

## EVALUATION OF PERFORMANCE OF ELECTROPLATED Cu-Ni-Cr AND DOUBLE LAYER Ni-Cr COATINGS ON MILD STEEL

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### ABSTRACT

Various types of decorative copper-nickel-chromium electrodeposits were produced on mild steel substrates and their corrosion resistance evaluated by means of CASS and Corrodokote accelerated tests and also by exposure tests at Mandapam Camp, a locality with a tropical marine atmosphere. The behaviour of the electrodeposits was examined by anodic polarisation in CASS and Corrodokote media. The results of all the above investigations are presented in this paper.

**Key words:** corrosion resistance, copper-nickel-chromium coating.

### INTRODUCTION

The protection given by and the corrosion behaviour of various combinations of electroplates have been extensively studied by field tests and accelerated laboratory tests [1]. It has been generally accepted that failure of electroplate combinations is related to the differences in potentials among the different metals constituting the electroplated systems [2]. However, it is only in recent years that the importance of a closer understanding of the galvanic relationship that exists between various electrodeposits and the substrate in different electrolytes has come to receive increasing attention [3]. Polarisation curves may be used to predict and interpret galvanic effects (4). Typical corrosion diagrams of electroplate combinations have been studied [5,6] along with the reactivities of various nickel electrodeposits. The distribution of galvanic current between bright and semibright nickel in double layer nickel systems have been investigated [7,8].

This paper deals with production of various types of multilayer coatings viz. (i) bright nickel + chromium (ii) semibright nickel + bright nickel + chromium (iii) copper + semibright nickel + bright nickel + chromium and with steel as substrate and chromium, either conventional or microporous, assessment of their performance in CASS and Corrodokote accelerated tests besides field exposure at Mandapam Camp and polarisation measurements.

### EXPERIMENTAL

Cleaned cold-rolled steel specimens of 0.25 mm thickness and of 8 x 5 cm size were subjected to plating of bright nickel, semibright nickel or copper on both sides and taken through the full sequence of decorative nickel-chromium plating, the duration of plating being properly adjusted to obtain the desired thickness as indicated in column 1 of Table I. Plating solutions of 25 litres volume prepared with LR grade chemicals were used. Pure copper and nickel anodes were employed for copper and nickel plating respectively and anodes of lead alloy carrying 7% tin for chromium plating. The source of current for electrocleaning, copper plating or nickel plating was a single-phase rectifier and that for chromium plating a three-phase rectifier.

The following preplating sequence was followed: (i) Solvent degreasing with trichloroethylene (ii) Electrocleaning in a sodium hydroxide (35 g/l)

and sodium carbonate (25 g/l) at 70°C at a current density of 700A/m<sup>2</sup>, cathodically for 2 minutes and anodically for 1 minute respectively (iii) Washing well in running tap water and (iv) A dip in 5% sulphuric acid for 10 seconds.

### Copper plating

The copper undercoat was applied by making use of cyanide copper strike (solution A, 0.5 μm) and acid copper plating (solution B, 9.5 μm) respectively as indicated below:

A. Cuprous cyanide	: 22.5 g/l
Sodium cyanide	: 7.5 g/l
Current density	: 100 A/m <sup>2</sup>
Time	: 3 min
Temperature	: 30°C

B. Copper sulphate	: 228 g/l
Sulphuric acid	: 99 g/l
Temperature	: 30°C
Current density	: 200 A/m <sup>2</sup>
Time	: 22 min

A wash under running tap water followed by a 5% sulphuric acid dip for 10 seconds and subsequent washing and rinsing respectively was employed after copper deposition from cyanide, but before acid copper plating. The copper deposit was buffed to a bright finish before nickel plating.

### Semibright nickel plating

The composition and operating conditions of semibright nickel bath are as follows:

Nickel sulphate	240 g/l
Nickel chloride	40 g/l
Boric acid	30 g/l
Sodium lauryl sulphate	0.1 g/l
Saccharin	0.15 g/l
Temperature	50°C
Current density	310 A/m <sup>2</sup>
Rate of build up	40 μm/h

**Bright nickel plating**

Bright nickel plating was carried out in the bath of the following composition and operated under conditions as below:

Nickel sulphate	240 g/l
Nickel chloride	40 g/l
Boric acid	30 g/l
2-Butyne, 1,4-diol	0.5 g/l
Saccharin	1.5 g/l
Sodium lauryl sulphate	0.15 g/l
Temperature	50°C
Current density	310 A/m <sup>2</sup>
Rate of build up	40 μm/h

**Conventional chromium plating**

Chromic acid	250 g/l
Sulphuric acid	2.5 g/l
Trivalent chromium	0.1 g/l
Temperature	50°C
Current density	1550 A/m <sup>2</sup>
Rate of build up	9.9 μm/h

**Microporous chromium**

In the case of a certain number of nickel plated panels, thin overlays of decorative chromium with micropores were applied. Typical chromium plated panels examined microscopically for porosity had pore densities ranging 10000 - 40000 micropores/cm<sup>2</sup>. A solution for direct deposition of microporous chromium and prepared from chromium trioxide, sulphuric acid and fluosilicic acid was used in this case.

**Coating systems studied**

Eight different combinations of deposits with mild steel as substrate were prepared -

1. Bright nickel (25 μm) + chromium (conventional, 0.3 μm)
2. Bright nickel (25 μm) + chromium (microporous, 0.3 μm)
3. Semibright nickel (12 μm) + bright nickel (8 μm) + chromium (conventional 0.3 μm)
4. Semibright nickel (12 μm) + bright nickel (8 μm) + chromium (microporous, 0.3 μm)
5. Semibright nickel (17 μm) + bright nickel (8 μm) + chromium (conventional 0.3 μm)
6. Semibright nickel (17 μm) + bright nickel (8 μm) + chromium (microporous, 0.3 μm)
7. Copper (10 μm) + semibright nickel (12 μm) + bright nickel (8 μm) + chromium (conventional 0.3 μm)
8. Copper (10 μm) + semibright nickel (12 μm) + bright nickel (8 μm) + chromium (microporous, 0.3 μm)

**Evaluation of the performance of nickel-chromium plated specimens against corrosion**

The plated panels were subjected to two widely adopted and effective accelerated corrosion tests, namely the CASS and Corrodokote. Another batch of specimens was exposed to the tropical marine atmosphere at Mandapam Camp. The nickel-chromium plated specimens were also subjected to anodic polarisation studies in the CASS and Corrodokote media. Details of the different tests are given below.

**CASS TEST**

Cupric chloride was introduced to the extent of 0.26 g/l into a 5 percent (w/v) salt spray solution and the solution pH adjusted to 3.2 with acetic acid. The test conditions were almost the same as for salt spray exposure except that a higher temperature of 49°C was maintained as recommended in the specifications.

The surface of the specimens was thoroughly degreased before the test.

The specimens were subjected to CASS test in a Canning salt spray cabinet for a period of 72 hours. They were then taken out and carefully washed in tap water, rinsed with distilled water and dried.

**CORRODKOTE TEST (9)**

The Corrodokote slurry was prepared generally in accordance with the BS specifications. The slurry, prepared from Kaolin (30 g) and a mixture of solutions of cupric nitrate (7.0 ml of 5.0 g/l solution), ferric chloride (33.0 ml of 5.0 g/l solution) and ammonium chloride (10.0 ml and 100 g/l solution), was applied on the plated panels with a brush in a circular motion so that an adequately uniform coating was obtained. The panels were dried and kept in a humidity cabinet at a temperature of 38°C and 95-98% relative humidity.

After exposure for 48 hours in the humidity chamber, the specimens were removed, carefully washed and dried. A fresh Corrodokote slurry was again applied and the specimens were reexposed in the humidity chamber for another 24 hours.

Thus after a total exposure period of 72 hours, the specimens were taken out, and the paste was carefully removed in running tap water. The specimens were then kept in the humidity chamber for a further period of 24 hours, after which they were evaluated for their corrosion resistance.

**Polarisation studies in CASS and corrodokote media**

Cold-rolled steel panels of 1 cm<sup>2</sup> size with different combinations of copper, nickel and chromium respectively as applied, were anodically polarised in CASS and corrodokote solutions using a counter electrode of platinum of 1 cm<sup>2</sup> area. In the case of the latter solution, no kaolin was added. A constant current generator was used as the source of D.C. current and the potential of the working electrode measured by means of a digital multimeter with reference to a saturated calomel electrode. An anodic current up to 10 mA was applied.

**Exposure tests at Mandapam Camp**

Cold-rolled steel specimens with different combinations of copper, nickel and chromium deposits were exposed for a period of three months during May to July 1983 to the tropical saline atmosphere near seashore by positioning them at an angle of 45° in a monel frame. At the end of the three month period, the panels were removed and the corrosion performance of each deposit system evaluated.

**RESULTS AND DISCUSSION**

Table I gives the results of the accelerated and atmospheric tests. The contribution of microporous chromium towards improved corrosion resistance is clearly brought out by the generally lower percentages of the corroded area in the case of specimens with microporous chromium top coats in the static exposure tests in Table I, column 4. It is also worthy of note that

Table I: Corrosion performance of different systems in terms of percentage of area affected

System	Corrodkote 72 hours	CASS 72 hours	Exposure for 3 months at Mandapam Camp
1. BNi (25 $\mu$ ) + C.Cr (0.3 $\mu$ )	14	7	50
2. BNi (25 $\mu$ ) + MPCr (0.3 $\mu$ )	70	17	46
3. SBNi (17 $\mu$ ) + BNi (8 $\mu$ ) + C.Cr (0.3 $\mu$ )	91	26	79
4. SBNi (17 $\mu$ ) + BNi (8 $\mu$ ) + MPCr (0.3 $\mu$ )	80	5	39
5. Cu (10 $\mu$ ) + SBNi (12 $\mu$ ) BNi (8 $\mu$ ) + C.Cr (0.3 $\mu$ )	12	10	17
6. Cu (10 $\mu$ ) + SBNi (12 $\mu$ ) + BNi (8 $\mu$ ) + MPCr (0.3 $\mu$ )	86	21	6
7. SBNi (12 $\mu$ ) + BNi (8 $\mu$ ) + C.Cr (0.3 $\mu$ )	84	2	67
8. SBNi (12 $\mu$ ) + BNi (8 $\mu$ ) + MPCr (0.3 $\mu$ )	62	6	67

Cu - Copper, BNi - Bright nickel, SBNi - Semibright nickel  
C.Cr - Conventional chromium  
MPCr - Microporous chromium

the extents of corrosion in terms of area are considerably lower for panels subject to CASS test. Good corrosion performance is obtained with application of duplex nickel and microporous or conventional chromium respectively in presence of copper undercoat. The significant influence of microporous chromium could be observed when thickness of nickel is 25  $\mu\text{m}$  with duplex nickel (lines 3, 4, Table I) whereas with decreasing thickness of nickel, microporous chromium does not have favourable influence (lines 7, 8 Table I). Similarly microporous chromium does not show any significant influence in corrosion resistance (lines 1 and 2 of Table I). However, no correlation appears to exist between the laboratory tests and the exposure tests at Mandapam Camp. The percentage affected by Corrodkote test is more severe than CASS test and the test has been carried out for 72 hours instead of 48 hours. However, it is also quite interesting to observe that Corrodkote test simulates the static exposure tests fairly reasonably excepting in line 6 of Table I which could not be easily explained.

To understand the mechanism of corrosion, anodic polarisation studies with individual foil deposits have been carried out, coupling it with cathode of different areas. By superposing the individual anodic polarisation curves on the cathodic polarisation curves of chromium the galvanic effects of multilayers coatings has been explained (5). So the anodic polarisation of multi-layer coatings were carried out by the present authors with platinum as counter cathode. But no conclusive informations could be obtained from these studies, because there is no clear correlation between accelerated tests and polarisation curves.

### CONCLUSION

Considering the static exposure tests as standard for evaluation of corrosion

performance studies, from the Table I column 3, it can be concluded that duplex nickel with microporous chromium and a copper undercoat can be considered as a better system for corrosion protection. It can also be concluded that there is no clear correlation between the polarisation studies as carried out by us and the corrosion tests.

### REFERENCES

1. F L Laque, *Proc Amer Soc Test Mat* 51 (1951) 495
2. F L Laque, *Proc Amer Electropol Soc* 46 (1959) 141
3. W A Wesley and B B Knapp, *Trans Inst Metal Finish* 31 (1954) 24
4. W A Wesley, *Proc Amer Electropol Soc*, 50 (1963) 9
5. J V Petrocelli, V Hospadonk and C A Dibray, *Plating* 49 (1962) 50
6. J V Petrocelli and V Hospadonk, *Plating* 48 (1961) 479
7. S A Melbourne and J N Flint, *Trans Inst Metal Finish*, 39 (1962) 50
8. S A Watson, *Trans Inst Met Finish*, 39 (1962) 91
9. B S No. 5466 (1977)