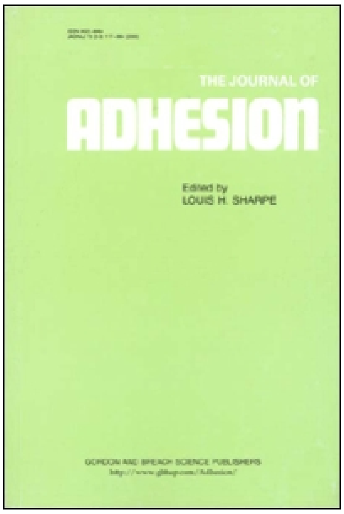

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Mechanistic Aspects of the Cathodic Delamination of Organic Coatings†

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The literature apertaining to XPS studies of three classes of organic coatings (polybutadiene, epoxy co-polymers, and fusion bonded epoxy) on steel are reviewed in the light of the current theories of cathodic disbondment. All three mechanisms (oxide reduction, polymer hydrolysis, and interfacial failure) are readily identified by XPS, and guidelines are presented for assessing the failure mechanism from kinetic data, without the added confidence provided by the surface analyses. In some systems two of the mechanisms are shown to be involved, either simultaneously, or in a two-stage manner. It is concluded that all three mechanisms currently advocated in the literature have their own realms of applicability, and both physical and electrochemical parameters will determine which of them will be dominant for a particular coatings system.

KEY WORDS Cathodic delamination; organic coatings; surface analysis; polybutadiene; epoxy; X-ray photoelectron spectroscopy (XPS).

INTRODUCTION

In recent years the phenomenon of cathodic disbondment (or delamination) has been widely studied with a view to obtaining a more complete understanding of the mechanism(s) responsible for this mode of coatings failure. In this paper it is intended to present all the analytical information concerning the interfacial chemistry of cathodic disbondment, and establish the prevailing rate-controlling steps in the failure process and relate them to type of coating, condition of the substrate, and mode of testing.

Before reviewing the available literature it is informative to discuss the cathodic disbondment process itself in a little more detail. The phenomenon is not new and was described as long ago as 1929 by U. R. Evans in a paper entitled "The Electrochemical Corrosion of Painted Steel With Special Reference to the *Alkaline Peeling* of the Coat."[1] Most paint failures, whether they be associated with a salt-fog test or a stone chip on automobile bodywork, show a certain

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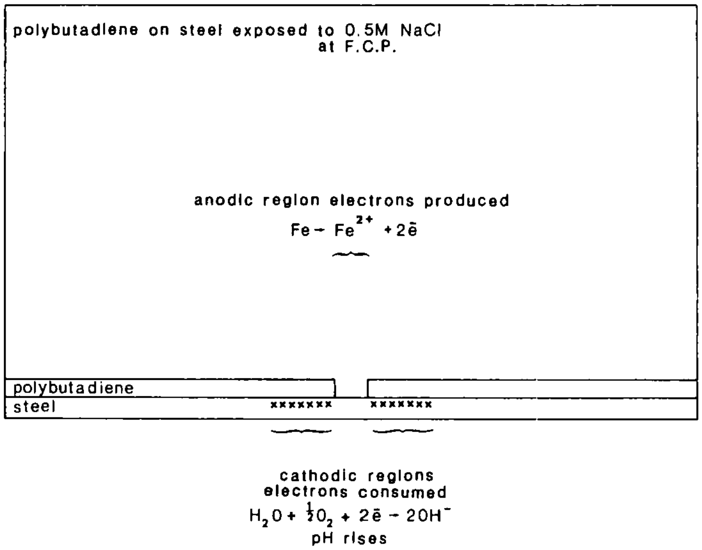

FIGURE 1 Electrochemical reactions at a defect on a coated steel surface.

proportion of the disbonded coating to have been associated with a localised cathodic potential. When a small defect occurs in a paint film on a mild steel surface, exposed to the atmosphere or an aqueous solution, a series of electrochemical reactions are set up as shown in Figure 1. At the defect rusting will occur and this anodic reaction will be balanced by a cathodic reaction which will take place close to the defect but under the paint film, the cathodic reduction of water and oxygen to provide hydroxyl ions. This reaction scheme presupposes the ready availability of water and oxygen but as most paint films are readily permeable to both these species this does not seem an unreasonable assumption. As the concentration of hydroxyl ions increases so the underfilm pH rises and eventually disbondment occurs, the exposed metal now becomes anodic, rusting occurs and so the process goes on.

The area most easily identified is the rusted region but often, on carefully peeling back the coating, a clean metal surface can be observed. This is the zone of cathodic influence which, until the early 1970s, was ignored. The quality of the paint film under investigation was merely reported as the distance of adhesion loss from the initial defect; the smaller this parameter the better. At about this time the problem of cathodic disbondment was recognised, both as a legitimate topic for academic research[2] and as a subject of commercial concern. The former was brought about by the realisation that by separating anodic and cathodic sites the mechanism of coatings failure could be investigated more thoroughly, and the practice arose of investigating the failure mode of coated steel panels that were cathodically polarised, either by coupling to a more active metal such as zinc or, by the use of an impressed current, the cathodic potential could then be varied at will. The commerical concern arose as a result of the increasing trend, within the oil and gas industries, to use a combination of impressed current cathodic protection and high performance organic coatings (such as fusion–bonded epoxy) to ensure corrosion-free operation of their transmission linepipe. In the majority of cases such a combination proves to be reliable and trouble-free in use, but problems can occur at holidays in the coating. At such regions rapid delamination of the coating is observed, a condition which is exacerbated by the presence of the cathodic potential. As a result, standardised cathodic disbondment tests were developed in both the UK[3] and the USA[4] to assess the susceptibility of such heavy-duty coatings to cathodic disbondment.

The advent of surface analysis methods some two decades ago provided the investigative scientist with a means of measuring the very thin surface layers important in corrosion, catalysis, polymer characterisation and so on. Such methods had clear ramifications for those interested in the adhesion of polymers to metal surfaces as discussed elsewhere.[5,6] For the present discussion it is sufficient to say that following failure the presence of very thin overlayers can be detected, chemical modification identified, and the segregation of specific ions or molecules to the failure interface followed. The most widely used surface analysis technique in these type of investigations is X-ray photoelectron spectroscopy (XPS or ESCA),[7] although both Auger electron spectroscopy[8,9] and static secondary ion mass spectrometry[10] have important roles to play.

The main aspect of controversy in the studies of cathodic disbondment has centred around the manner in which adhesion loss occurs, so a brief description of the three candidate mechanisms is included below.

MECHANISMS OF FAILURE

In the literature there is a plethora of work on a wide variety of systems and, at first sight, there seems to be little agreement amongst the various investigators. However, on closer insepection it becomes apparent that there are three mechanisms that are being advocated for cathodic disbondment. They have one feature in common; that cathodically generated alkali, produced in the manner described above, leading to high pH excursions in the environs of the polymer/metal interface, is responsible for failure. The mechanisms can be summarised as follows:

Oxide reduction

That is, the dissolution of the substrate oxide phase to which the polymer adheres, leaving a void at the interface and hence blistering. This method has been identified by ellipsometry used in conjunction with underfilm pH probes which indicate the very high alkalinity attained.[11,12]

Alkaline hydrolysis of the polymer

Attack of the polymer close to, but not at, the interface by underfilm or interfacial hydroxyl ions, (sometimes referred to as saponification). This will invariably leave a very thin layer of polymer adhering to the substrate, and it is only with the application of XPS to adhesion studies that this mechanism has been identified.[13,14,15] This type of failure requires gross permeation of the coating by hydroxyl ions, and their metal counter ions, which does not always occur. A closely-associated failure mechanism, and one which is indistinguishable spectroscopically, occurs as a result of the ingress of water molecules to the polymer/metal interface.

Interfacial failure

This is the classical form of alkaline-induced failure as described by Evans,[1] and advocated more recently by other authors.[16,17] It is only with the advent of surface-specific analysis methods such as XPS that it has proved possible to identify such a failure mechanism unambiguously.

The main difficulty that has arisen in recent years is that experimental data have been presented which establish the applicability of one of the above mechanisms, which has then been applied to a different system, invariably by a different group of research workers. In this manner a mechanism developed for, and apertaining to, one particular system, has been applied in an uninformed way to another coating. In this way, each mechanism has been seen to be all encompassing, each with its supporters and protagonists. The main thrust of this paper is to establish the realms of applicability of each particular mechanism described above.

ORGANIC COATINGS INVESTIGATED

Polybutadiene

One of the first organic coatings to be studied comprehensively was polybutadiene,[18] and it now seems clear that the complex behaviour of this simple material is well understood.[18] The question of which failure mode is operational is convoluted by the existence of all three possibilities. The adhesion of polybutadiene to steel is complex and involves the formation of an interphase zone containing iron carboxylate[19,20,21] as illustrated in Figure 2. Thus, the possible loci of failure are between oxide and interphase (a true adhesive or interfacial failure), between interphase and polymer leaving some polymer residue on the metal oxide surface (akin to polymer hydrolysis), or within any of the phases present.

The failure of this polymer is represented schematically in Figure 3; the test employed has been described elsewhere[22] but, essentially, a pre-damaged panel is exposed to 0.5 M NaCl solution at a potential of −1500 mV as required by the appropriate test specification.[3] The visual appearance following testing was of a blistered central region and weakly-adhering outer zone. At the edge of the blistered region oxide reduction could be identified by XPS as shown in Figure 4. The appearance of the metallic components in the upper spectrum indicates that

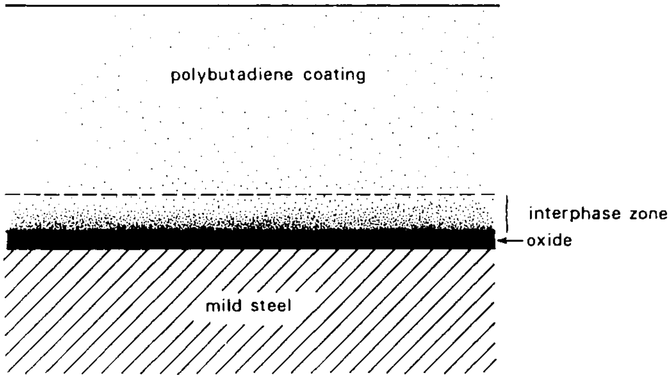

FIGURE 2 Schematic representation of the interaction between polybutadiene and a steel substrate.

the oxide thickness has been substantially reduced compared with that of the centre of the blistered zone. Clearly, the pH excursions at the crevice tip lead to oxide dissolution but as the crevice grows so the pH falls and the oxide thickens again. The survey XPS spectra from the blistered region, Figure 5a, are from a very clean surface, indicating interfacial failure—the interphase zone segregating with the disbonded polymer surface. This results from the lateral diffusion of the hydroxyl ions from the exposed metal surface where they are produced. The small amount of carbon results from the usual atmospheric contamination observed in XPS. In its dry state the interface is mechanically strong,[22] and failure

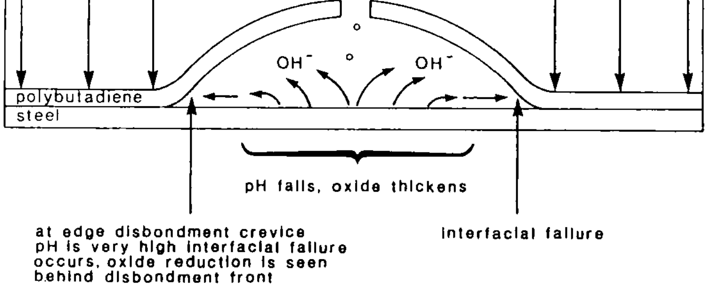

FIGURE 3 Mode of failure of polybutadiene on steel when cathodically polarised. All three mechanisms of cathodic disbondment are observed as discussed in the text.

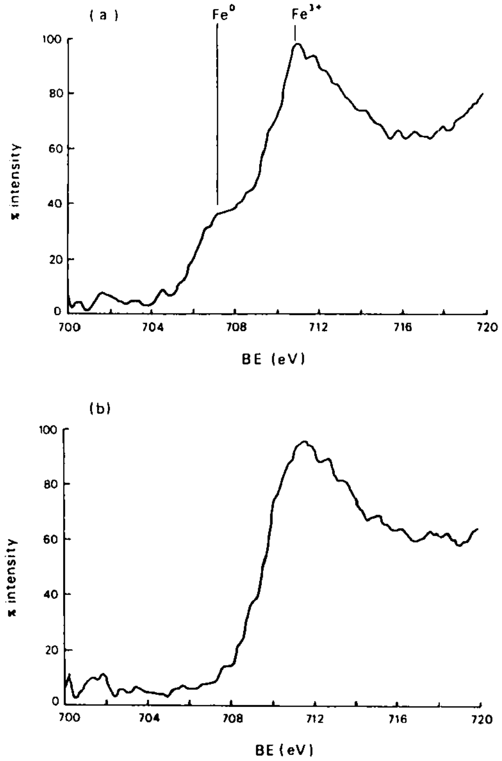

FIGURE 4 Iron $2p_{3/2}$ spectra from the disbondment zone of Figure 3. (a) reduced thickness of oxide at the crevice tip, (b) regrown oxide.

occurs within the polymer, thus indicating the absence of weak boundary layers which might otherwise account for the presence of such a carbon signal.

Outside the blistered region the polymer can be peeled easily from the substrate but does not spontaneously disbond. The XPS spectrum reveals large quantities of carbon (Figure 5b), and a strongly attenuated iron signal. This failure is associated with the interphase zone remaining at the substrate surface and can be classified as a case of coating hydrolysis, resulting from the downward diffusion of water molecules through the thickness of the polymer film. However, the effect of solution composition and, in particular, the influence of the cation to which the coating is exposed is still not clear. By using a series of Group 1 and Group 2 metal chlorides it is apparent that the rate of failure depends on the size of the hydrated cation, but NOT the presence of the cation at, or close to, the interphase zone.[23] The presence of cations at the interphase, brought about by the mass transport of solvated ions through the polymer film, allows water ready access to this region, which brings about rapid failure. In the case of the slower failures, the solvated cations are larger and migrate more slowly to the interface, in turn impeding the migration of water to this point. In essence, the water is

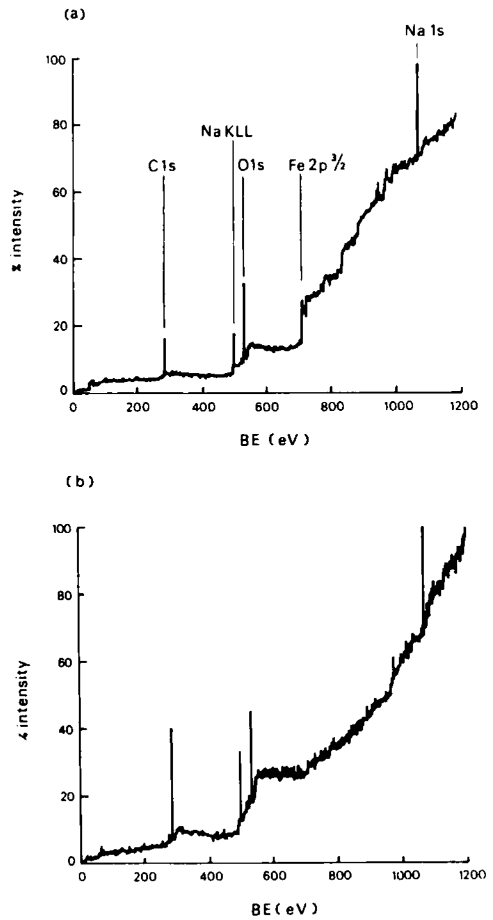

FIGURE 5 XPS survey spectra of the metal surface following cathodic disbondment of polybutadiene from mild steel. (a) blistered zone of Figure 3 showing interfacial failure, (b) metal with a thin polymeric overlayer as a result of polymer hydrolysis.

responsible for the damage but the rate at which it arrives at the interfacial region is controlled by considerations of ionic size and substrate potential. If the substrate is unpolarised the failure will occur much more slowly. This scenario is in stark contrast to the interfacial failure described above where it is the hydroxyl ions that are primarily responsible for failure.

Thus, in this polymer system the oxide reduction is irrelevant to the failure process as it occurs after the polymer has separated from the substrate. The blistering phenomenon represents interfacial failure, the kinetics of which are directly proportional to exposure time once the process has been initiated.[18] The outer zone represents damage inflicted by water aggregating close to, but not at, the polymer metal interface, as a result of downward transport through the thickness of the film.[24] The definition of a single failure mechanism for polybutadiene would be misleading, although correct, and failure routes can be inferred from kinetic and electrochemical observations although it is only by using the appropriate analytical method that the locus of failure can be accurately defined.

Epoxy co-polymers

The disbondment of epoxy co-polymers by cathodic potentials has been the subject of several XPS investigations.[13,15,25] In the latter work the thickness of organic residue remaining after mechanical failure and aqueous exposure was measured and found to vary between 2 and 5 nm but was not related to the method of inducing failure. The C1s spectra was shown to vary quite dramatically with failure as shown in Figure 6, and was interpreted in terms of subtle differences in the loci of failure. The spectra obtained from the polymer and metal failure surfaces of the dry test are very similar, indicating that the composition of the thin organic layer remaining on the metal surface is the same as the bulk polymer (the C1s spectrum presented by the polymer failure surface). On aqueous exposure, however, the intermediate component of the C1s spectrum represent C-O species (epoxy groups) is depleted; the displacement of epoxy groups from such a metal-oxide surface is consistent with the thermodynamics of this system. The conclusion to be drawn from this investigation was that, although

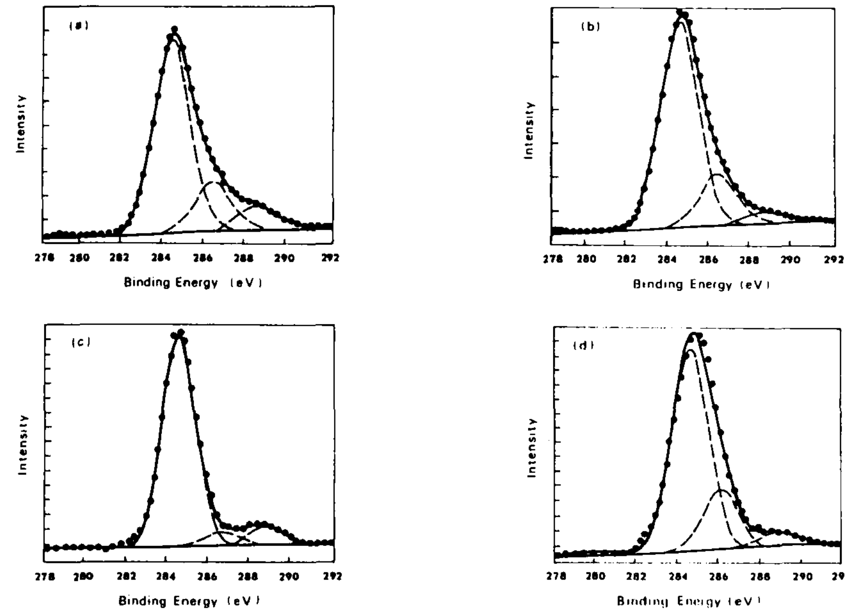

FIGURE 6 Carbon 1s spectra of epoxy-phenolic coated steel. (a) and (b) are from a mechanical test, (c) and (d) following aqueous exposure. (a) and (c) are substrate surfaces, (b) and (d) coating surfaces. The components of the spectrum are alkane (C—H), epoxy (C—O), and carboxyl (C=O).

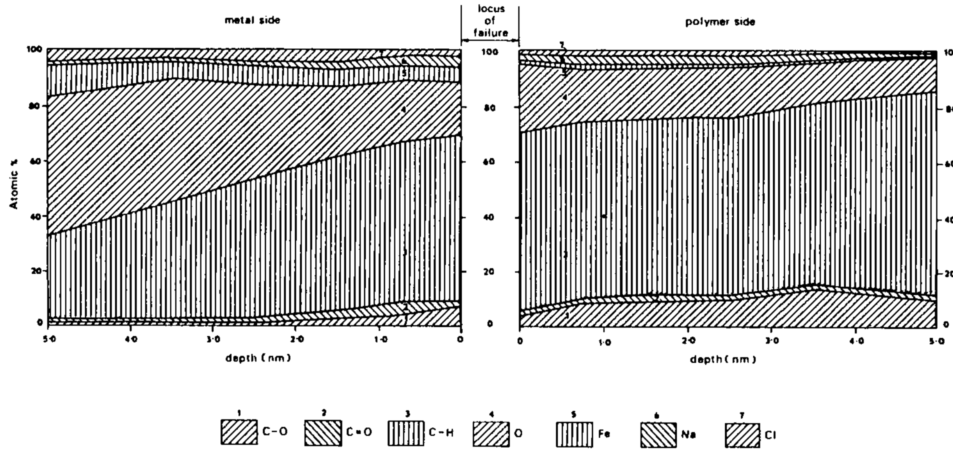

FIGURE 7 Compositional depth profile, away from the locus of failure, by angle XPS.

the overlyaer thicknesses were comparable, the polymer composition was different, an apparently characteristic hydrophobic surface being produced by aqueous exposure. The investigation was extended further, by the use of angular-resolved XPS, to determine the orientation of the organic molecules at the failure surface following saline exposure.[26] A depth profile obtained in this manner is shown in Figure 7. On the metal side of the failure the C-O species are concentrated in the outer 1 nm, whilst on the polymer side there is a complementary depletion. These data are consistent with a failure occurring adjacent to the epoxy groups of the bisphenol-A chain which then segregate with the substrate on failure.

Thus, although the use of XPS in a standard manner allows us to follow changes that occur in an integral depth of approximately 5 nm, the use of angular-resolved XPS allows additional composition information to be obtained within that sampling depth.

The failures described above are clearly associated with cathodic polarisation of the substrate, and the more noble the potential the greater the rate of delamination (an observation that is also true for polybutadiene).[18] These observations have been traditionally ascirbed to damage of the organic coating by cathodically-generated alkali, brought about by the cathodic reduction of water and oxygen at the metal surface. However, there are other factors which must be considered. The failure surfaces are spectroscopically very similar to those obtained in a wet adhesion test where water is regarded as being the prime cause of damage.[27] The theory described above for polybutadiene[23] seems to be applicable in this case as well, that water diffusion through the polymer film can be blocked by the uptake of highly solvated ions. The potential field from the substrate will tend to pull such ions into the D-type regions of the film, where the cross link density is lower, thus accounting for the larger delamination rate when a cathodic potential is externally applied. The true interfacial failure of the type observed for polybutadiene proceeds very slowly, if at all, although a small amount of blistering is generally observed at the exposed metal.

Fusion-bonded epoxy

In most of the studies described above the physical condition of the substrate, *i.e.* the surface roughness, did not appear to have a significant effect on the delamination kinetics, although the times employed were generally too short to undertake a rigorous investigation of the parameter. This was not the case with fusion-bonded epoxy coatings where the coatings are much more resistant to cathodic disbondment. In this study XPS provided information concerning the locus of failure and the manner in which it varied with substrate topography. The failure mode observed was predominantly adhesive[28] but, as the surface roughness increases, so there is a trend towards mixed-mode failure. This is a result of protruding oxide asperities fracturing in the polymer phase. There is, however, one feature that is characteristic of the failure of this system and that is the large amount of oxide reduction that occurs at the pre-damage prior to the onset of adhesive failure. If the cathodic disbonding test is carried out according to the British Gas Specification,[3] this defect takes the form of a 6 mm parallel-sided hole through the coating into the substrate. The substrate oxide is a characteristic golden colour following coating as a result of oxide growth that has occurred during the preheating. Oxide reduction is readily recognised as a silver-coloured halo around the defect; XPS shows the oxide to be 2–3 nm thick. Once this precursor process has taken place the mechanism of failure changes to interfacial separation, and it is thought that the change is brought about by residual stresses in the coating lifting it from the substrate and allowing the cathodically-generated alkali direct access to the interface. The shape of the defect and the steepness of the sides seems to affect the extent of the halo region. Figure 8 shows the variation of this halo effect with defect size obtained using a series of twist drills to obtain shallow craters as well as parallel-sided defects of high aspect ratio. The details of the mechanical damage is provided in Table I, other types of damage which present a small area of exposed metal were also studied.

Considering the circular (or near circular) defects first, it seems clear that the larger the aspect ratio the greater the area of reduced oxide; this is consistent with the stress patterns around such defects. The same is true of the non-symmetrical damage inflicted by a knife or similar; thus it seems apparent that the type of standardised tests employed in laboratory screening tests[3,4] do not give the same results as the type of field damage they are intended to simulate, although they most probably do present the same ranking order. Two of the specimens of Figure 8 (Nos. 1 and 7) went open circuit for a short time and this can be identified from the deposits seen in the halo region.

Although the failure mechanism passes from oxide reduction to interfacial failure, the rate controlling step remains the same; that is the rate of production of hydroxyl ions which is a function of the exposed cathode area. From this reasoning, a logarithmic dependence of disbondment area with time can be

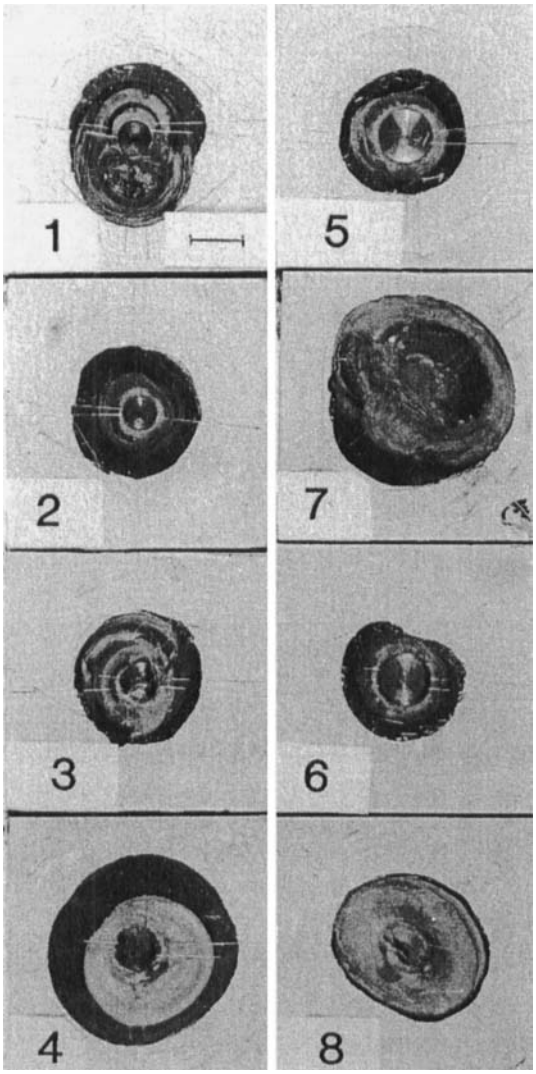

FIGURE 8 Cathodic delamination of a fusion bonded epoxy on polished steel surfaces in 0.5 M Nacl at a potential of −1500 mV. Time of test was 11 days.

predicted and this is indeed the case.[28] However, the disbondment of heavy-duty coatings is a three-stage process and in the final stage linear, rather than logarithmic, kinetics are predicted and the rate-controlling step passes from cathode area to interfacial path length. A series of substrate surface profiles all produced a constant delamination velocity once a tortuousity factor had been defined to account for the differing path lengths.

The failure mode for these types of coatings is complex and can only be fully understood by combining the data obtained by XPS with kinetic results. Once this

TABLE I
Dimensions of the pre-damage used in the cathodic disbondment experiment of Figure 8

Specimen No (see Figure 8)	Diameter of defect at polymer/metal interface (mm)	Bevel through polymer (vertical = 0°)	Aspect ratio in polymer (diameter/thickness)
1	6.6	0	17
2	6.9	0	18
3	7.1	60	19
4	7.5	70	20
5	10.0	60	26
6	10.1	55	27
7	1.5 × 10.5 chisel damage		
8	0.25 × 10.86 knife cut		

is done it is possible to define fully the manner in which failure has occurred, even when it does rely on two different loci of failure and two rate-controlling steps that overlap.

CONCLUDING REMARKS

The three mechanisms of cathodic disbondment proposed in the literature have been discussed in the light of evidence obtained from XPS investigations from a series of markedly different coatings. In the case of the oxide reduction and interfacial failure it is clear that the underfilm alkalinity produced by the cathodic reduction of water is responsible for failure; in the former case the oxide is dissolved in conditions of high pH and very noble potential, in the latter the polymer-to-metal-oxide bonding is attacked directly by the alkali. The final failure mechanism (hydrolysis of the polymer) is not unequivocally attributable to the action of hydroxyl ions on the polymer. The magnitude of the cathodic potential plays an important role but it is the downward diffusion of water molecules that is responsible for the damage to the polymer. This type of damage has now been reported in studies of both adganic coatings.[23] Further studies in this area are necessary for a complete understanding of the aggregation of water molecules in polymers and the damage they bring about.

The three mechanisms are in competition in any particular system and the physical properties of the polymer and the electrochemical conditions will determine which one becomes dominant. On the basis of the polybutadiene and fusion-bonded epoxy studies cited above there can be regimes in which one or other becomes dominant in the same system. As a guide to the assessment of the mechanism which is responsible for failure, it appears that for oxide reduction to occur the potential must be very noble; for interfacial failure the kinetics will show a dependence on interfacial path length, so the disbondment area will be directly proportional to the time of the test; and, for polymer hydrolysis to dominate, downward diffusion through the polymer *i.e.* failure of all polymer exposed to the aqueous phase), as in the wet adhesion test, must be observed.

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