH being adjusted to 3.0 with AR glacial acetic acid. A salt spray cabinet (M/s. Canning Ltd. Birmingham) was used. The test specimens were arranged inside the cabinet by means of glass hooks in such a way that the surfaces were exposed freely to the fog. The test schedule included 8 hrs spray and 16 hrs rest successively and the experiment was conducted up to 240 hrs of spraying. Periodical observations were made after every 8 hrs spraying.

In regard to corrosion performance rating, the ASTM method (B537-70) [13, 14] has been used in this paper. The method uses a two number system in which the first number denotes protection of the substrate and the second number is descriptive of appearance. A perfect specimen showing no deterioration is rated 10/10. Progressive degrees of failure are denoted by lower numbers. A rating below 7 for either protection or appearance is frequently considered unsatisfactory [5, 15].

RESULTS AND DISCUSSION

Acetic acid salt spray is a recommended test method for studying the corrosion performance of electroplated coatings of nickel and chromium. The exposure periods recommended for mild, moderate, severe and very severe service conditions are 8, 24, 96 and 144 hrs respectively [16].

Single layer nickel and nickel-iron alloy coatings of 15 μm thickness and regular chromium topcoats were tested for their suitability for service grades 1 and 2. For an exposure period of 8 hrs all the panels were intact with no trace of corrosion whereas after a test duration of 24 hrs, there was onset of corrosion (Fig. 1) leading to rating numbers above 7 for all. This indicates that coatings of single layer nickel or nickel-iron alloys with iron contents up to 35% and with a regular chromium topcoat in each case are suitable for mild and moderate service conditions such as indoor applications. Similar conclusions had been reported earlier from acetic acid salt spray test [17] and CASS test [8, 18].

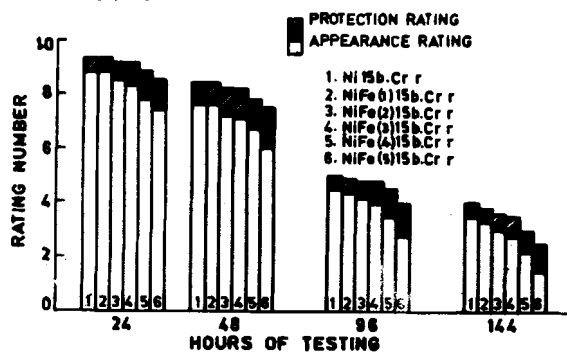


Fig. 1: Effect of iron content on the performance of nickel iron (15 μm) alloy coatings.

Nickel-chromium or nickel iron-chromium systems with 25 μm thick coatings do not satisfy the requirement for service condition 3, namely, 96 hrs spray (Fig. 2). For both 15 μm and 25 μm thick deposits continued exposure shows that the difference in performance between nickel and nickel iron increases as corrosion proceeds. This can be explained in terms of the increased corrosion rate of nickel iron as evidenced by its static potential (Table V) and increase in its staining which increases with an increase in iron content.

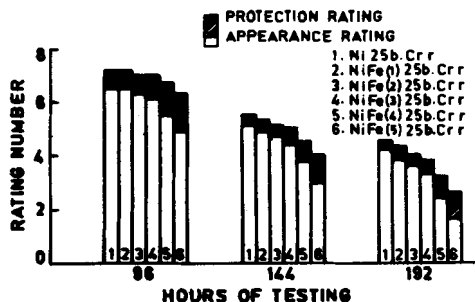


Fig. 2: Effect of iron content on the performance of nickel-iron (25 μm) alloy coatings

Table V: Static potential of electrodeposited foils in 5% sodium chloride solution of pH 3.0

Electrodeposited foil	Potential V (V_s SCE)
Nickel	-0.290
Nickel-iron (20% iron)	-0.340
Nickel-iron (25% iron)	-0.350
Nickel-iron (35% iron)	-0.410
Copper	-0.275

The improvement in corrosion performance of nickel/nickel-iron system brought about by means of a microporous layer of chromium is illustrated in Fig. 3 and 4. The nickel systems show a consistently better performance than nickel-iron systems though the influence of staining is less with lower iron contents.

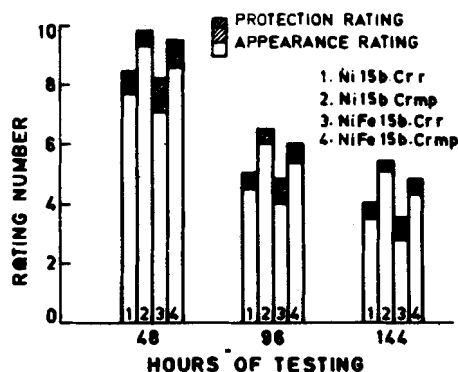


Fig. 3: Corrosion performance of nickel and nickel-iron coatings (15 μm) with regular & microporous chromium topcoats

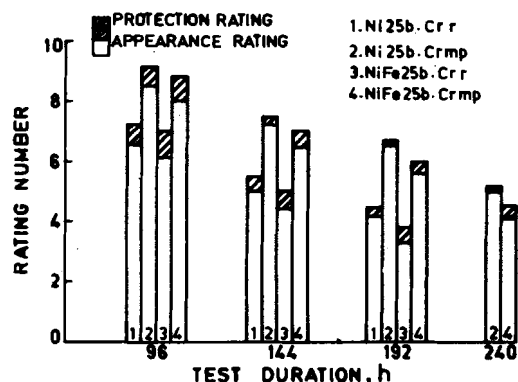


Fig. 4: Corrosion performance of nickel and nickel-iron coatings (25 μm) with regular & microporous chromium topcoats

Results of acetic acid salt spray tests on the effect of copper undercoats on nickel/nickel-iron-conventional-chromium systems are shown in Fig. 5 and 6. The difference in behaviour between nickel and nickel-iron is to be attributed to the possibility that though nickel remains anodic to copper initially, as corrosion proceeds, there is a reversal of corrosion behaviour which means copper corrosion occurs in copper-nickel-chromium systems resulting in loss of appearance, blister formation and penetration to the basis metal. This type of a polarity reversal may not be possible in nickel-iron because of its more anodic character. The advantage of copper undercoats of adequate thickness (10 μm) is borne out by the better performance of the nickel-iron system than the nickel system. This is also in agreement with the observations of Claus [5]. Failure due to corrosion is to be traced to the greater porosity of copper coating [8] when applied in low thicknesses.

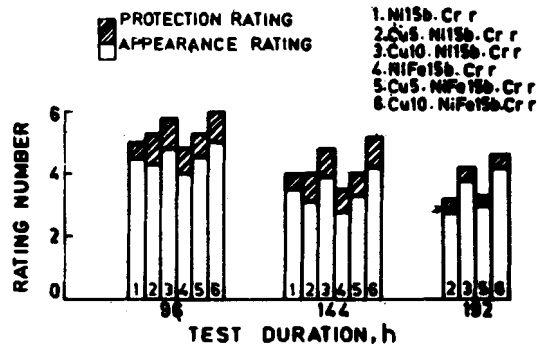


Fig. 5: Effect of copper undercoats on the performance of Ni/Ni-Fe (15 μm) regular chromium coatings

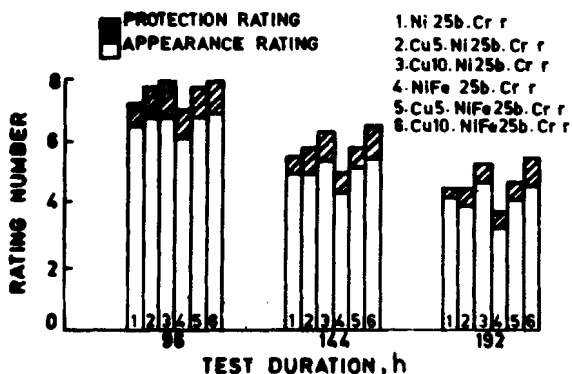


Fig. 6: Effect of copper undercoats on the performance of Ni/Ni-Fe (25 μm) chromium coatings

The combined effect of a copper undercoat and a microporous chromium topcoat may be considered now. Fig. 7 and 8 show that copper undercoats improve the corrosion performance of nickel/nickel-iron-microporous chromium systems in conformity with literature reports [19-21]. With sufficiently thick copper layers (10 μm) initially applied, nickel-iron coatings are found to perform better than the corresponding nickel systems when basis metal protection is considered. However, the appearance is slightly inferior.

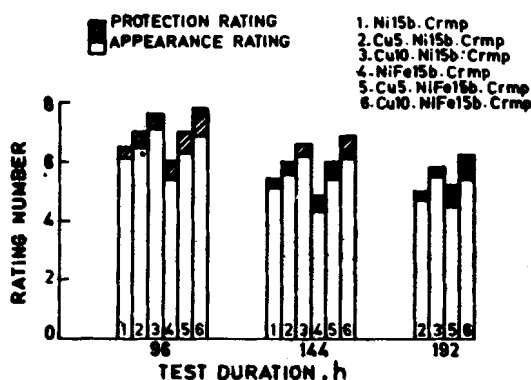


Fig. 7: Effect of copper undercoat on the corrosion performance of Ni/Ni-Fe (15 μm) microporous chromium coatings

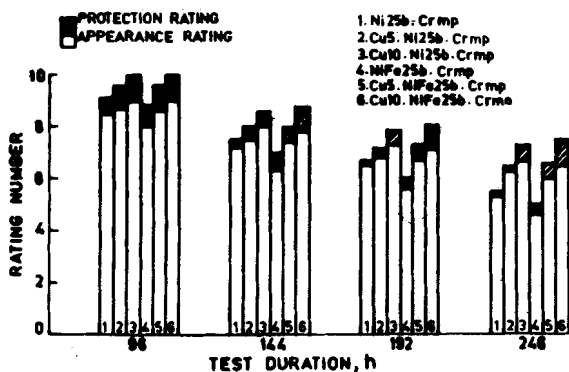


Fig. 8: Effect of copper undercoat on the corrosion performance of Ni/Ni-Fe (25 μm) microporous chromium coatings

The effects of copper undercoats and chromium layers on the corrosion performance are summarised in Tables VI and VII. Multilayer systems consisting of copper undercoats of adequate thickness and microporous chromium topcoats have as acceptable a corrosion protection performance as the system based on nickel.

Table VI: Effect of copper undercoat on the corrosion performance ratings after 96 hours of exposure

Thickness of copper undercoat μm	Type of Cr topcoat	Ratings for 15 μm coatings	
		Nickel	Nickel-iron
0	r	5.0* / 4.5 §	4.8 / 4.0
0	mp	6.5 / 6.1	6.0 / 5.4
5	r	5.3 / 4.3	5.3 / 4.5
5	mp	7.0 / 6.5	7.0 / 6.3
10	r	5.8 / 4.8	6.0 / 5.0
10	mp	7.6 / 7.1	7.8 / 6.9

* Protection rating

§ Appearance rating

Table VII: Effect of copper undercoat on the corrosion performance ratings after 144 hours of exposure

Thickness of copper undercoat μm	Type of Cr topcoat	Ratings for 25 μm coatings	
		Nickel	Nickel-iron
0	r	5.5* / 5.0 §	5.0 / 4.4
0	mp	7.5 / 7.2	7.0 / 6.5
5	r	5.8 / 5.0	5.8 / 5.2
5	mp	8.0 / 7.5	8.0 / 7.4
10	r	6.3 / 5.4	6.5 / 5.5
10	mp	8.6 / 8.0	8.8 / 7.8

* Protection rating

§ Appearance rating

CONCLUSIONS

Single layer nickel iron-chromium systems with iron contents of up to 35% pass the acetic acid salt spray test for indoor applications though their performance is slightly inferior to that of nickel-chromium systems. Modification of the chromium topcoat by inducing microporosity improves the corrosion performance of nickel-chromium and nickel iron-chromium systems. A copper undercoat of adequate thickness is highly favourable for the nickel-iron system. Protection ratings equal to those of nickel systems were obtained for acetic acid salt spray exposure for smaller duration, the corrosion protection offered by the nickel-iron systems appears to be slightly better than the nickel systems when longer exposure periods are involved.

REFERENCES

1. R.J Clauss and R.A Tremmel, *Plat Surf Finish*, **66** (1973) 803
2. R.J Clauss, R.A Trammel and R.W Klein, *Trans Inst Metal Finish*, **53** (1975) 22
3. R.J Clauss and R.A Tremmel, *Proc Int Metal Finish Congr Interfinish*, **76** (1976) 239
4. R.A Tremmel, *Plat Surf Finish*, **82-1** (1981) 22
5. R.J Clauss, *Atmospheric Corrosion of Metals*, ASTM Special Technical Publication, (1982) 767, 214 pp
6. R.A Tremmel, *Prod Finish (Cincinnati)*, **44-9** (1980) 42
7. R.A Tremmel, *Plat Surf Finish*, **82-2** (1981) 30
8. Malathy Pushpavanam, Sobha Jayakrishnan, SR Natarajan and R Subramanian, *Int Symp Advan Electrochem Sci and Technol*, 3rd Dec. (1984) Madras

Sobha Jayakrishnan et al – Copper undercoats on the corrosion resistance of Ni-Cr and Ni-Fe-Cr electrodeposits

9. Malathy Pushpavanam, Sobha Jayakrishnan, SR Natarajan and R Subramanian, *Symp Corro Prev*, Varanasi, Oct. (1984)
10. Vidyalakshmi Raman, Malathy Pushpavanam and BA Shenoi, *Plat Surf Finish*, **69** (1982) 132
11. Malathy Pushpavanam, Vidyalakshmi Raman and BA Shenoi, *J Electrochem Soc India*, **31**-1 (1982) 18
12. Malathy Pushpavanam, Vidyalakshmi Raman, Sobha Jayakrishnan and BA Shenoi, *Corros Bull*, **3** (1983) 322
13. 1982 Annual Book of ASTM Standards, p 364
14. A Kenneth Graham (Ed), *Electroplating Engineering Handbook*, Van Nostrand Reinhold Company, Third Ed. (1973) p 323
15. GA DiBari, G Hawks and EA Baker, *Atmospheric Corrosion of Metals*, ASTM Special Technical Publication, (1982) 767, p 186
16. 1982 Annual Book of ASTM Standards, p 271
17. JS Hadley and JO Grady, *Trans Inst Metal Finish*, **59**-3 (1981) 89
18. H Chessin, EJ Seyb and PD Walker, *Plat Surf Finish*, **63**-12 (1976) 32
19. S A Watson, *Proc Symp Recent Develop Nickel-Chromium Plat*, March (1973) Bombay
20. RJ Clauss and RW Klein, *Proc Int Metal Finish Congr Interfinish*, **68** (1968) p 124
21. NW Phasey, *Trans Inst Metal Finish*, **49** (1971) 48