CORROSION BEHAVIOUR OF COPPER METAL TREATED WITH HYDROXYSTYRYL CYANINE DYE

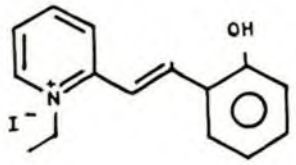
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The effect of 2-(o-hydroxystyryl)pyridinium-1-methyl iodide cyanine dye on the corrosion behaviour of copper metal in nitric acid solution has been studied. Weight loss measurements, galvanostatic polarization curves, open-circuit potential variation of copper electrode with time and the cathodic protective current values, indicate that styryl cyanine dye gives an anti-corrosive character. The inhibition effect is more pronounced in case of copper metal coated by thin film of the dye than that dipped in medium with the dye.

Cyanine dyes are widely used as photosensitizers especially in photographic industry[1,2], in photo chemical splitting of water [3] and in spectral sensitization of zinc oxide film electrode for solar cells of cyanine dyes. Styryl cyanines responded to membrane potential changes by an electrochromic mechanism and are used as charge-shift probes of membrane potential [7].

The work given in this article is devoted to examine the effect of simple 2-(o-hydroxystyryl) pyridinium-1-ethyl iodide cyanine dye (I) on the corrosion behaviour of copper metal in nitric acid solutions.



I

EXPERIMENTAL

The effect of investigated cyanine dye on the corrosion of copper in 2 M nitric acid was carried out by two ways:

(i) Adding different concentrations of the dye to the corrosion medium, and (ii) forming a thin film of the dye on copper surface by treatment of the surface in aqueous dye solutions, washing thoroughly with bidistilled water, drying and immersing in the corrosive medium. The effect of styrl dye on the corrosion process of copper metal, in both methods has been studied using weight loss technique [8]. Each experiment was carried out using 50 ml of the aerated corrosive solution and without stirring at 30 ± 0.1° C. All corrosion tests were made in duplicate.

The shift in anodic potentials at copper electrode surface was determined by anodic galvanostatic polarization studies.

RESULTS AND DISCUSSION

Weight Loss Experiments

The effect of dye concentrations in the corrosion medium (2 M HNO_3) on the weight loss of copper specimens are tabulated in Table 1. It is observed that, the higher the concentration of styryl cyanine dye in the corrosion medium, the greater the inhibition percentage i.e. the lower is the loss in weight at small interval of immersion (45 & 120 min) but, after immersing time of 240 min, the dye is not effective. The inhibition effect is attributed to the higher adsorbability of the dye molecule [1] on the copper surface.

Table 1 shows the effect of treating copper metal surface, in different concentrations of aqueous dye solutions for a fixed time before its immersions in the aggressive medium. The minimum effective concentration was found to be 0.5 mM. This effect is due to the formation of a thin protective film of the dye which retards the attack of the aggressive nitric acid to the metal surface. The efficiency of the protective film depends mainly on the time of immersion in the corrosion medium.

At a definite styryl cyanine dye concentration, the inhibition effect of the adsorbed film is greatly affected by the time of treatment before immersing in the corrosion medium. The inhibition percentage increased with time up to 10 hr, then decreased again. This behaviour may be attributed to the orientation of the adsorbed dye molecules from aggregates

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TABLE 1

EFFECT OF THE DYE CONCENTRATION ON WEIGHT LOSS OF COPPER METAL IN 2 M NITRIC ACID SOLUTION

Cone dye mM	After 45 min A	B	120 min A	B	240 min A	B
(a) Dye in corrosion medium						
0.0	850	-	1350	-	2900	-
0.1	770	9.4	1420	(-ve)	3620	(-ve)
0.2	740	13.0	1247	8.14	4010	(-ve)
0.5	640	24.7	1150	14.8	4250	(-ve)
0.8	520	38.8	1070	20.7	4040	(-ve)
1.0	540	36.5	990	26.7	4490	(-ve)
(b) Dye in treatment solution						
0.0	845	-	1340	-	2970	-
0.1	930	(-ve)	1355	(-ve)	2975	(-ve)
0.2	830	1.80	1370	(-ve)	2960	(-ve)
0.5	750	11.2	1280	4.5	2880	3
0.8	200	76.3	1050	21.6	2630	11.4
1.0	160	81.0	930	30.6	2440	17.8
2.0	90	89.3	850	36.6	2390	19.5

A = weight loss in mg/dm^2 B = % inhibition

form [4] to vertical ones by long time of treatment. This new orientation form leads to uncovered surface area, which facilitate the attack of the aggressive medium (c.f.Table 2). The treatment of copper metal surface in 2 mM of aqueous dye solution for 10 hr gave an inhibition percentage higher than that obtained by adding the same concentration to the corrosion medium, as given in Table 3. This is probably due to either the competition between the aggressive effect of nitric acid and the adsorption of cyanine dye at the metal surface, or due to the oxidation of liberated iodide ion from the dye molecules by nitric acid.

Both decrease the adsorbability of protective dye molecules relative to that obtained by treatment of metal surface in a dye solution before the immersion in corrosion medium.

Polarization Studies

The influence of dye concentration on the anodic galvanostatic polarization curves of copper electrode in 2 M nitric acid has been investigated. The anodic potential is shifted to more positive values on increasing the current density (Fig.1) both in presence and absence of the dye. This indicates that the corrosion process is inhibited by the application of an external current.

The potential values are shifted to more positive values in presence of the dye. Higher the concentration, larger the positive shift (Fig. 1). This explains the inhibition action of the dye.

The shift of anodic potential is greatly affected by the time of treatment, with 1 mM dye solution of the copper electrode immersion in corrosive medium (Fig. 2). The polarization curves in case of treated electrodes (i.e.in

TABLE 2

EFFECT OF TREATMENT IN 2 mM STYRYL CYANINE DYE SOLUTION ON THE WEIGHT LOSS OF COPPER METAL IN 2 M NITRIC ACID (VALUES IN BRACKETS IS THE INHIBITION PERCENTAGE).

Time of immersion	Weight loss mg/dm^2 using copper specimens treated for a time of							
	0.0 hr (untreated)	1 hr	5 hr	10 hr	20 hr	30 hr	40 hr	45 hr
30 min.	430	310(28.0)	220(48.8)	0.0(100)	95(78)	270(37.2)	315(26.7)	380(11.6)
90 min.	920	640(30.4)	540(41.3)	180(80.4)	390(57.6)	600(34.8)	570(38.0)	555(39.7)
120 min.	1335	1250(6.4)	1010(24.6)	660(50.6)	830(37.8)	990(25.8)	1120(16.1)	1300(2.6)

TABLE 3

EFFECT OF IMMERSION TIME ON THE WEIGHT LOSS OF COPPER METAL IN 2 M NITRIC ACID AT DIFFERENT CONDITIONS (VALUES IN BRACKETS IS THE INHIBITION PERCENTAGE)

	Weight loss mg/dm^2 after immersing for					
	15 min.	30 min.	50 min.	75 min.	100 min.	125 min.
I.	0.0 (100)	0.0 (100)	90 (83.9)	310 (68.4)	480 (61.9)	1050 (26.6)
II.	0.0 (100)	110 (56.0)	280 (50.0)	770 (21.4)	1150 (8.7)	1380 (3.5)
III.	120	250	560	980	1260	1430

I. Specimen treated in 2 mM dye solution fn 10 hrs immersed in 2 M nitirc acid medium.
II. Untreated specimen is immersed in 2 m nitric acid medium containing 2 mM dye
III. Untreated Specimen immersed in 2 M nitric acid plain.

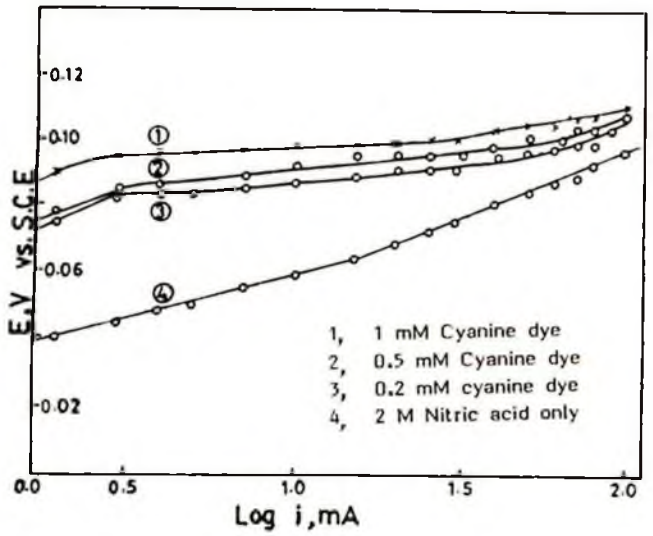


Fig. 1 The effect of cyanine dye concentrations on the anodic galvanostatic polarization of copper electrode in 2 M nitric acid at 30 ± 0.1 °C.

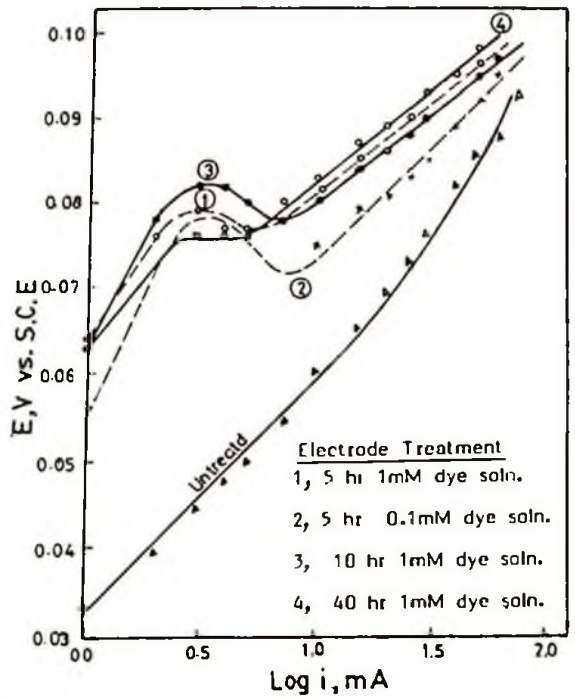


Fig. 2 The effect of time of treatment on the anodic galvanostatic polarization of copper electrode in 2 M nitric acid at at 30 ± 0.1° C

presence of adsorbed dye film) consists of three parts- (i) a rapid shift of potential to more positive values with increasing the current densities; (ii) potential change to less positive values over a small range of currents and (iii) finally an another shift to more positive ones. The slight shift to less positive values of potential may be due to destruction of the protective film of dye by the aggressive nitric acid. The shift of potential to more positive values in case of copper electrode previously treated in dye solution for 10 hr is higher than the one treated for 5 hr which in turn is more than that for 40 hr treatment. This supports the data obtained in weight loss measurements given in Table 2.

The treatment of coper electrode by 1 mM dye solution for 5 hr gives a more positive shift of potential than the one treated in lower concentration (0.1 mM) for the same time. This indicates that the inhibition action of protective film is concentration dependent.

Open Circuit Potential-Time Relation

Fig. 3 shows the effect of different concen-

tration of the styryl cyanine dye, in the corrosion medium, on the open-circuit potential variation with time. The potential of copper electrode is shifted to more positive values up to 40 min, then followed by a slight shift to less positive values

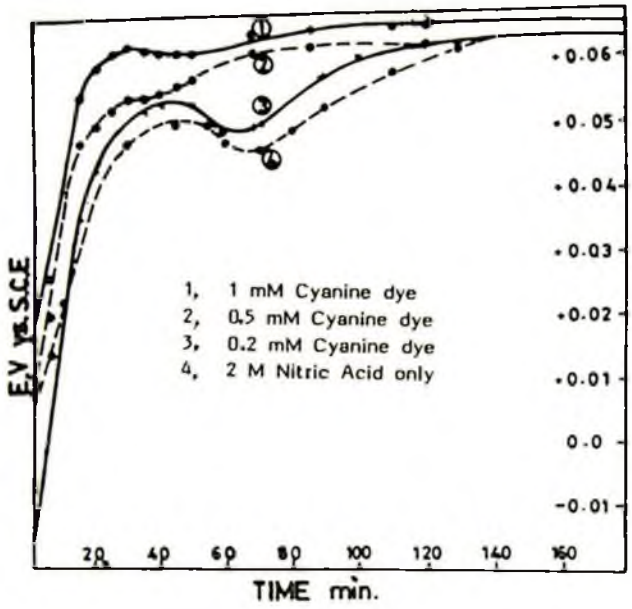


Fig. 3 The effect of cyanine dye concentrations on the potential time relation of copper electrode in 2 M nitric acid at 30 ± 0.1° C

specially in corrosion medium free from cyanine dye and in presence of its lower concentration (0.2 mM)and finally reached the steady state values. The shift in potential to more positive values by increasing the dye concentration explains the increase of inhibition action.

The steady state potentials of the electrode in the medium with or without cyanine dye are approximately the same. This behaviour supports the observation in weight loss experiments that the inhibition action of studied dye is greately decreased after a long time.

Previous treatment of copper electrodes in dye solutions reflects itself on the potential variation with time (Fig. 4). These relations confirm the weight loss data. Thus, the adsorbed film formed after 10 hr of treatment is the more protective one, which gives the higher shift of potential to positive value by time.

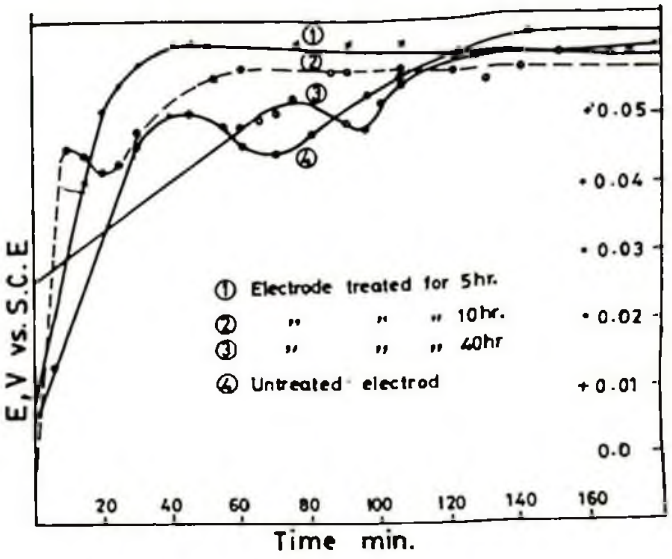


Fig. 4 The effect of treatment time on the potential-time relations of copper electrode in 2 M nitric acid at 30 ± 0.1° C

Cathodic Protection

The protective effect of styryl cyanine dye observed so far is supported by the protection behaviour of the impressed cathodic current. The Table 4 shows that, 374 mA/dm^2 current is needed to afford complete protection of copper in 2 M nitric acid. The cathodic current required for complete protection of copper

TABLE 4

CATHODIC PROTECTIVE CURRENT FOR COPPER METAL PREVIOUSLY TREATED IN 2 mM SOLUTION OF STYRYL CYANINE DYE FOR TIME INTERVALS BEFORE IMMERSION IN 2 M NITRIC ACID AS AGGRESSIVE MEDIUM

Treatment Time (hr)	Cathodic protective current mA/dm^2	Potential (mV)
0.0	374	-127.5
1.0	325	-102.0
5.0	260	- 85.5
10.0	95	- 25.5
20.0	230	- 75.5
30.0	235	- 88.5
40.0	315	- 97.5
45.0	355	-115.5

metal previously treated in 1 mM dye solution decrease as the treatment time increases up to 10 hr (95 mA/dm^2) then the current subsequently increases. It may be recalled that weight loss measurements shows maximum protection for metal treated with dye for 10 hrs (Table 2).

These protective current values reveal also that the inhibition action of adsorbed dye film does not change under the effect of cathodic current. This is because the order of current required follows the same pattern as indicated from the weight loss data. Therefore, the cathodic protection of copper metal, previously treated in relatively lower concentration of studied styryl cyanine for 10 hr, can be considered as a practical suggestion.

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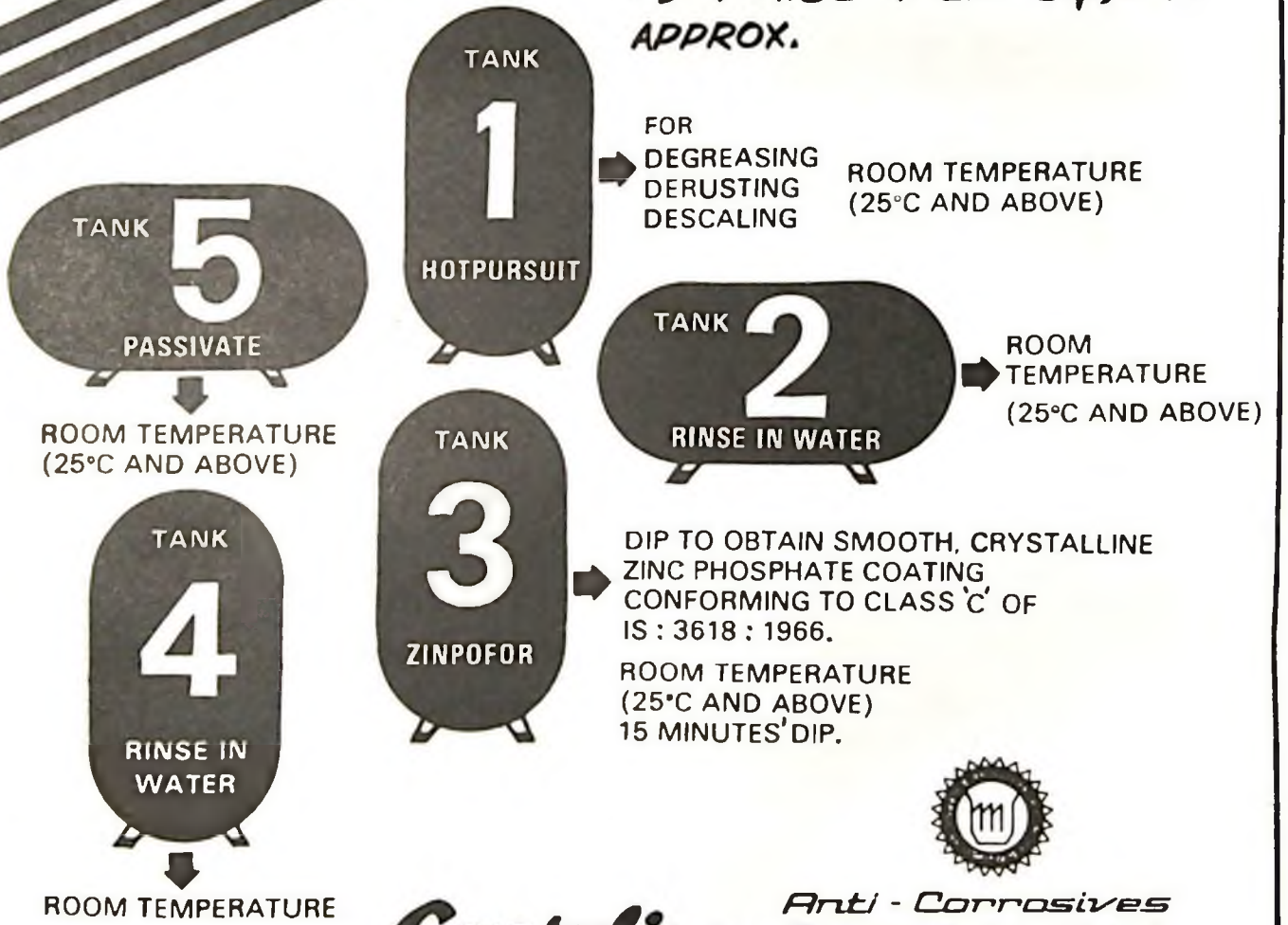
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