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CATHODIC TREATMENT OF COLOURED STAINLESS STEEL

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An attempt has been made in this work to improve the abrasion resistance of the coloured film by cathodic treatment in a suitable oxidising solution at different current densities and temperatures. The cathodic polarisation of the coloured film is studied in chromic acid/sulphuric acid mixture at constant current density and the potential-time behaviour is reported.

Key words: Colouring of stainless steel, cathodic treatment, abrasion resistance, chromic acid-sulphuric acid solution

INTRODUCTION

Stainless steel is notable for its corrosion and tarnish resistance at ambient temperatures due to the presence of a thin, tenacious oxide film of the order of 200 to 800 A° on its surface. When this film is further thickened, different colours are formed due to interference [1]. The thickening of the film can be carried out by thermal oxidation in air at specific temperatures [2], chemical oxidation [3-6] or electrolytic oxidation using [7] (AC or DC) in oxidising solutions.

Thermally formed films give very light colours whereas films formed by both chemical and electrochemical oxidation give deep and intense colours. The films formed by the above three methods are soft, easily damageable, porous and possess poor abrasion resistance. The films need protection against the above drawbacks and one such has been reported [8], which prevents staining, marring and masking, but it does not improve the abrasion resistance of the film. In the present work, the thickening of the natural oxide film was done in chromic acid-sulphuric acid system, by immersion, followed by cathodic treatment in a suitable oxidising solution, in order to improve the abrasion resistance of the film. The results of the effect of cathodic treatment at different current densities and temperatures on the abrasion resistance of the coloured film and the cathode potential-time behaviour of the coloured stainless steel at a constant current density have been reported.

EXPERIMENTAL

Stainless steel (AISI 304) panels of 12 cm x 4 cm size were mechanically polished, buffed, degreased and electrolytically cleaned in hot alkaline cleaner. The panels were coloured blue in chromic acid (200 g/l) and sulphuric acid (375 g/l) at 348 + 1K. These coloured panels were cathodically treated in a bath containing: chromic acid (250 g/l) and sulphuric acid (0.75 g/l) at current densities of 20, 30 and 40 $mA.cm^{-2}$ for 20 minutes at temperatures of 333K, 323K and 313K respectively. The counter electrode used was chemically pure lead sheet.

The cathodically treated coloured stainless steel panels were tested for their abrasion resistance using the arrangement shown in Fig.1.

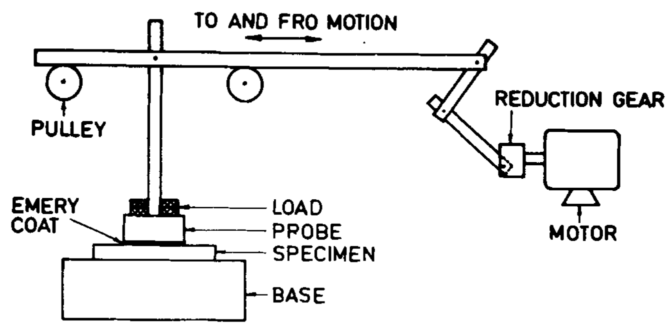

Fig. 1: Arrangement for measuring abrasion resistance

The probe coated with 4/0 emery at its bottom moves over the coloured film to and fro with a load of 250 g acting on 0.75 cm^2 area. For one to and fro motion the probe travels a distance of 150 cm per minute. The time required for the removal of the film from the surface i.e. appearance of plain stainless steel surface, was noted for each panel. The results are given in Table - I.

The variation of cathode potential with time at a constant current density of 20 $mA.cm^{-2}$ and at 323K was measured (vs SCE) in a bath containing varying ratios of chromic acid and sulphuric acid as given in Table-II and the results are shown in Fig.2.

The scanning electron micrographs of the coloured stainless steel with and without cathodic treatment are shown in Fig.3.

RESULTS AND DISCUSSION

While colouring stainless steel by immersion in chromic acid-sulphuric acid bath at 348 $\pm$ 1K, the following colours are obtained: brown, blue, yellow, magenta and finally green, in that order. The colours so formed are dependent on the temperature and composition of the bath, nature and the surface finish of the steel. In the potential-time behaviour of the stainless steel, two inflections have been reported [9] one at the beginning and the other at the end of the curve. Between these inflections, the formation of different colours takes place.

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It is seen from Table I that the abrasion resistance of the cathodically treated film at 323K and 333K and at current densities of 20 and 30 $mA.cm^{-2}$ are better than at 40 $mA.cm^{-2}$. However, the cathodic treatment at 323K at 20 $mA.cm^{-2}$ gives the maximum value. At 313K, the abrasion resistance of the film is lower than that at 323K and 333K at the same current densities. But prolonged treatment slightly improves the abrasion resistance. Below 313K the abrasion resistance of the film is still poor which is indicated by rubbing test with conventional washing powders.

TABLE-I: Abrasion resistance of the cathodically treated coloured film

Solution composition: Chromic acid 2450 gpl; sulphuric acid 0.75 gpl; Treatment time = 20 minutes

Temperature (K)	Current density ($mA.cm^{-2}$)	Time required for the removal of the film from the stainless steel (sec)
333	20	100
	30	80
	40	60
323	20	250
	30	240
	40	150
313	20	30
	20*	120
	30	40
	40	50

* Treatment time = 60 minutes

TABLE-II: Cathodic treatment-Bath composition

Current density = 20$mA.cm^{-2}$; Temperature = 323K

A	Chromic acid (125 g/l)
B	Chromic acid (125 g/l) + Sulphuric acid (0.75 g/l)
C	Chromic acid (250 g/l)
D	Chromic acid (250 g/l) + Sulphuric acid (0.75 g/l)
E	Chromic acid (250 g/l) + Sulphuric acid (2.5 g/l)

It is evident from Fig.2 that the cathodic potential increases with time for all solutions studied (Table II), but the addition of sulphuric acid is found to bring down the potential values, in general. The abrasion resistance of the coloured film treated in the bath-B is better than in the bath-A as revealed by rub test

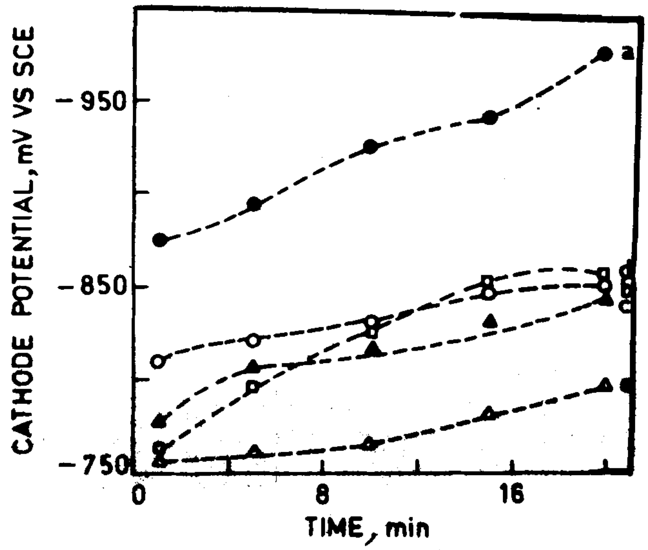

Fig.2: Cathode potential-time behaviour at 20 mA cm^{-2}; a = Bath A; b = Bath B, c = Bath C, d = Bath D, e = Bath E

with proprietory washing powders. Again, the abrasion resistance of the film treated in bath-D is better than in the bath- C and bath-B. Higher the concentration of chromic acid in the bath, better is the abrasion resistance of the film. The result from bath-E, which contains more sulphuric acid, is inferior to the one from bath-D, apart from the deposition of metallic chromium on the film especially at high current density areas.

Since the cathodic treatment of the coloured stainless steel in the bath D gives better abrasion resistance compared to the other baths, the concentration and its ratio of chromic acid and sulphuric acid are important factors apart from other parameters. Similar observations were made in the preparation of metal hydroxide sols, particularly chromium hydroxide sol, where the chromic oxide-sulphate ratio is the most important in producing tiny and spherical shaped particles [10]. The bath "D" is, probably, the one which produces the tiny and spherical shaped particles of chromium oxide-hydroxide with much access to enter into the pores of oxide film of the stainless steel. However, this interesting aspect requires further investigation.

During cathodic treatment of the coloured films of stainless steel, hydrogen evolution takes place resulting in pH increase and reduction of Cr^{6+} to Cr^{3+}, according to the reaction

$$Cr_2O_7^{-} + 14H^{+} + 6e \longrightarrow 2\,Cr^{3+} + 7H_2O$$

The Cr^{3+} formed during cathodic treatment produces oxides and hydroxides of chromium due to hydrolysis at oxide film solution interface. These hydrolysed products of chromium are cathodically precipitated in the pores of the oxide film on stainless steel [11] and it is responsible for the improved abrasion resistance.

It is reported [12,13] that the cathodic treatment of chromium plated zinc die castings in dichromate solutions improves abrasion resistance and corrosion resistance of the chromium deposit, which has been attributed to the presence of oxides and hydroxides of chromium in the pores of the thin chromium deposit. The electron diffraction studies had shown that increase in thickness due to cathodic treatment is more than 50 A°.

Fig.3(a) and 3(b) show the scanning electron micrographs of the coloured stainless steel with and without cathodic treatment. In Fig.3(b) the grain boundaries are visibly seen whereas in Fig.3(a) they are absent. This shows that during cathodic treatment the thickening of the film takes place as reported in the case of chromium plated zinc die casts.

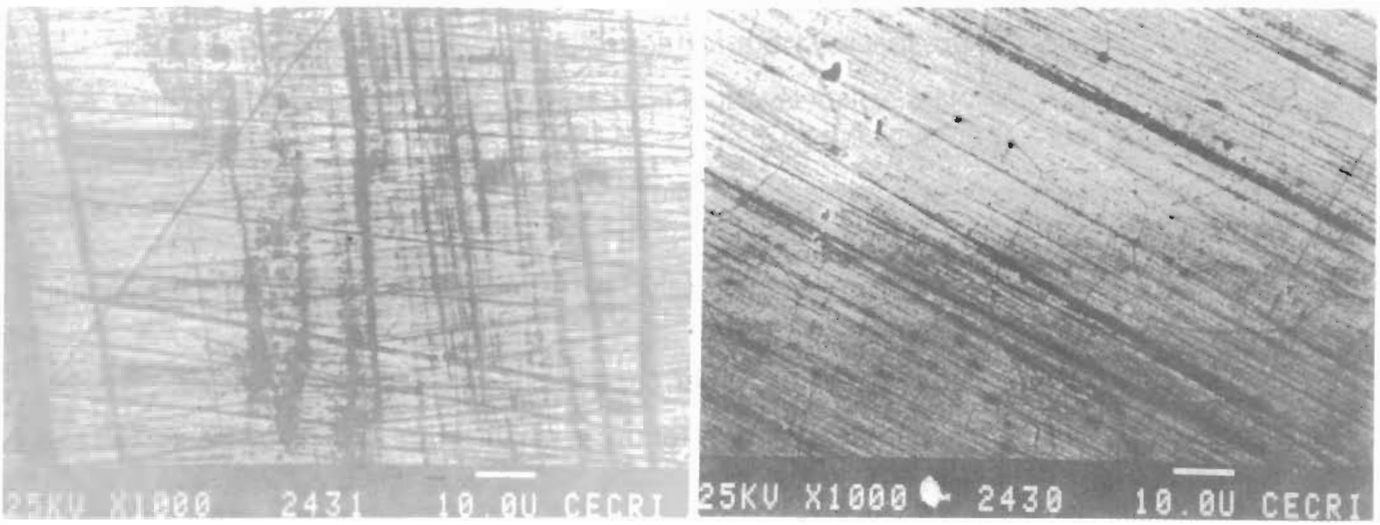

Fig.3: Microstructure of coloured stainless steel;
(a) With cathodic treatment *(b) Without cathodic treatment*

CONCLUSION

The abrasion resistance of the coloured film of stainless steel is improved by the cathodic treatment in the bath containing chromic acid 250 g/l and sulphuric acid 0.75 g/l under the operating conditions of current density of 20 $mA.cm^{-2}$ at 323K for 20 minutes. In spite of several decorative and functional applications, the blue coloured stainless steel finds unique application as absorber plates for solar collectors with absorption above 90%.

REFERENCES

1. C E Naylor, *Plating*, **37**-2 (1950) 153
2. S A Sygeoda, Belg. Pat. 869, 885 (Feb 1979); *CA*, **91** (1979) 43346
3. R L Hornak and J J Halbig, U S Pat. 2,521,580 (1950)
4. T E Evans, H James and C G Smith, U S Pat. 1,122,173 (1968)
5. K K Rasakogyo, Jap. Pat. 5316328 (1976)
6. I Hideki and S Kastuaki, Jap. Pat. 6227596 (1987)
7. T E Evans and W H Sutton, Brit. Pat. 1,402,184 (1975)
8. D F Esler and E G Choby, U S Pat. 3,703,419 (1972)
9. T E Evans, A C Hart and A N Skedgell, *Trans Inst Met Finish*, **51** (1973) 108
10. J O'M Bockris, O A J Rand and B J Welch, (Ed) *Trends in Electrochemistry*, Plenum Press, New York (1977) p 177
11. A N Skedgell, V A Smith and T E Evans, U S Pat. 3850767 (1975)
12. W H Safranek and H R Miller, *Plating*, **52** (1965) 873
13. W H Safranek , H R Miller and C L Faust, *Plating*, **50** (1963) 507