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EFFECT OF THIOCYANATES OF ALKALI METALS ON CORROSION PROTECTION BEHAVIOUR OF ORGANIC COATINGS IN ACRYLIC FIBRE INDUSTRIES

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Due to the reduction in costs and elimination of process steps, industries manufacturing acrylic fibres prefer solution polymerization. In this technique, the fibres are prepared in a form suitable for wet and dry spinning. The commonly used solvents include aqueous solution of thiocyanates of alkali metals at higher concentrations. It is reported that the structures and reactors in the manufacturing plant suffer from severe corrosion leading to huge costs for replacement of the same. To find the suitable coating material to protect the structures in such atmosphere, four representative film forming polymers were chosen and the performance of their coatings was studied under different conditions of concentrations and temperatures. Four coatings based on polyacrylates, polyamide cured epoxy, polyurethane and chlorinated rubber were evaluated and among them the coating based on chlorinated rubber resin is found to give better protection in thiocyanates atmosphere.

Keywords: Acrylic coatings, corrosion protection and thiocyanates

INTRODUCTION

The acrylic fibres are usually manufactured by solution polymerization technique because of the advantages like cost reduction and elimination of process steps. In this process, acrylic polymeric fibres are prepared in a form suitable for wet and dry spinning. Commonly, aqueous solutions of thiocyanates of alkali metals at higher concentrations are used as solvents.

In an official communication, an acrylic fibre manufacturing industry in Thailand reports that the severe corrosion of steel structures caused due to the spillage of aqueous thiocyanate solution results in frequent replacement of the structures and thereby industrial losses.

The literature was surveyed to find suitable organic coatings which could provide adequate protection to metals in corrosive atmosphere. A few formulations based on vinyl ester and thermosetting polyesters were reported suitable for this purpose [1-6]. However, the former is reported to be more resistant in comparison to the latter. A few proprietary products based on vinyl ester (mostly epoxy based) and polyesters are commercially available [4-6]. However, much data are not found in the literature on use of coatings based on polyacrylates, epoxy- polyamides, polyurethanes and chlorinated rubbers for the protection of metals from the attack of thiocyanates.

Four coating systems based on polyacrylates, polyamide cured bisphenol. A based epoxies, polyurethanes and chlorinated rubber plasticized with chlorinated paraffin were chosen for the study. Mild steel panels coated with these materials were subjected to the thiocyanates atmosphere in two different electrolyte concentrations to study the effect of concentration over the corrosion rate. The tests were conducted at ambient and at an elevated temperature to match the industrial processing temperatures.

EXPERIMENTAL

Materials

Four different polymeric coating materials listed below were chosen for this study.

1. **ACR:** Polymethacrylate resin, Single pack type, (Self plasticizeable), Proprietary product of CECRI
2. **EPX:** Bisphenol A based epoxy resin cured with Polyamide resin. Two pack system. Commercial product.
3. **PUR:** Polyurethane(Polyester polyol and aromatic polyisocyanates). Two pack system
4. **CRB:** Chlorinated rubber plasticized with chlorinated paraffin.

The physical properties of liquid materials and of their coatings are given in the Table I.

Preparation of the Test specimens

Panels of size 7.5 x 5 cm cut from cold rolled mild steel sheet were sandblasted to Swedish standard Sa 2 1/2. Immediately after sandblasting, the cleaned panels were coated with individual resins by brush and cured for one week. Specimens were then tested for pinholes with a holiday detector and the dry film thickness (DFT) of the coating was measured. The edges of the specimens were sealed with Araldite adhesive to an extent of 0.5 cm. For each test, a set of three specimens were used. After the test, the painted surface of one of the panels was scribed diagonally as per standard method specified for the determination of adhesive of a coating. The degree of loss of adhesive during the test period was determined by pulling the cut painted. The specimens were also subjected to other simulated laboratory tests.

Description of Tests

In all the tests uncoated mild steel specimens were used as control to determine the corrosion rates. The following tests were conducted on coating and uncoated test specimens.

Immersion test

The specimens were immersed in aqueous solutions of sodium thiocyanates of 10 and 20% (by weight) concentrations at ambient and at 328 - 333 K. The test was conducted for a period of 500 hours and the specimens were periodically observed for failures.

Salt spray (fog) test

A 10% (by weight) aqueous solution of sodium thiocyanate was used in place of salt solution of specified as per ASTM B-177 for this test.

Potential vs time measurements

The change in the potential vs time was measured by immersing the test specimens in 10 and 20% aqueous thiocyanate solutions. The specimen of an area of 1 sq.cm was used as working electrode and SCE as reference electrode. A digital multimeter with an accuracy ± 0.01% was used for potential measurements.

RESULTS AND DISCUSSION

The data in Table II indicate that the rate of corrosion of mild steel is least affected by the concentration of thiocyanate in solution as well as by the temperature of the test. Moreover, the rate is slightly higher in 10 % thiocyanate solution at ambient temperature. The rate of corrosion in hot solution of 20 % thiocyanate is fairly low (23.80 mpy) whereas in cold 10 % solution of thiocyanate, the rate is higher (28.98 mpy). During the immersion test in hot conditions was observed the formation of a thin film blanketed over the surface of the solution which might have decreased the dissolved oxygen and thus reduced the corrosion rate.

In salt spray test, the rate of corrosion is higher i.e. 51.85 mpy which may be due to the well known nature of aggressive attack existing inside the chamber under 100 % RH and at ambient conditions.

The data on the performance of the coatings in immersion tests are listed in Table III to IV. No change was observed in the surface of the coatings after 120 hour immersion of coated panels in 10 and 20 % aqueous solutions of thiocyanate. Except for the chlorinated rubber coating, the coatings of other resins developed blisterings at the end of

TABLE I: Properties of coatings used

Property	ACR	EPX	PUR	CRB
1. Colour	#	#	#	#
2. Solids (wt)	55%	52%	48%	55%
3. DFT (microns)	55 ± 5	55 ± 5	50 ± 5	55 ± 5
4. Drying time	6 hrs	3 hrs	2 hrs	45 mts
5. Density (gm/ml)	1.01	1.10	0.98	1.23
6. Viscosity (Sec.) (Fordcup No.4)	45-50	50-55	40-45	50-55

= Transparent

TABLE II: Corrosion rates of mild steel in thiocyanate solution

Environment	Corrosion rates (mpy)
Immersion (Cold)	
10% solution	28.980
20% solution	28.040
Immersion (Hot)	
10% solution	27.800
20% solution	23.800
Salt (fog) spray	51.845

TABLE III: Results of immersion test (10% thiocyanate solution at 303 ± 2K)

Coating	After 120 hrs	After 240 hrs	After 360 hrs	After 480 hrs
ACR	No change	Slight blisters	Blistering increased	Heavy blistering/ rust all over the panel failed
EPX	No change	Little blistering	Blistering/ rust spots over the panel	Failed
PUR	No change	Little blistering	Blistering/ rust spots over the panel	Failed
CRB	No change	No change	Rust along scribes/ rust spots	A few rust spots over the panel surface only

240 hours. Heavy blistering has been observed in the coating of the resins after immersion for 360 hours and the coatings failed after 480 hours in 10 or 20 % solution of thiocyanate solutions.

In the case of chlorinated rubber coatings, specimens in 10 and 20 % solutions showed rust along scribes but did not show signs of failure excepting for a few spots over the coated surface. In the hot solution of thiocyanate at 328 - 333 K, the performance of chlorinated rubber coatings was found to be better in comparison to that of other coatings.

TABLE IV: Results of immersion test (20% thiocyanate solution at 303 ± 2K)

Coating	After 120 hrs	After 240 hrs	After 360 hrs	After 480 hrs
ACR	No change	Slight blisters	Blistering increased	Heavy blistering/ rust all over the panel failed
EPX	No change	Little blistering	Blistering/ rust spots over the panel	Failed
PUR	No change	Little blistering	Blistering/ rust spots over the panel	Failed
CRB	No change	No change	Rust along scribes/ rust spots over the surface	A few rust spots over the panel surface only

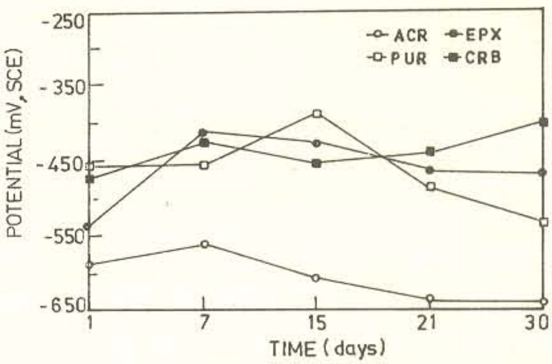

Fig. 1: Potential vs time data for coated mild steel electrodes in 10% NaSCN

The data reported in Tables V and VI indicate that the elevation in the temperature 328 - 333 K has no significant effect over the performance of coatings in comparison in that at low temperature 303 ± 305 K.

The salt spray (fog) test data indicate the failure of all the coatings after exposure for 480 hours (Table VII). However the chlorinated rubber coatings was found to be comparatively more resistant than other coatings.

The plots in Figs. 1 and 2 show that the potentials of test panels coated with ACR become more negative with the increase of the duration of test whereas the potential of the test panels coated with chlorinated rubber and epoxy resins (CRB & EPX) become more positive. This indicates that the

TABLE V: Results of immersion test (10% thiocyanate solution at 328-333 K)

Coating	After 120 hrs	After 240 hrs	After 360 hrs	After 480 hrs
ACR	No change	Slight blisters	Heavy blistering/ rust all over the panel	Failed
EPX	No change	Little blistering	Blistering/ rust spots over the panel	Failed
PUR	No change	Little blistering	Blistering/ rust spots over the panel	Failed
CRB	No change	No change	Rust along scribes/ rust spots	Blistering/ rust along the scribes only

TABLE VI: Results of immersion test (20% thiocyanate solution at 328-333K)

Coating	After 120 hrs	After 240 hrs	After 360 hrs	After 480 hrs
ACR	No change	Slight blisters	Heavy blistering/ rust all over the panel	Failed
EPX	No change	Little blistering	Blistering/ rust spots over the panel	Failed
PUR	No change	Little blistering	Blistering/ rust spots over the panel	Failed
CRB	No change	No change	Rust along scribes/ rust spots	Blistering/ rust along the scribes only

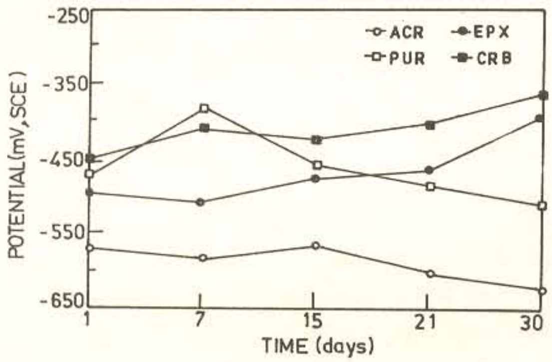

Fig. 2: Potential vs time data for coated mild steel electrodes in 20% NaSCN

coatings of CRB & EPX may protect the steel structures better in industries manufacturing acrylic fibres.

CONCLUSION

Out of four clear coatings based on polyacrylates, polyamide cured epoxy, polyurethanes and chlorinated rubber, the coating based on chlorinated rubber is found to protect the mild steel substrate better in thiocyanate atmosphere in

TABLE VII: Results of spray (fog) test (Thiocyanate solution)

Coating	After 120 hrs	After 240 hrs	After 360 hrs	After 480 hrs
ACR	No change	Blistering	Heavy blistering/ rust all over the panel	Failed
EPX	No change	Little blistering	Blistering/ rust spots over the panel	Failed
PUR	No change	Heavy blistering/ rust spots all over the panel	Failed	
CRB	No change	Rust along scribes/ rust spots seen	Blistering/ rust spots over the panel increased	Heavy blistering/ rust spots all over panels: Failed

comparison to the coatings of other resins. It is expected that, the corrosion resistance of these resins could be enhanced by suitable pigmentation. The performance assessment of pigmented coatings in thiocyanates atmosphere is under study.

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