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Disbonding of Epoxy Resin Coatings

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Measurements are reported of the rate of cathodic disbonding of 2 ethyl,4 methyl imidazole cured epoxy resin coatings with variation of the electrolyte system. Parallel studies of the elemental distribution in the disbonding region, using EDAX§ indicate that significant permeation of electrolyte occurs ahead of the detached zone. The changes of rate of cathodic disbonding are discussed with respect to the changes in the type of electrolyte being used.

INTRODUCTION

Cathodic disbonding of epoxy resin coatings is one of the precursors to catastrophic oxidation of the substrate. Breaks or “holidays”^{||} in pipe coatings allow the metal to be exposed and also lead to enhanced corrosion in the exposed areas.^{1,2} The exposed metal surface is usually covered by an electrolyte, the composition of which reflects the surrounding soil type. Disbonding of polymer coatings from metal substrates occurs in the presence of water.^{3–6} Added protection is usually provided for the substrate by the use of cathodic bias potentials. In these conditions, cathodic protection is found to accelerate disbond-

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§ (energy dispersive X-ray analysis).

|| Pin holes continuous between the surface of the coating and the metallic substrate.

ment, the mechanism responsible for the enhanced rate is not clear.⁷

Examination of the surface using ESCA indicate that, in the presence of sodium hydroxide, saponification of the coating occurs with the formation of sodium carboxylate.⁷ It has been proposed by Hammond⁷ that the generation cathodically of hydroxide ions is correlated with the disbonding process. Using X-ray photoelectron spectroscopy (XPS) Watts and Castle⁸ have examined hot cured epoxy to abraded steels. An hierarchy of surface layers appears to exist and remains after surface treatment (and disbonding) and consists of metal, metal oxide, hydroxide, polar organic, hydrocarbon and water in ascending order towards the surface. Heating in air at the maximum epoxy cure temperature causes significant oxide growth and reductions in absorbed water and hydrocarbon contaminant. Studies of cathodic disbondment of butadiene coatings from steel in the presence of Na⁺ ions indicate that ions have permeated ahead of the disbonded coating. It was proposed that the disbondment can be associated with the saponification. The modified surface generated prior to complete hydrolysis is believed to lower the cohesive energy ahead of the disbondment front. The initial step in the disbonding mechanism requires the hydrolysis of ester type bonds. Watts and Castle⁸ have found evidence for Fe—OOCR bonds which supports this mechanism.

In this study, we report the effects of changing the nature of the electrolyte and also analysis of the spatial composition variation using energy dispersive X-ray analysis (EDAX).

EXPERIMENTAL

Materials

Three commercial coatings were investigated in these studies; 3M Scotchkote 206N, Berger Eparzit S and International Paints, International 1827. These are diglycidyl ethers of bisphenol A cured using imidazole, the coatings are filled and pigmented. A list of fillers is presented in Table I. The films were prepared by spraying the powder on preheated steel panels, the panels having been preheated to approximately 473K. The films were post cured in an oven. The final glossy film was examined for imperfections prior to being used in these studies.

TABLE I
Typical commercial fillers and pigments for epoxy resin coatings

Fillers	Pigments
Aluminium silicate	1. <i>Inorganics</i>
Calcium carbonate	Fe ₂ O ₃
Magnesium silicate	Fe ₃ O ₄
Aluminium powder	Cr ₂ O ₃
Tabular alumina	Pb ₃ O ₄
Mica	CoO, Al ₂ O ₃
Silica	NiO, TiO ₂
Zirconium silicate	FeNH ₄ Fe(CN) ₆
Hydrated alumina	2. <i>Organic</i>
Lithium aluminium silicate	Azo
Colloidal silica	Non-azo

Cathodic disbonding apparatus

The experimental configuration used in the disbonding tests is shown in Figure 1. The cathodic potential is applied to the cell *via* a potentiostat and intermittently monitored to ensure stability of the voltage. A "holiday" is introduced by drilling a hole 6 mm in diameter through the coating into the metal substrate. Plastic pipe sections, for use as electrolyte vessels were fixed to the coating surface using a silicone based adhesive. The plastic vessels were filled with 3% w/v electrolyte

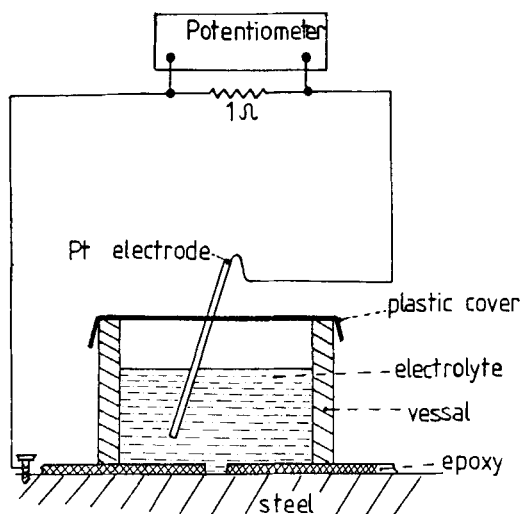


FIGURE 1 Apparatus used in the cathodic disbonding tests.

to a depth of 5 cm. The applied voltage was set at -1.5 V with respect to the calomel reference electrode; a platinum counter electrode was placed 1 cm from the "holiday". The tests were carried out for 28 days after which the disbonding of the coating was investigated by detaching the base film by cutting radially through the film and peeling back to the interface. The extent of peel was recorded. The exposed metal surface was then tested with acid/base indicators.

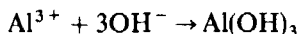
SCANNING ELECTRON MICROGRAPH AND ELECTRON DISPERSIVE X-RAY ANALYSIS

The surfaces exposed during the disbonding were examined using a Phillips PSCN 500 scanning electron microscope equipped with a Links EDAX analysis system.

RESULTS AND DISCUSSION

Cathodic disbonding tests

The increase in the size of the initial defect "holiday" was monitored as a function of time, Figure 2. It was observed that over a period of 33 days the variation of the size was linear. The variation in pH was monitored as a function of time, Figure 3. In all cases, except $\text{Al}_2(\text{SO}_4)_3$, an initial rise in pH was observed corresponding to the generation of hydroxyl ions from the reduction of water. Ultimately, an approximately constant pH value is observed. In the case of $\text{Al}_2(\text{SO}_4)_3$ electrolyte, the following additional reaction occurs



which removes the cathodically generated OH ions and results in the retention of an acidic solution.

Initial cathodic disbonding tests using electrolytes with common anions and cations found in soil indicated that significant differences can be observed, Table II. A more comprehensive study of chloride ion electrolyte shows a variation which must be associated with the counter ion. It appears that potassium chloride again has the most deleterious effect on the adhesion of the coating. Studies of variation in the method of application of the powder to the metal did not produce a significant

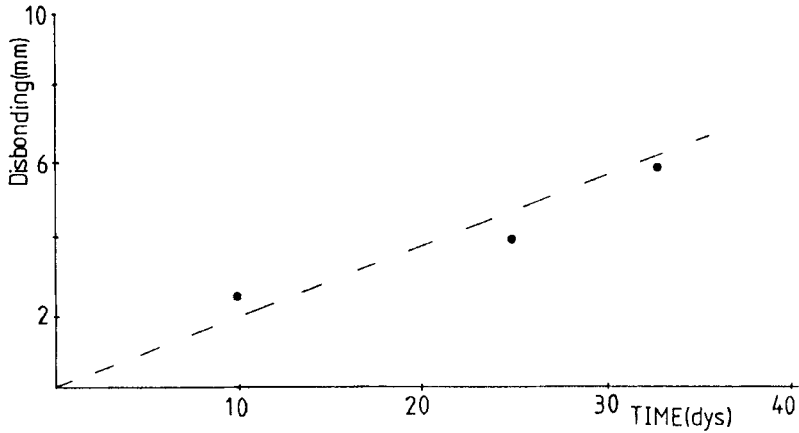


FIGURE 2 Extent of disbonding as a function of time in a cathodic disbonding situation.

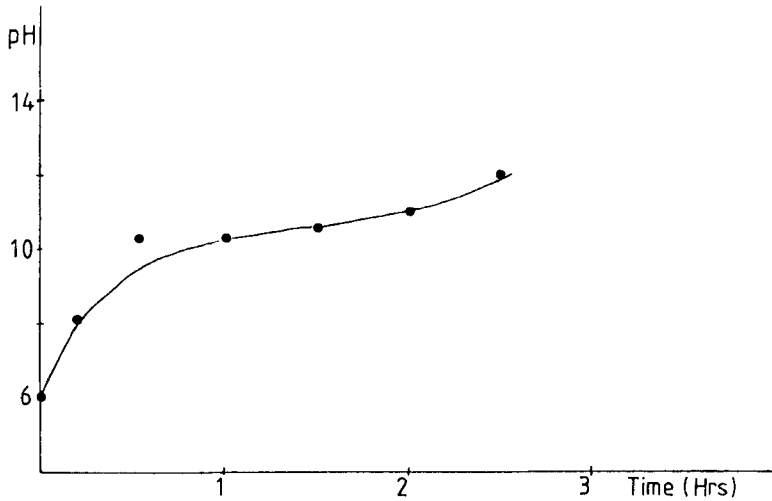


FIGURE 3 Variation of pH with time during cathodic disbonding.

variation in the disbonding rate. It was found however that differences in the preparation of the steel substrate as a consequence of variants in the short blasting lead to changes in the absolute values of the disbonding. This is illustrated in a study of the effects of counter ion, the anion has little effect and potassium ion is the important factor in the observed accelerated disbonding. Two factors may be considered

TABLE II
Cathodic disbonding of epoxy resin coatings

Effect of variation of electrolyte		Coating disbonding (mm) after 28 days			
Electrolyte	Coating disbonding (mm) after 28 days				
	Skotchkote 206N		Eparzite		
NaCl	5.5		3.5		
KCl	6.5		5.5		
CuCl ₂	3.0		4.5		
Al ₂ SO ₄	3.5		1.5		
H ₂ O (deionized)	—		1.5		
Effect of holiday size		Skotchkote 206N disbonding (mm)			
Electrolyte	2 mm holiday		6 mm holiday		
	3.5		3.5		
Effect of variation of cation		Skotchkote 206N disbonding (mm)			
Electrolyte	CaCl		3.5		
	KCl		8.5		
	NaCl		4.5		
	NaBr		4.5		
	Effect of post cure		Disbonding (mm)		
Electrolyte	Skotchkote 206N		Eparzite		
	Cure 245°C/ 3 min	Postcure 255°C/10 min	Cure 255°C/ 1 min	Postcure 260°C/15 min	
NaCl	5.5	3.5	3.5	3.5	
KCl	6.5	4.5	5.5	—	

to influence the rate of disbonding; firstly, the size and mobility of ions in the bond and secondly, the electrochemical potential of the interface. The effects of cure and post cure on disbonding are shown in Table II. From these limited results it is observed that a slight improvement in resistance to disbonding occurs when the coating is post cured. Improvement of the adhesive strength in lap joints constructed with aluminium has been reported previously⁹ and is associated with changes in the chemical structure of the epoxy resin.

Energy dispersive X-ray analysis

Analysis of the elemental composition in the region of the holiday are shown in Figure 4. A series of electrolyte systems were analysed including NaCl, KCl, Na₂SO₄, K₂CrO₃ and Na₃PO₄. Three different areas of the specimen can be identified; the initial defect, the disbonded

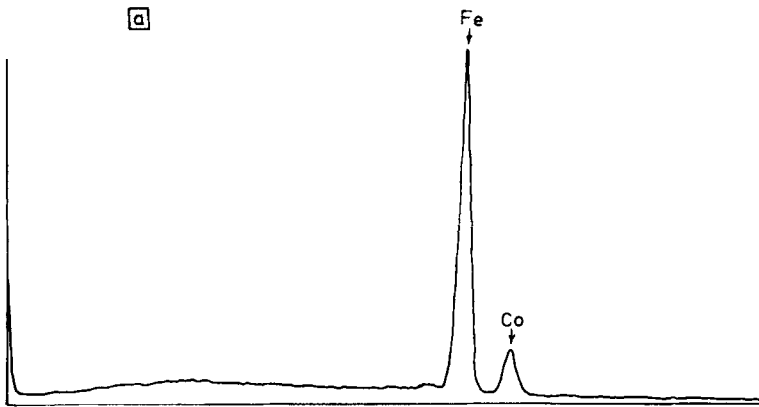
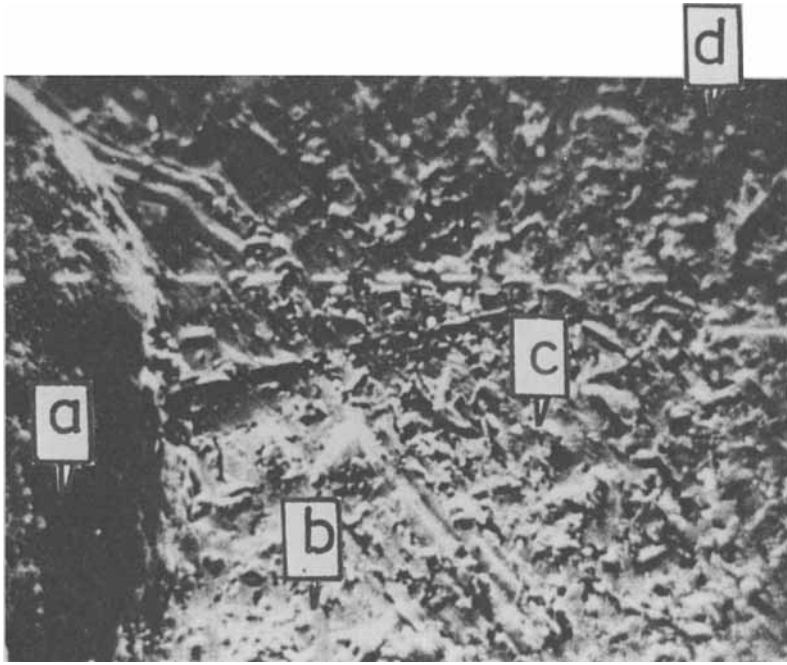
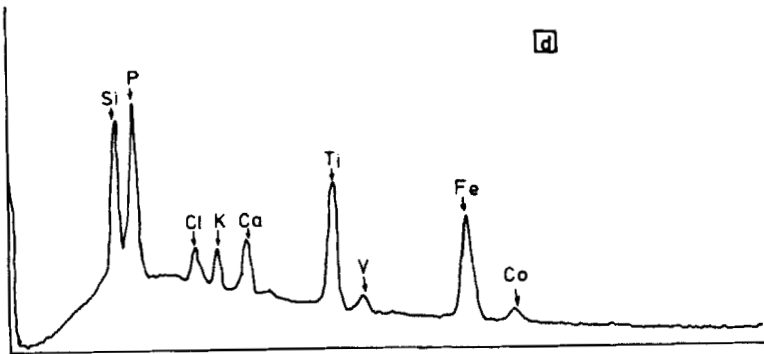
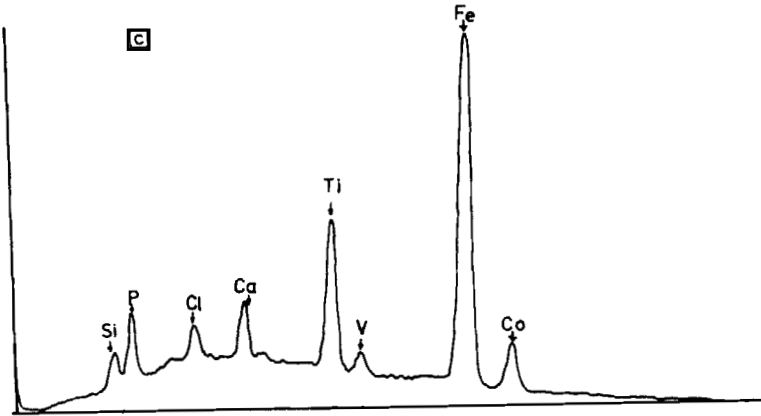
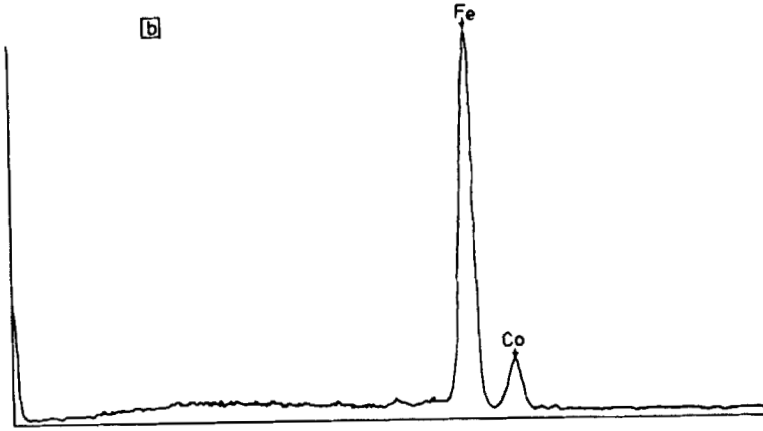


FIGURE 4 Electron micrograph of the disbonded region and EDAX analysis of various regions—KCl as electrolyte.

- a) analysis of the holiday
- b) analysis of the exposed steel surface
- c) analysis of attached epoxy coating
- d) analysis of area ahead of disbonded region.



area and the non-disbonded area where the coating was physically removed.

Analysis of the "holiday" In all cases the analysis indicates the composition of the substrate and shows no significant concentration of electrolyte retained in the surface, Figure 4a.

Analysis of the disbonded region The analysis is almost identical with that of the "holiday". The exposed surface corresponded to bare oxidised steel with occasional area of retained epoxy resin. The epoxy resin can be identified by the presence of alumina and silicate fillers identified by characteristic peaks in the spectrum, Figure 4c.

Analysis of region beyond disbonded region In this region the epoxy resin is still retained by the substrate and as a result the analysis reflects not only the filler and the substrate but also the electrolyte. The presence of the electrolyte in the region ahead of the disbonding was observed in all the systems examined, Figure 4d.

These observations are similar to those previously reported by Watts and Castle⁸ for studies of polybutadiene disbondment from steel.

A recent paper¹¹ has considered the mechanism of disbonding of coatings from metallic substrates. In this system the coating was polybutadiene and the study explored the effects of oxygen concentration, cathodic potential, coating thickness, nature of substrate, pretreatment of substrate, electrolyte type, concentration and temperature. From these studies it was concluded that the rate determining step for the disbondment is associated with the diffusion of cations to the interface. Once the cation has arrived in the oxide layer it undergoes catalytic generation of hydroxide ions leading to changes in the nature of the oxide-polymer interface. The diffusion of cation can occur either through the coating or along the interface. The data presented here would appear to support the latter mechanism.

CONCLUSIONS

Two important points emerge from these studies. Firstly, that disbondment is accelerated by the presence of potassium in the electrolyte system and secondly that the permeation of the electrolyte into the region ahead of the region of detachment is associated with disbondment. It is anticipated that the oxide growth which accompanies dis-

bonding is influenced by the nature of the cation, which points to electrochemical effects rather than to stress related processes associated with oxide build up being important in controlling the rate of detachment. The study further reflects the effect of post cure on the adhesion of the coating and correlates well with earlier studies on lap joints.

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