Some Dyes as Corrosion Inhibitor for 1100 Al in Trichloroacetic Acid

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The inhibition efficiency of the dyes increases with their concentration. At a concentration of 500 ppm in 0.1 M CCl_3COOH, efficiency of inhibition of corrosion of 1100 Al alloy is in the order; Bismarck brown > Naphthol blue black-B > Auromine O > Congo red > Brilliant green > Crystal violet > Methyl orange > Safranine T > Indigo carmine. Potentiostatic polarization studies suggest that both anodic and cathodic reactions are polarized in the presence of these inhibitors. These dyes appear to be mixed type of inhibitors. The inhibitors appear to follow the Langmuir adsorption isotherm.

Nitrogen and sulphur containing organic compounds have long been used as corrosion inhibitors [1-3], although their exact inhibition mechanism is still unknown becuase of the complexity of corrosion process. Out of the many proposed mechanisms of corrosion inhibition, surface adsorption theory is most pertinent. The proper selection of a suitable inhibitor depends on many factors, such as the behaviour of metal, nature of corrosive environment, the magnitude of charge at metal solution interphase and the nature of the cathodic reaction [4]. In the present communication, some dyes have been reported as corrosion inhibitor for 1100 aluminium alloy in trichloroacetic acid.

EXPERIMENTAL

Ortho phosphoric aicd (A.R. grade) was used as a corrodant. All the organic dyes were of A.R. grade. Solutions were prepared in double distilled water. The specimen used for the present study has the following % composition:

S:0.13; Fe 0.32; Mn 0.07; Mg 0.02; Cu 0.01; Al remainder. Electrochemical and weight loss techniques were used to study the inhibitor efficiency of different dyes.

Square coupons of 5 cm length (50 cm^2 area) were cut, polished with emery paper grades 1/0 to 4/0 (John okay), cleaned with teepol (detergent) solution and finally surface was degreased in acetone. 200 ml of corrodant was taken in a 250 ml glass beaker and maintained at a specified temperature in an electronically regulated thermostat. The degreased specimen was immersed in this corrodant for 12 hrs and weight loss determined. Generally duplicate (in some cases triplicate) experiments were performed and the mean value of weight loss was

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taken to calculate the inhibition efficency of different dyes. The inhibition efficiency (E) was calculated using the following equation:

$$E = \frac{W_u - W_i}{W_u} \times 100$$

where W_u is the average weight loss of aluminium samples in trichloroacetic acid solution without inhibitor and W_i is the average weight loss of the samples in trichloroacetic acid solution containing dyes.

Polarization experiments were carried out in 250 ml pyrex glass cell using flag shaped aluminium electrode with 2 cm^2 working area. An auxiliary platinum electrode and saturated calomel reference electrode with luggin capillary completed the cell. The distance between the luggin capillary tip and working electrode was very small and constant throughout the experiment. The corrosion current was obtained by extrapolating the anodic and cathodic polarization curves.

RESULTS AND DISCUSSION

Weight Loss Studies

Table 1 shows the percentage inhibition efficiency towards 1100 Al alloy of different dyes and at different concentration at 30° and 40° C. In plane solution of trichloroacetic acid, heavily pitted area was observed but in the presence of these dyes, a uniform and bright appearing metal surface was left behind. The inhibition efficiency increases with increse in inhibitor concentration. It can be noticed that these inhibitors possess a good inhibition efficiency at 300-500 ppm concentration. During the initial period of immersion, protection efficiency is lower; it increases considerably with time. Bismarck brown, naphthol blue black B, congo red and auromine O provide an efficiency > 95% at 500 ppm concentration. The inhibition efficiency of other inhibitors are nearly the same. In most of the cases, the metal surface was found to be covered with a film of almost similar colour as dyes in which it was immersed. It may be due to the formation of a thin layer of the corresponding inhibitors by simple adsorption.

Polarization Studies

It is found that in the presence of inhibitors, mostly the open circuit potential shifts slightly in negative direction; only in a few cases it shifts in the positive direction as can be seen in the cathodic and anodic polarization curves (fig.1). Both cathodic and anodic current densities decrease with increase in inhibitor concentration. The maximum decrease was observed at 500 ppm of each inhibitor. The nature of the cathodic polarisation curves indicates that the hydrogen evolution reaction is the same in inhibited and uninhibited acid solution. The inhibition action is probably due to the blocking of the metal surface and this decreases the cathodic current densities. It is observed that at higher concentration, the shift of anodic polarization curves is predominant

Table 1

Corrsion of 1100 Al and its inhibition by some dyes

Medium 0.1M Trichloro acedic acid(TCA); Exposure period 12hrs. Wt.loss at 30°C 840mg; at 40°C 2250 mg;

	100 ppm		200 ppm		300 ppm		400 ppm	
	30	40	30	40	30	40	30	40
Methyl Red								
Wt.loss (mg)	344	1237	244	877	126	630	42	427
E%	59	45	71	61	85	72	95	81
Methyl Organge								
Wt.loss (mg)	470	1462	344	1286	277	1080	126	562
E%	44	35	59	43	67	52	85	75
Crystal violet								
Wt.loss (mg)	378	1462	302	1012	244	900	92	652
E%	55	41	64	55	71	60	89	71
Naphthol blue black B								
Wt.loss (mg)	320	1238	202	787	101	562	17	427
E%	62	45	76	65	88	75	98	81
Safranine T								
Wt.loss (mg)	294	1013	252	913	210	787	160	630
E%	65	55	70	61	75	65	81	72
Malachite green								
Wt.loss (mg)	373	1530	328	1238	235	788	185	720
E%	55	32	61	45	72	65	78	68
Brilliant green								
Wt.loss (mg)	311	1080	185	855	160	720	67	427
E%	63	52	78	62	81	68	92	81
Bismark Brown								
Wt.loss (mg)	235	877	151	675	67	630	17	428
E%	72	61	82	70	92	72	98	81
Indigo carmine								
Wt.loss (mg)	521	1778	445	1470	378	1327	319	1193
E%	38	21	47	35	55	41	62	47
Auromine O								
Wt. loss (mg)	361	1260	294	1103	126	630	17	338
E%	57	44	65	51	85	72	98	85

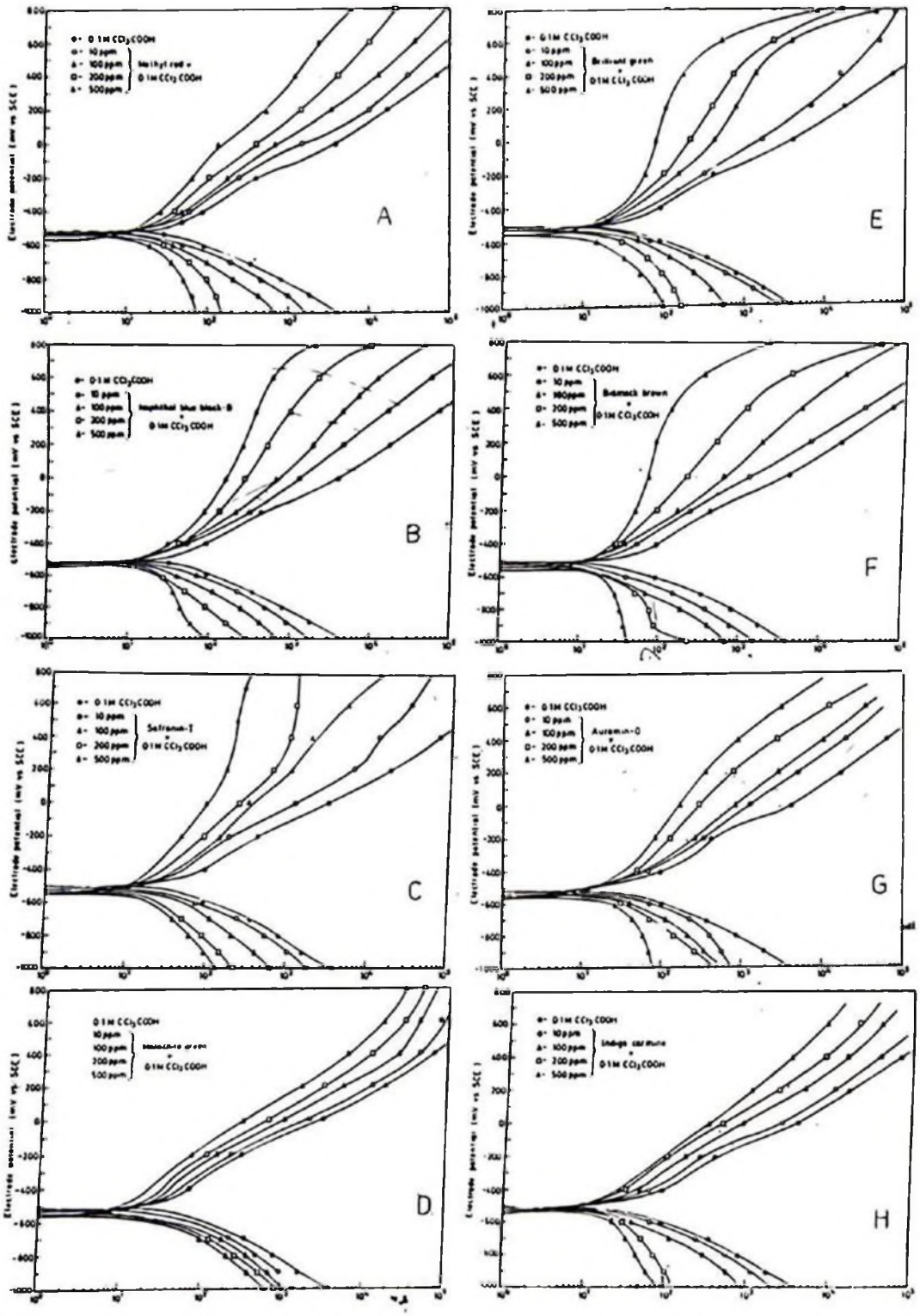


Fig.1 Anodic Polarisation behaviour of 1100 alloy in 0.1M CCl_3 COOH with different concentration of inhibitors

y axis - Electrode Potential (mv vs SCE); x axis - current density (μA/cm²)

A Methyl red; B Napthal blue black -B; C Saframin - T; D Malachite green; E Brilliant green; F Bismark brown; G Auromine O; H Indigo carmine

◆ No Inhibitor; ○ 10 ppm Inhibitor; △ 100 ppm Inhibitor; □ 200 ppm Inhibitor; ▲ 500 ppm Inhibitor

over the shift observed in cathodic curves. No passivation is observed at any concentration of the inhibitor. Different corrosion parameters obtained by extrapolating the anodic and cathodic polarization curves are presented in Table 2

Table 2

Effect of inhibitors on electrochemical corrosion parameters
Specimen 1100 Al; Medium 0.1 M (TCA)
Inhibitor concentration 500 ppm

Inhibitor	E_{Corr} (mV/SCE)	I_{Corr} ($\mu A/cm^2$)	%E
None	- 500	30	-
Methyl red	- 540	0.66	82
Methyl Oragne	- 535	5.4	78
Crystal violet	- 570	13.8	35
Napthol Blue Black-B	- 520	9.6	82
Safranine T	- 535	1.8	79
Malachite green	- 530	2.4	94
Brilliant green	- 550	0.42	92
Bismarck Brown	- 555	5.4	98.7
Indigo carmine	- 620		54
Auromine O	- 570		98

Mann and co-workers [5] examined aliphatic and aromatic amines and proposed that the positively charged inhibitor ions got attached to the metal surface through forces acting positively on charged nitrogen atom in the molecule. Mann and others [6,7] proposed that specific adsorption of positively charged inhibitor ions at the cathodic site resulted in inhibition by the hindrance of discharge of hydrogen ions. It was observed that inhibition efficiency increased in the case of inhibitors with non symmetrical substitution of alkyl groups in the benzene ring. Bockris and Conway [8] have attributed the action of such inhibitors to increase in hydrogen over voltage in presence of the inhibitor rather than protection by an adsorbed film.

The inhibition of 1100 aluminium in the presence of such dyes may be attributed to the adsorption of these dyes on the reactive sites as Al - Dye complex. The number of such active sites blocked by the adsorption of dyes is proportional to the concentration of the dye. At high concentration, all these active sites can be completely blocked by the Al - dye film.

The nature of the inhibitor interaction with the metal surface during corrosion inhibition in the present case has been deduced from the adsorption characteristics. In most cases the adsorption of inhibitor from the corrosive medium is a quasi-substitutional process [9].

$$Inhibitor_{(soln)} + nH_2O_{(ads)} \longrightarrow Inhibitor_{(ads)} + nH_2O_{(soln.)}$$

Thermodynamics of this process depends on the number n of water molecules (diploes) displaced by an inhibitor molecule during adsorption at the metal/ solution interface. The value of n for a given inhibitor depends on the mode of adsorption. The standard free energy of adsorption of such a process has been evaluated using an adsorption isotherm [10] from the configurational expression :

$$\Delta G_a^{\circ} = -2.303\,RT \times \log\left[\frac{55.4\,\theta}{C_{org}(1-\theta)^n} \quad \frac{[\theta + n(1-\theta)]^{n-1}}{n^n}\right]$$

where C_{org} is the concentration of inhibitor in the bulk solution.

Generally, Langmuir adsorption occurs in cases where good corrosion inhibition is observed. Assuming that the inhibitor forms a unimolecular layer on the metal surface at the maximum inhibition, the surface coverage, at each case was calculated from the results of weglht loss test using the equation

$$\emptyset = \frac{W_u - W}{W_u - W_m}$$

where W_o and W_i are weight loss in uninhibited and inhibited solution and W_m is the weight loss in case of maximum inhibition.

Fig.2 shows a plot of log (θ/1-θ) vs log C for 1100 alloy in case of some dyes. A linear relationship is observed in all cases. This suggests that the inhibitors undergo adsorption following Langmuir adsorption isotherm. The inhibiting effect of these dyes on 1100 aluminium in chloroacetic acid medium can be ascribed to the formation of a protective and stable complex between Al^{3+} ions and dyes [11].

Most of the dyes investigated in the present case has nitrogen atom of the azo group or the hetero atom of the ring. These are easily available for N - Al boding. The complex of base form of

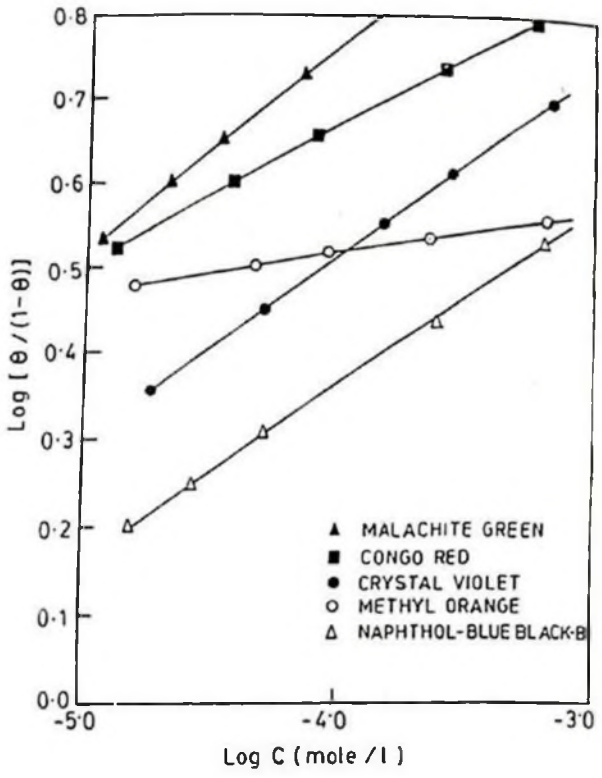
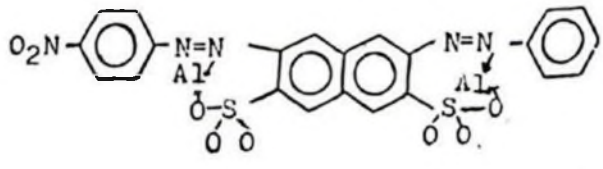


FIG. 1 - LANGMUIR PLOTS FOR INHIBITORS STUDIED IN 0·1M CCl_3COOH AT 30°C

methyl red with Al^{3+} may be represented as this complex ion becomes integrated in the oxide layer to increase its strength.

Methyl orange forms unidentate complex with the Al^{3+} ion becuase only N - Al bond is possible in this case. Since, unidentate complex is less stable than bidentate complex, inhibition efficiency of methyl orange is less than that of methyl red.

The probable complex ion formed with the anionic form of naphthol blue black has the following structure:



This complex ion, incorporating two aluminium ions in one molecule provides > 98% inhibition to 1100 aluminium.

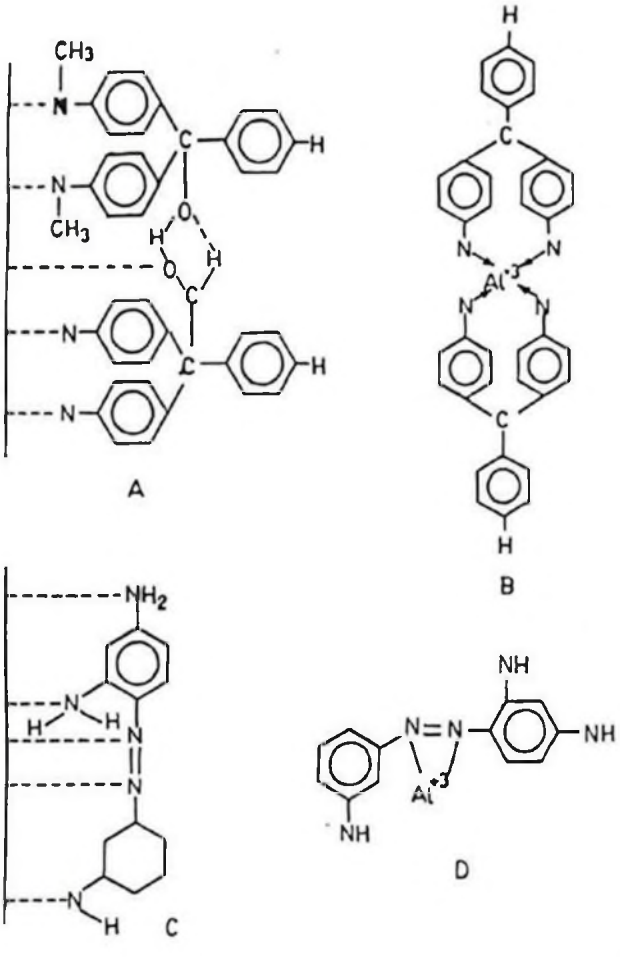


Fig. 3 Models of adsorption of inhibitors on aluminium surface and structures of aluminium-dye complex.

A Malachite Green on Al surface
B Malachite Green - Al complex
C Bismarck Brown on Al surface
D Al complex of Bismarck Brown

Similarly, congo red forming a monodentate ligand with the aluminium ions has less inhibition efficiency than naphthol blue black-B, but its considerble efficiency is due to the presence of higher number of N, O and S atoms.

Fig.3 shows some proposed models of the dyes on metal surface and the structure of aluminium dye complex. It is observed that adsorption model of malachite green and brilliant green are similar but corrosion inhibition efficiency of brilliant green is higher. This may be attributed to the presence of ethyl group which increases the electron density on N atoms. A better efficiency of Bismarck-brown may be explained on the basis of its adsorption mode as shown in fig.3C. The number of active adsorption sites in Bismarck-brown is higher than those of malachite green and brilliant green. Indigo carmine and auromine-O work in the similar fashion.

In a few cases, it was observed that the colour of the dyes disappeared due to the corrosion reaction. This may be due to the reduction of azo compounds and their dissociation to the corresponding amines. Hydrogen arising from the corrosion reaction [12] is responsible for the reduction of the dyes and their dissociation proceeds through electrochemical phenomenon following the reduction [13]. Evolution of hydrogen occurs by the following reaction -

$$2H^{+} + 2e \longrightarrow H_2 (g)$$

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