

INFLUENCE OF DICYCLOHEXYLAMINE NITRITE IN EPOXY PRIMER

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Epoxy resins have many advantages over other binders in the formulation of primers to protect steel structures from various corrosive environments. Recent studies showed that inhibitor incorporated epoxy primers protect structures for longer duration than plain epoxy primers. In the present investigation, different concentration of dicyclohexylamine nitrite (DCHAN) (0.5-2%) were incorporated in epoxy primers and coated on steel surfaces. The performance of the primers were evaluated by salts spray and electrochemical evaluation tests in 3% sodium chloride solution. The performance of the primer in presence the inhibitor showed that the inhibitor protected the steel surface for a particular period and thereafter the inhibitor efficiency was in decreasing trend. In this study, the ratios of the DCHAN was optimized in the epoxy resin based primer and the performance of the optimized primer was evaluated by accelerated and electrochemical techniques.

Keywords: Dicyclohexylamine nitrite, epoxy primer, impedance measurement, salts spray tests.

INTRODUCTION

In general inhibitive pigments are used in primer formulation to protect the metal surface from corrosion. The inhibitive pigments are generally toxic and hazardous to human beings and so most of the inhibitive pigments are banned through out the world [1]. The inhibitors such as (DCHAN), morpholine, hexamine, Ammonium benzoate etc are generally used in very low percentage to protect the metals from corrosion in liquid as well as in vapour form [2].

Epoxy - polyamide coatings perform well on metal surface, where excellent adhesion and corrosion resistance are required [3]. Moreover coatings based on this binder can be used as primer, undercoat and finish coat formulations. A major limitation of this resin is poor exterior durability and so a sealant coating is required for protecting it from direct sunlight exposed areas.

A recent study shows that the inhibitor incorporated epoxy primer protects the structures for longer duration than the primer without inhibitors [4]. On the basis of this study, we have incorporated DCHAN in epoxy resin and evaluated the performance of the primer by both accelerated as well as electrochemical techniques.

EXPERIMENTAL

70 wt% solution of epoxy resin with epoxide value 475 - 500 (supplied by CIBA GEIGY Ltd., Mumbai) was prepared by using methyl isobutyl ketone, xylene and butyl cellosolve solvents. Another pack contains 70 wt% solution of polyamide with amine value 280-320 (supplied by Synpol Pvt. Ltd., Odhav, Ahmadabad) was prepared by using xylene as solvent. This coating was a two pack system and so the resin and hardener are mixed at the time of application. The mixing ratio of the resin and hardener was 70:30.

The inhibitor DCHAN was incorporated in the hardener part in the ratio of 0.5, 1, 1.5 and 2 to the total 100 parts of the primer. Primers with 35 pigment volume concentration (PVC) were prepared by using the required volume of epoxy-polyamide binder with and without inhibitor. The formulation was Iron oxide and Titanium di oxide as main pigments of equal part each 20 volume of the total pigment present in the formulation. The primers were applied on sand blasted mild steel substrate by brush to get dry film thickness of 40 ± 5 microns. These primer coated panels were used for the following tests after drying in air for seven days.

Tests
 Primer coated panels in tri-
 atch at the center of the panels were
 for 300 hours. In the salt spray ch
 sodium chloride solution was automatized by
 number for create a fog. This test was conducted a
 per ASTM specification B 117.
 Electrochemical impedance measurements
 Impedance measurements were carried out with PAR model
 '68 - 1 system at frequencies from 100 KHz to 0.1 Hz and
 applied signal amplitude was 10 mVs. The surface to
 chemical cell used for this study consisted of 3% by
 m chloride solution as electrolyte, primer coated
 'king electrode, platinum foil as counter electrode
 'ed calomel electrode (SCE) as reference
 impedance measurements were done with 0.5% and 1% DC
 5 and 10 days of immersion. The charge and with high
) was obtained directly from the Bode incorporated coatings in salt s,

so.
 over the
 The test pane.
 are no rust spots
 seen on the scratch
 the salt spray chambr
 at high
 incorporated coatings in salt s,

Behaviour of 40 micron epoxy coatings with and without inhibi
 mild steel in different chemical solutions

Coating with 0.5% inhibitor	Coating with 1% inhibitor	Coating with 1.5% inhibitor	Co.
No blisters	No blisters	No blisters	inhib.
No blisters	No blisters	Small blisters are seen on the surface	Few blis on the sur.
No blisters	No blisters	Few blisters are seen on the surface	The size of b. are higher than the previous one
No blisters but our adding is red	Few blisters are seen on the surface	Few corrosion spots are seen on the surface	Corrosion spots are seen on the surface
Corrosion are seen on the edges	Corrosion spots are seen on the surface	Corrosion spots are seen on the surface	Corrosion spots seen through the surface

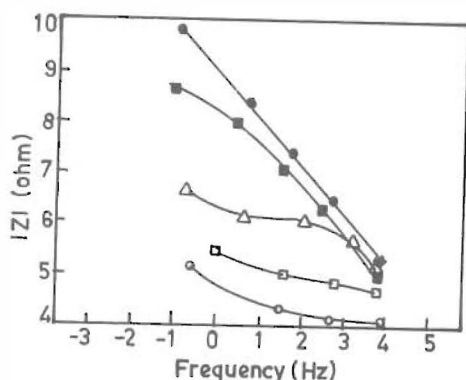


Fig. 1: Bode plots of epoxy primer and DCHAN incorporated primer on mild steel in 3wt% NaCl solution after 1 day (•) primer without DCHAN; (+) primer with 0.5% DCHAN (†) primer with 1% DCHAN; (□) primer with 1.5% DCHAN (×) primer with 2% DCHAN

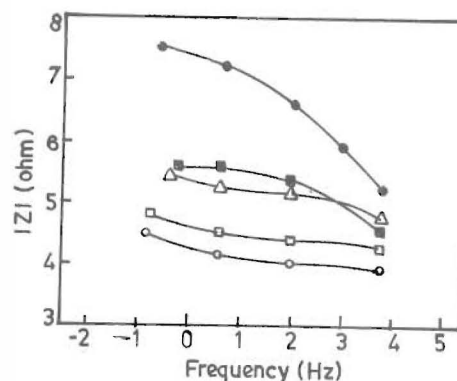


Fig. 2: Bode plots of epoxy primer and DCHAN incorporated primer on mild steel in 3wt% NaCl solution after 5 days (•) primer without DCHAN; (+) primer with 0.5% DCHAN (†) primer with 1% DCHAN; (□) primer with 1.5% DCHAN (×) primer with 2% DCHAN

duration. In the case of low percentage of inhibitor incorporated coatings, the rust products are observed in the scratched area only but it was not spread. This result clearly shows that the coating is strongly adherent on the metal substrate and does not allow the penetration of the corrosive ions into the substrate. While in the case of higher concentration of DCHAN incorporated coatings, the corrosion products are spread into the surface from the scratched area. Also small reddish brown rust spots were observed on the surface. This result indicates that the higher concentration of DCHAN produces pores on the surface by vaporization or by leaching.

Fig. 1 shows the impedance plots of epoxy primer with and without of DCHAN incorporated coating on mild steel in 3 wt% sodium chloride solution after 24 hours. It is seen that importance behaviour of the epoxy primer with 1% of DCHAN is capacitive and there is no diffusion of electrolyte into the substrate. This indicates that the coating is well intact on the steel surface and acts as a good inhibitive barrier in the chloride sodium medium. After 24 hours the resistance produced by the coating without inhibitor is 8.3×10^8 ohms.cm², which is within the limit of good coating to protect the surface for longer duration [6]. The resistance produced by the coating with 0.5% DCHAN is 10×10^6 ohms.cm². This also indicates that the coating protects the surface from the sodium chloride electrolyte medium. But the resistances produced by the coatings with 1.5% and 2% of DCHAN inhibitor are 5.1×10^5 and 4.1×10^4 ohms.cm² respectively. This shows that these coatings allow the electrolyte into the substrate and so the corrosion process is started in these panels surface. Similar

to the salt spray results, the impedance studies also indicate that the coating contains upto 1% of DCHAN protects the steel surface from sodium chloride solution, there after, the excess quantity of DCHAN leaches out from the surface and produces pores on the surface, which initiate corrosion process.

Fig. 2 shows the impedance plots of epoxy primer without and with different percentage of DCHAN inhibitor incorporated coating on mild steel surface in 3 wt% of sodium chloride solution after 5 days duration. It is seen from the figure that the resistance produced by the coatings with 1% DCHAN is much higher than the other coatings, that is 7.2×10^7 ohms.cm². The resistances produced by the coatings without and with 0.5%, 1.5% and 2% DCHAN are 5.3×10^5 , 5.1×10^5 , 4.3×10^4 and 4.1×10^4 ohms.cm² respectively. This clearly shows that the coating with 1.5 and 2% of the inhibitor failed to protect the surface from sodium chloride medium. The coating with 1% inhibitor, protects the surface from sodium chloride medium since of the passive layer produced by this inhibitor is intact on the surface. The resistance produced by coating without inhibitor and with 0.5% inhibitor shows that these coatings protect the surface from the solution but in a low profile, compared with 1% DCHAN incorporated coating.

Fig. 3 shows the impedance plots of epoxy primer without and with different percentage of DCHAN inhibitor incorporated coating on mild steel surface in 3 wt% of sodium chloride solution after 10 days of immersion. It is seen from the figure that the resistance produced by all the systems are below the protective level, that is below

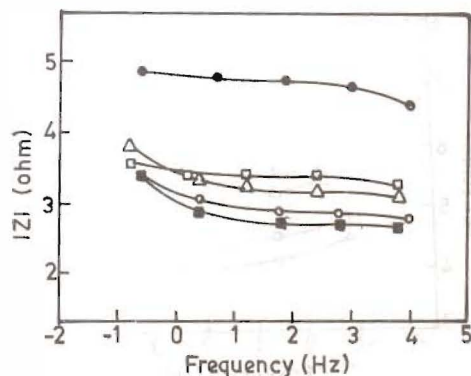


Fig. 3: Bode plots of epoxy primer and DCHAN incorporated primer on mild steel in 3wt% NaCl after 10 days
 (*) primer without DCHAN; (+) primer with 0.5% DCHAN
 (∧) primer with 1% DCHAN; (□) primer with 1.5% DCHAN
 (×) primer with 2% DCHAN

1×10^5 ohms.cm². The resistance offered by the coating with 1% inhibitor is much higher than the other system, that is 4.6×10^4 shows cm², still it is on the side of failure system [7]. Impedance measurement studies thus reveal that the epoxy primer incorporated with 1% of DCHAN inhibitor will protect the surface for longer duration than the other systems.

CONCLUSION

DCHAN as a admixture of epoxy primer has mixed effect on the corrosion resistance. At low concentration upto 1% it is having beneficial effect and at higher concentration it is having detrimental effect.

REFERENCES

1. John D Keane, *Good Painting Practices*, Vol 1, Published by Steel Structures Painting Council, Pittsburgh, PA 15213-3728 1 (1994) 138
2. E G Stroud and W H J Vernon, *J Appl Chem*, 2 (1952) 166
3. Zenow Wickles, Jr Frank N Jones and S Petes Papas, *Organic Coatings Sci and Technology*, Vol 1, John Wiley & Sons, New York, (1992) 163
4. Rom Patent, RO-87580 30 No (1985)
5. A Wachter, T Skei and N Stillman, *Dicyclohexylamine nitrite avolalite inhibitor for corrosion preventive packaging - presented at the Seventh Annual Conference and Exhibition, National Association of Corrosion Engineers, New York, March 13- 16, (1951)*
6. M Selvaraj, *Anticorrosion Methods and Materials*, 44 (1997) 13
7. B S Skerry and D A Eden, *Prog Org Coatings*, 15 (1987) 269