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The application of X-ray photoelectron spectroscopy to the study of polymer-to-metal adhesion

Part 1 *Polybutadiene coated mild steel*

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The nature of polybutadiene to mild steel adhesion has been characterized by X-ray photoelectron spectroscopy (XPS) used in conjunction with a novel oxide stripping/argon ion bombardment technique for interface analysis. It is concluded that the interface is more correctly described as an interphase region. The failure mode of the polybutadiene/steel couple has been determined for mechanical delamination, and corrosion induced failure; both at the free corrosion potential (FCP), and when cathodically protected. Cohesive failure of the polymer occurred in the two former instances, but when cathodically protected the film is observed to separate in two stages. These results are discussed in relation to underfilm pH and the possible importance of oxide reduction to coatings delamination from cathodically protected structures.

1. Introduction

The nature of the metal-to-polymer interface is important in many contexts, the polymer may be a simple organic coating or a load bearing adhesive; the metal may be mild steel or an exotic titanium alloy for aerospace applications. In this paper we report the investigation of the bonding, and subsequent failure of a polybutadiene coating on a mild steel substrate.

As adhesion is a local phenomenon involving only a few atom layers of adherend and adherate, an analysis technique such as XPS is ideal. XPS was chosen in preference to Auger electron spectroscopy (AES) for its ability to yield chemical state information and its applicability to polymers.

In an investigation of polymer-to-metal adhesion it is desirable to obtain chemical information about the interface before mechanical or corrosion induced failure has occurred. The usual method of depth profiling in surface analysis is by argon ion bombardment (AIB) but such an approach is not feasible in this case, owing to problems associated with polymer degradation in the ion beam. A method of approaching the interface has now been devised; by chemically stripping the oxide/polymer film from the parent metal it is possible to approach the interface through the oxide by ion bombardment. Model experiments have also been carried out in which curing of the polymer is inhibited and the uncured polymer dissolved from the substrates to reveal any interface modification which may have occurred.

The locus of failure of a polymer-to-metal joint will indicate the quality of the interfacial bond. Lap shear tests were carried out on the coated steel followed by XPS analysis to assess this parameter.

Cathodic delamination occurs when a coated metal surface is polarized and may be due to an externally applied potential (as in the case of cathodically protected structures such as ships or pipelines), or the development of discrete anodic and cathodic sites on the metal surface (this situation occurs in the salt spray test used in the paint industry). The cathodic disbondment of polybutadiene on steel has been investigated for both types of polarization.

XPS spectra were obtained using a V.G. Scien-

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tific ESCA 3 Mk II operating at a vacuum of $\sim 5 \times 10^{-10}$ torr, using Al$K\alpha$ radiation ($h\nu = 1486.6$ eV), pass energy of the analyser was set at 50 eV, 2 mm entrance and exit slits were used. The spectrometer was interfaced to a V.G. 3040 data system based on a DEC PDP8e computer. Each specimen was examined by a combination of 1000 eV survey spectra, together with 20 eV high resolution scans of all the major elements. Quantitative analyses were calculated from the peak areas, following a linear background subtration, using the appropriate sensitivity factors [1].

2. Bonding of polybutadiene to mild steel

2.1. Mechanical failure

The polybutadiene coating employed in this investigation was a commercial can coating manufactured by Du Pont [2]. The coating was applied to the mild steel substrate, using a wire wound bar coater, to a thickness of 17 ± 2 μm after stoving in air at 200° C. The substrates were prepared by emery abrasion to a 120 grit finish. Surface preparation methods have been investigated previously and this method was found to give the cleanest surfaces [3].

The delamination of this material has been extensively studied by Leidheiser and co-workers [4–8], using electrochemical techniques and it is intended that the present XPS studies are complementary to these.

To assess the quality of the interfacial bond and define the locus of failure under mechanical loading conditions, lap shear test specimens were produced from coated panels bonded with cyanoacrylate ester adhesive; the area of the lap was 10 mm × 8 mm. Tests were carried out in quadruplicate, failure loads of approximately 2 kN were obtained.

"Metal" and "polymer" surfaces of a failed coated panel are shown in Fig. 1. Visual evidence alone would classify this failure as mainly adhesive with the "metal" surface showing just a few lumps of the coating still adhering. XPS analysis of these surfaces together with that of a polybutadiene standard are presented in Fig. 2 and the only elements identifiable in any of the spectra are carbon and oxygen due to the polymer. The similarity of these three survey spectra show the failure to be entirely cohesive, with the locus of failure in the polymer and an overlayer of the coating remaining on the substrate surface.

2.2. Examination of bond characteristics by an oxide stripping technique

As the polymer/metal interface remained intact after mechanical testing a means of investigating this region further was necessary. Approaching the interface by ion bombardment of the polymer is impractical owing to sample degradation. By employing a chemical stripping technique it is possible to remove the oxide/polymer layers as a

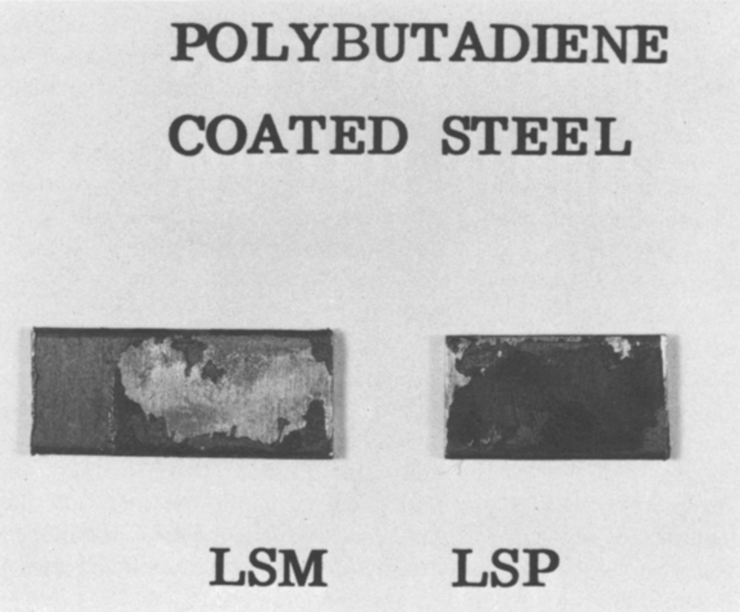
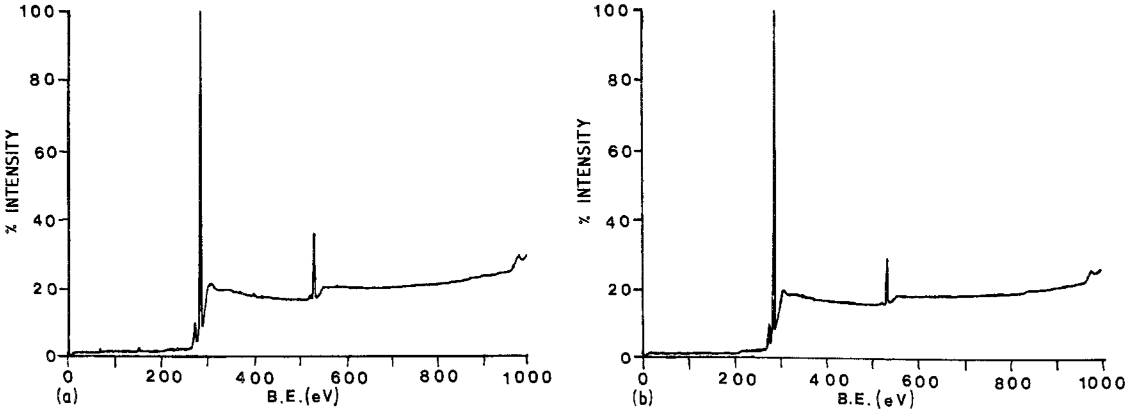


Figure 1 Metal (LSM) and polymer (LSP) surfaces of a failed lap shear test specimen.



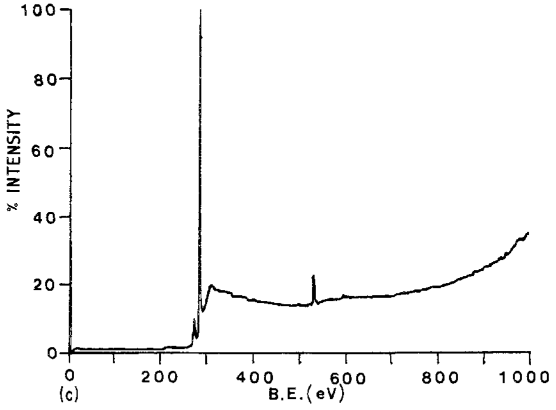


Figure 2 XPS survey spectra of (a) polymer surface (LSP), (b) metal surfaces (LSM) and (c) polybutadiene standard.

duplex film. Oxide stripping using a methanolic iodine solution was first described by Vernon *et al.* [9] who performed gravimetric analyses of the films. More recently Moseley *et al.* [10] have utilized this method and carried out electron diffraction studies of the stripped film. The application of the stripping technique to XPS where substantially larger, continuous films are required has been developed in our laboratory. Full details of the technique, together with potential applications will be published elsewhere [11].

Oxide stripping of the coated specimens is readily accomplished, without damage to the polymer in accord with thermodynamic calculations which show that the polymer/oxide bond is not disrupted by methanol [12]. Scanning electron microscopy (SEM) observations show the oxide film to remain intact on the polymer; not having fractured or spalled during the stripping process [3].

Once removed from the parent metal the composite polymer/oxide film is analysed from the oxide side by sequential AIB/XPS. The ion gun employed was a V.G. Scientific AG2 operating at 3 kV, with 1.5 kV focus potential and a residual argon pressure of 10^{-6} torr. Under these conditions the etch rate was 1.5 nm min^{-1} on a stainless steel oxide. The oxide stripping experiment, and subsequent analysis is shown schematically in Fig. 3 together with a scanning electron micrograph of the underside of the stripped film (oxide uppermost).

Several etch profiles of stripped oxide/polymer films have been obtained using different surface preparation methods and heat treatment schedules. The depth profile obtained from a 17 μm coating on alkali cleaned mild steel is shown in Fig. 4. Because of the roughness of the interface a sharp discontinuity is not observed in the depth profile but a general increase in carbon level was taken as an indication that the polymer had been reached in certain regions. The oxygen level remained fairly uniform throughout the oxide and started to fall as the interface was approached, i.e. as the carbon level rose. There was also slight broadening of the Fe2p3/2 peak due to a small quantity of iron in the ferrous state. The iron 2p3/2 spectra for the bulk oxide and that obtained at the interface region are shown in Fig. 5, together with a difference spectrum to indicate the magnitude of the ferrous component.

The appearance of this iron (II) component was always observed as the interface region was approached, *irrespective* of etch time. It is, therefore, due to a chemical modification of the iron oxide at the interface, rather than an ion induced reduction, which could occur during ion bombardment but is likely to depend on total charge deposited by the ion beam and hence on etch

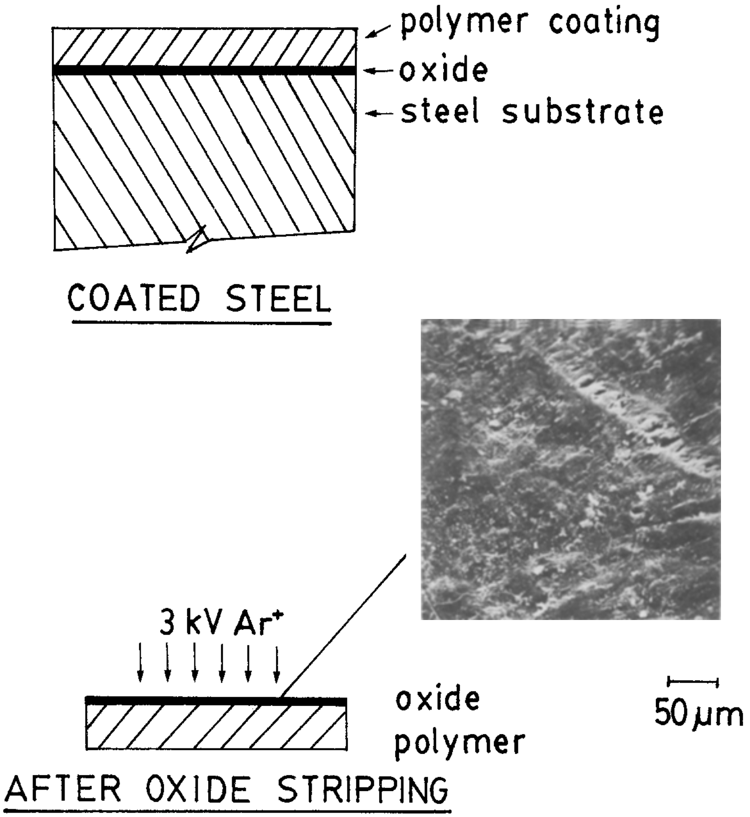


Figure 3 Schematic diagram of the oxide stripping procedure. The scanning electron micrograph illustrates the integrity of the underside of the stripped film.

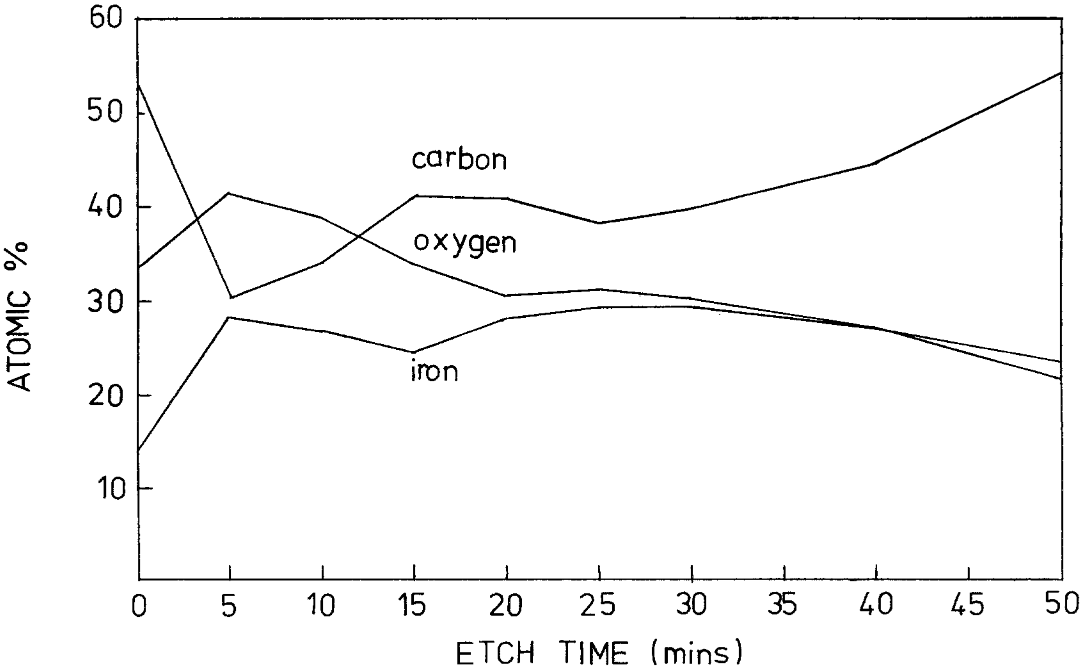


Figure 4 Depth profile of a stripped oxide/polymer film. Etch rate is approximately 1.5 nm min^{-1}.

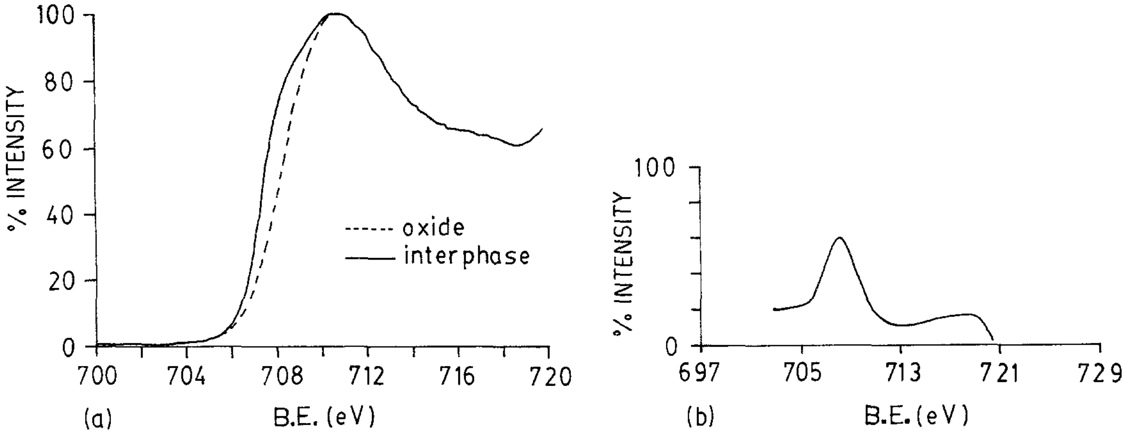


Figure 5 (a) Fe2p3/2 spectrum at the interphase showing broadening attributable to iron. (b) Difference spectrum of Fig. 5a indicating the magnitude of the Fe^{2+} component.

time. To illustrate this point further Table I presents, for several depth profiles, the time at which the iron (II) component can be first identified.

Analysis of a 1 μm diamond polished film was carried out to gain improved interface definition, and after only two minutes of ion bombardment the Fe^{2+} component was discernible, not as a broadening of the ferric peak but as a major component of the Fe2p3/2 spectrum as shown in Fig. 6. After a further three minutes etch time the iron (III) component can only be seen as a substantial broadening on the side of the ferrous peak.

Thus the evidence provided by the oxide stripping/AIB/XPS technique is that there is a layer of modified iron oxide/polymer at the interface, identified by the presence of divalent iron in the spectrum. Analysis of this region on a polished substrate to give improved interface definition shows it to be several namometres thick, thus the description of an oxide/polymer interface is better satisfied by the term interphase indicating a well-defined region between the bulk polymer and the oxide. XPS has shown that the interphase contains iron, mainly in the ferrous state, and organic carbon. The composition or thickness of this zone did not relate in any way to the substrate pretreatment.

TABLE I AIB time to appearance of Fe^{2+} in XPS spectrum for various combinations of surface preparation and stoving time

Surface preparation [3]	Coating thickness (μm)	Time at 200° C (mins)	Time to onset of Fe^{2+} in spectrum (mins)
alkali clean	17	20	20
alkali clean	34	40	50
emery abrasion	17	40	30
diamond polish	17	20	2

2.3. Direct examination of interphase chemistry

Polybutadiene cures by an oxidative mechanism [13, 14] and by curing in an inert environment it will be possible to inhibit the crosslinking which is promoted by oxygen from the atmosphere. Any chemical modification of the oxide surface at its interface with the polymer should however continue to occur in the absence of atmospheric oxygen. The developed interphase zone could then be exposed by removing the uncured polymer with a suitable solvent such as de-aerated carbon tetrachloride and would be amenable to XPS analysis.

Initial experiments of this type were carried out on mild steel coupons heated at 200° C in flowing oxygen free nitrogen for two hours. Removal of uncured polymer by solvent washing and subsequent surface analysis showed the presence of ferrous iron at the surface. It was realised, however, that a similar modification could arise by heating steel in nitrogen in the absence of polymer as a result of a solid state reaction between iron and its oxide. To distinguish this possibility from the alternative, the reduction of oxide by polymer, a rather more rigorous investigation was undertaken using solid ferric oxide (haematite, α-Fe_2O_3) as the substrate material.

The oxide specimens were produced by heating

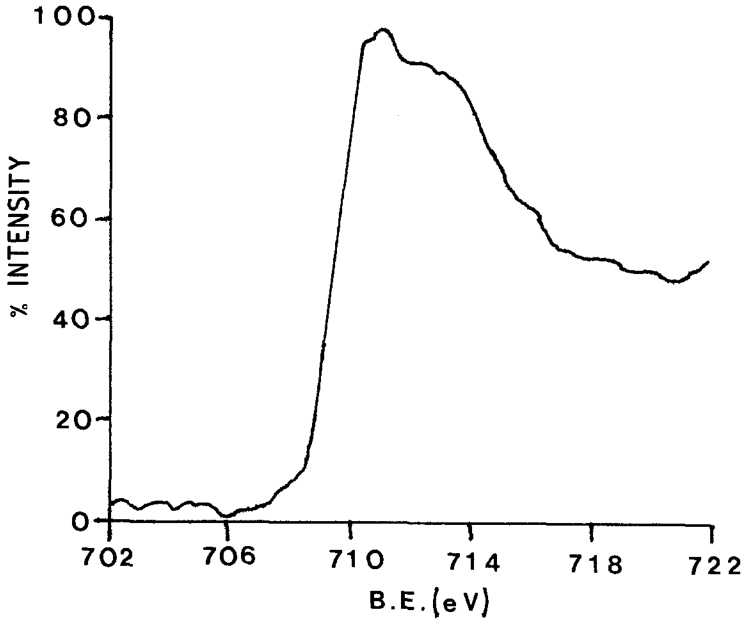


Figure 6 Fe2p3/2 region at the interphase of polybutadiene applied to polished steel. Etch time is two minutes.

pure iron (Specpure, ex Johnson Matthey Chemicals Ltd) in air at 850 to 900° C for several days, coupons were then ground to a 1200 grit finish on silicon carbide papers. Specimens were treated with polybutadiene and heated in nitrogen as described above. Reference spectra were also obtained from the "as-polished" oxide and from the oxide following swabbing with the de-aerated solvent; both showed the iron 2p3/2 peak to be completely ferric, indicating that, as expected, solvent washing had no effect on oxide chemistry.

When the oxide is heated with the polymer in place, a ferrous component appears on the rather weak iron signal. To establish the location of the Fe^{2+} bearing layer in relation to the bulk (Fe^{3+}) oxide photoelectron spectra were recorded at take-off angles from 10 to 45°, as shown in Fig. 7a, together with the bulk oxide as a standard; (the photoelectron take-off angle, θ, is defined as the angle subtended by the sample surface and analyser optics, thus a low value of θ will be more surface specific). The iron spectra from the oxide standard and the modified oxide surface ($\theta = 45^\circ$) were analysed in their Fe^{2+} and Fe^{3+} components, using an iterative non-linear least squares curve fitting procedure, (Gauss or Gauss–Newton method). The resultant fits show a large iron (II) component on the modified oxide surface, Fig. 7b, which was only a minor feature of the standard, Fig. 7c. The other spectra (Fig. 7a) show that the Fe^{2+} component is enhanced at low take-off angles, indicating it to be overlaying the bulk oxide as expected from an oxide modification due to polymer interaction. Further evidence of this interaction is found in the behaviour of the organic phase. As mentioned above the iron signal on the washed surface was weak and the organic carbon signal correspondingly large. Unlike the behaviour of the reference sample, this polymer is not washed away and has apparently been cured by contact with the ferric oxide which in the process is itself reduced.

Before commencing a detailed investigation of the corrosion induced delamination of this sytem some exploratory experiments were carried out using simple strip specimens. Strips of the coated panels 10 mm wide were immersed in sodium chloride solution to a depth of 40 mm, at either the rest potential or polarized cathodically. After the appropriate time of exposure the coating was peeled from the substrate with self-adhesive tape. The appearance of the cathodically protected strip specimen after 24 h is shown in Fig. 8. The coating has been peeled back to reveal the matt grey steel substrate adjacent to the adhering polymer. Near the edge of the specimen the substrate appears shiny and much lighter. The underside of the polymer shows complementary changes: a grey region corresponding to the shiny substrate surface while the polymer from the grey metal region is the characteristic golden colour of the crosslinked polymer. These observations point to a complex failure mode and, to simplify future references to these regions, the failure showing the dark grey surface adjacent to the adhering polymer will be referred to as a Type I failure whilst the failure which reveals the shiny region near the specimen edge will be designated Type II, Fig. 8.

In the case of the strip specimen immersed at rest potential considerable rusting at the edges is seen. Coating removal is effected using self adhesive tape and the predominantly shiny appearance (Type II failure) of the cathodically polarized specimen is replaced by the Type I failure surface. XPS examination of the failure surfaces of both coating and substrate are given in Table II.

The high level of carbon on the substrate surface and the corresponding low level of iron points to cohesive failure of the weakened polymer close to the metal surface. This view of Type I failure is also supported by the absence of iron on the polymer surface. The phenomenon of Type II failure occurring only during cathodic disbondment is investigated further in the next section.

3. Cathodic disbondment of polybutadiene on mild steel

3.1. Experimental details

The experimental set-up is shown schematically in Fig. 9, a seal is made between the electrolyte ring and a coated, mild steel panel, using silicone grease. A central initiating defect is made using a twist drill, the area of the defect is 10 mm^2. To obviate any effects brought about by defects in the coating (such as dust particles) each panel was coated

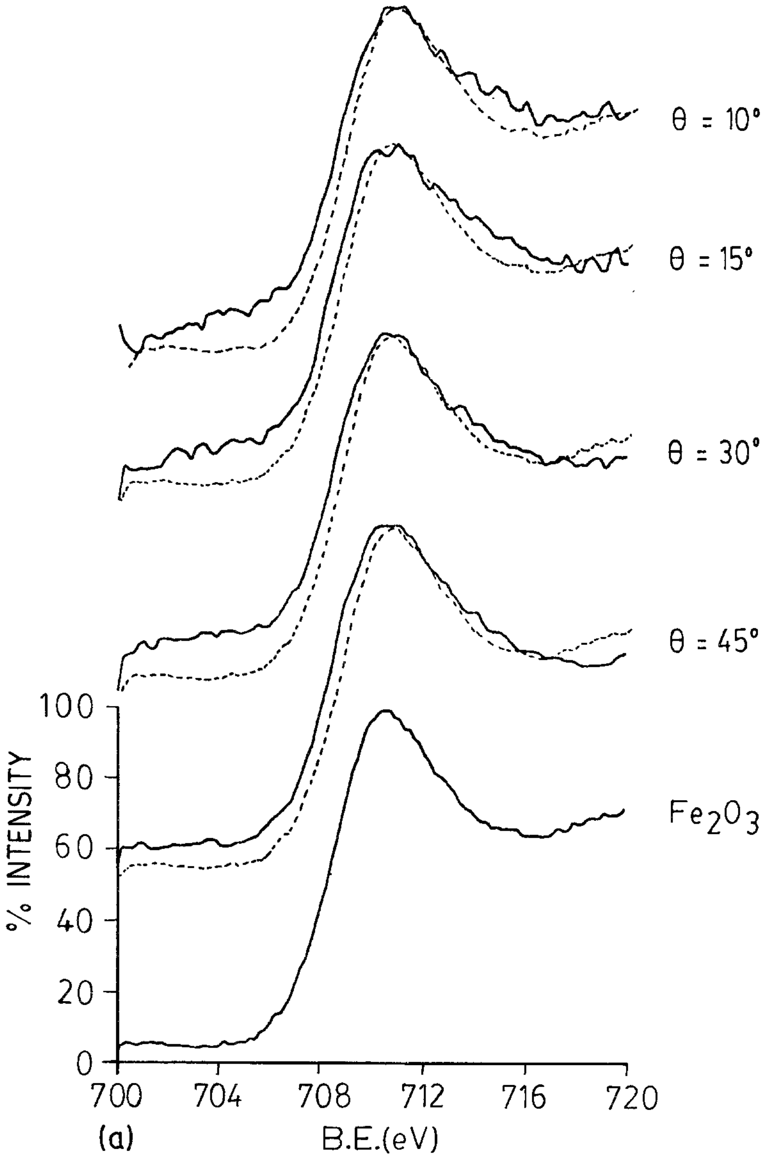
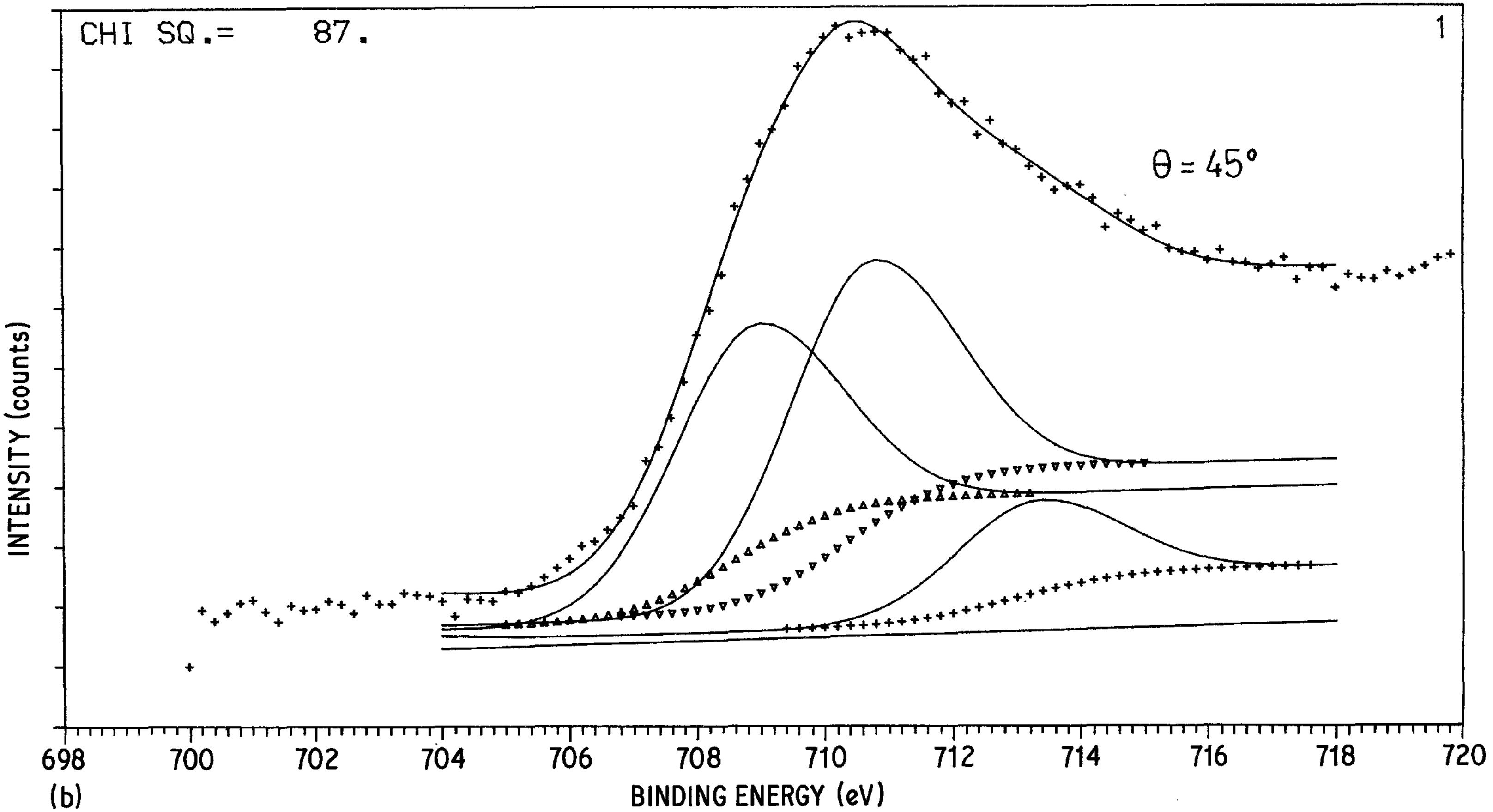


Figure 7 (a) High resolution XPS spectrum of a α-Fe_2O_3 standard together with the Fe2p3/2 region after stoving polybutadiene on the oxide in an inert atmosphere. Dotted line is the spectrum of the standard, θ the photoelectron take-off angle. (b) and (c) deconvolution of two of the Fe2p3/2 spectra from Fig. 7a. Components are (L to R) iron (II), iron (III), satellite contribution.



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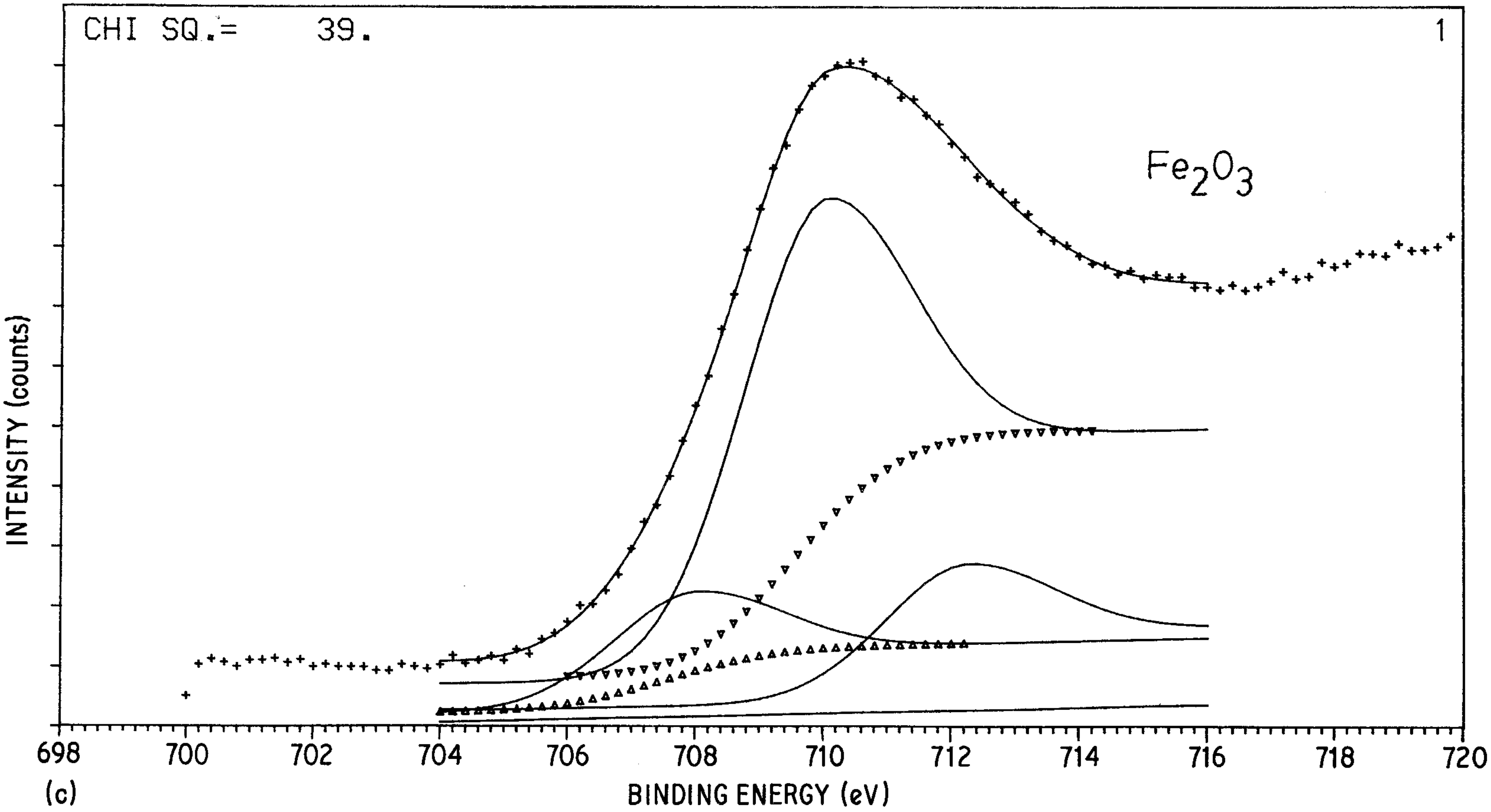

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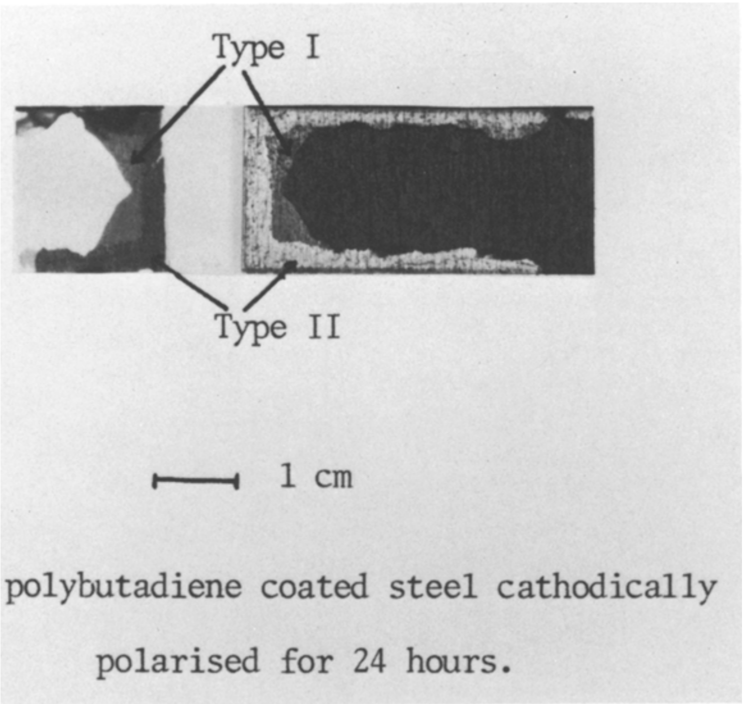

Figure 8 Cathodically polarized strip specimen showing Type I and Type II failure.

and stoved twice to give an effective thickness of 34 μm. The electrolyte employed was a 0.52 M NaCl solution.

3.2. Results

Tests were carried out on cathodically protected panels (− 1500 mV vs SCE) and panels at rest potential for 10 and 15 days. For the cathodically polarized panel exposed to saline solution for 10 days a disbondment zone could be visually identified by blistering over several square centimetres and had approached the electrolyte ring locally; the polymer could be lifted using a scalpel. This was Type II failure. The area between the disbondment front and the electrolyte ring was weakly adhering and could be removed using self-adhesive tape: this was Type I failure. In the case of the 15 day specimen the complete area enclosed by the electrolyte ring failed by Type II disbondment. For the panel at rest potential exposed for 10 days there was evidence of rusting at the defect and the disbondment front had advanced only 1 mm. The area of intact polymer again could be removed with self-adhesive tape. Specimens were cut from the test panels, and the polymer film, for XPS analysis, the results of these analyses and specimen identification information are presented in Table III. Fig. 10 shows representative survey spectra illustrating the dramatic difference in carbon and iron levels from the Type I and the Type II failure regions of the 10 day cathodically polarized specimen. Examination of the surface compositions for the substrate surfaces shows a clear difference between those removed from a disbonded region (Type II failure) which shows a high level of oxygen and iron and a low level of carbon (Fig. 10a), whilst those from which the polymer has been peeled (Type I failure) show a much higher level of carbon attenuating the oxygen and iron components (Fig. 10b). This high level of carbon is characteristic of the Type I failure described in Table II.

TABLE II XPS analysis of strip specimen immersed in saline solution following coating removal after Type I failure

	(At %)				
	C	O	Fe	Na	Cl
Substrate	62.6	28.3	1.2	5.8	2.0
Underside of coating	70.8	20.5	0	6.8	1.9

High resolution iron and oxygen spectra are shown in Fig. 11 for selected specimens. The O1s spectrum for a Type I failure (Fig. 11b) is broader than that observed from the Type II regions: this can be attributed to the presence of molecular water, and accounts for some 15% of the total oxygen signal. Since the film was removed after

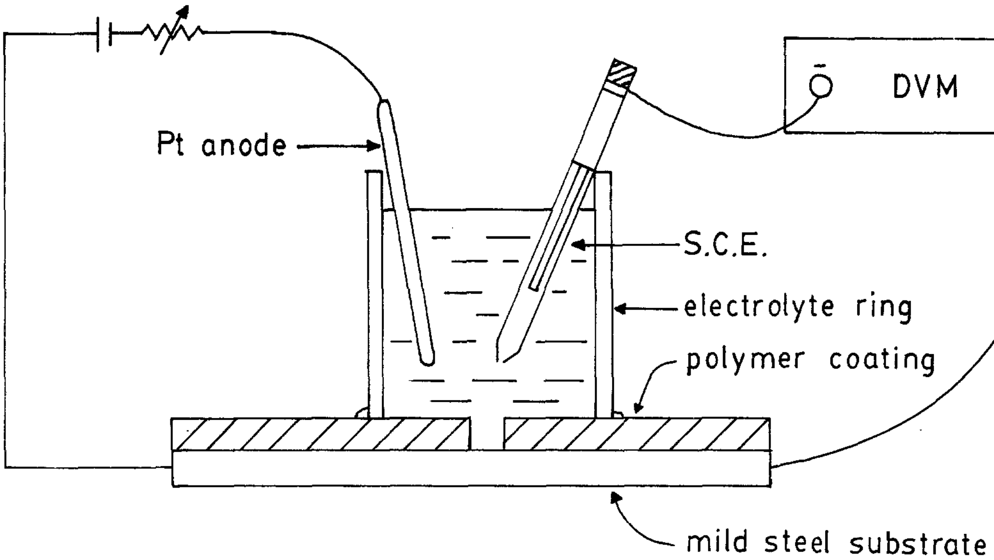

Figure 9 Schematic diagram of cathodic disbondment test.

the sample had been kept in a vacuum desiccator for a short time, the lack of water on the exposed Type II surface is not surprising. However the water on the Type I surface does show that water has access to this interface during the course of saline exposure.

The levels of iron on both specimens taken from within the disbonded zone of the 10 day specimen are similar but inspection of the Fe2p3/2 spectra shows the presence of metallic iron close to the disbondment front (Fig. 11d), indicating some reduction of the oxide under the coating during cathodic treatment. Although reduction appears at the disbondment front, it is not apparent near the defect; that is, the area which was first disbonded, indicating that oxide growth has occurred as the disbondment front moves outwards.

More important, possibly, than the question of oxide reduction is the fact that the levels of organic carbon remaining on the substrates within the disbonded region (Type II failure) are remarkably low. The low level does not result directly from the application of cathodic protection as is shown by the results presented in Table IV for uncoated mild steel surfaces. These analyses were obtained

TABLE III Identification and surface analyses of specimens from disbondment experiments

Code	Time (days)	Potential (mV)	Interfacial surface	Position	(At %)					Assignment of failure type
					C	O	Fe	Na	Cl	
D4M1	10	−1500	Metal	near defect	35.6	47.1	6.5	7.7	3.1	Type II
D4M2	10	−1500	Metal	near limit of disbond	36.7	43.8	6.5	9.2	3.8	Type II
D4M3	10	−1500	Metal	near electrolyte ring*	66.8	27.4	2.2	3.6	Tr	Type I
D5M1	10	FCP	Metal	near defect*	63.4	28.7	Tr	6.7	1.3	Type I
D5M2	10	FCP	Metal	near electrolyte ring*	58.0	30.8	1.0	7.4	2.9	Type I
D30M1	15	−1500	Metal	near defect	48.6	42.6	1.3	5.4	2.1	Type II
D30P1	15	−1500	Polymer	near defect	61.5	30.4	0.4	5.5	2.2	Type II
D30M1	15	−1500	Metal	near limit of disbond	48.4	43.6	3.9	3.4	0.7	Type II
D30P2	15	−1500	Polymer	near limit of disbond	61.0	31.7	1.0	6.0	0.4	Type II

* not disbonded, Tr – trace, FCP – Free Corrosion Potential.

by XPS from coupons of the steel prepared by emery abrasion or alkali cleaning [3], and immersed in a 0.52 M NaCl at − 1500 mV vs SCE for 30 h. Comparison with unexposed controls show that organic contamination is in the range 50 to 60% as is usual for surfaces that have been exposed to an aqueous phase.

Clearly then, during cathodic disbondment a total separation of the organic phase takes place. The increased level of carbon after cathodic treatment of the emery abraded specimen is analogous to the slightly higher levels of carbon observed on the substrate surface after the 15 day test. It seems likely, therefore, that after delamination the freshly exposed, clean surface, readsorbs carbonaceous contaminants from the test solution.

The underside of the polymer (D30P1, D30P2, Table III) shows a small amount of iron, seemingly associated with a visible darkening of the polymer (Fig. 8). These surface analyses are quantitatively very similar to those of the metal substrates remaining after Type I failure (D4M3, D5M1, D5M2 of Table III); this provides an important point to the location of the interphase zone following delamination which is returned to in the discussion.

The sodium level is high both in the Type II an and Type I zones indicating that cathodic conditions prevail for both types of failure.

3.3. Film stripping

To gain an insight into the initial stages of cathodic disbondment an alkali cleaned, coated panel was polarized cathodically for three hours, when the disbondment front was estimated to have advanced (≃ 1/2 mm). The area around the defect was stripped using the iodine/methanol technique, and the duplex film examined from the oxide side by scanning electron microscopy. A halo around the defect is apparent at low magnification (Fig. 12) and this corresponds to the disbondment zone. At higher magnification elliptical regions are seen, Fig. 13; these are due to areas of localized oxide reduction distributed randomly within the disbondment zone.

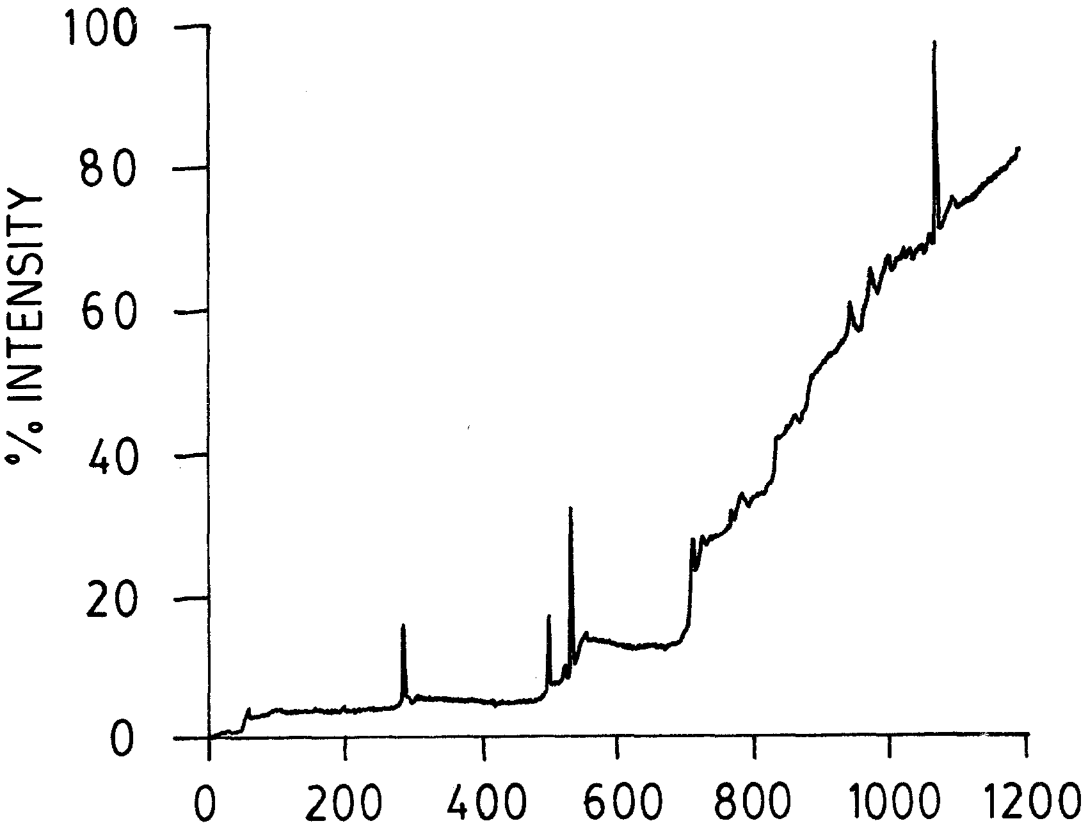

Figure 10 XPS survey spectra of substrate surfaces of (a) Type II failure (D4M2), and (b) Type I failure (D5M2).

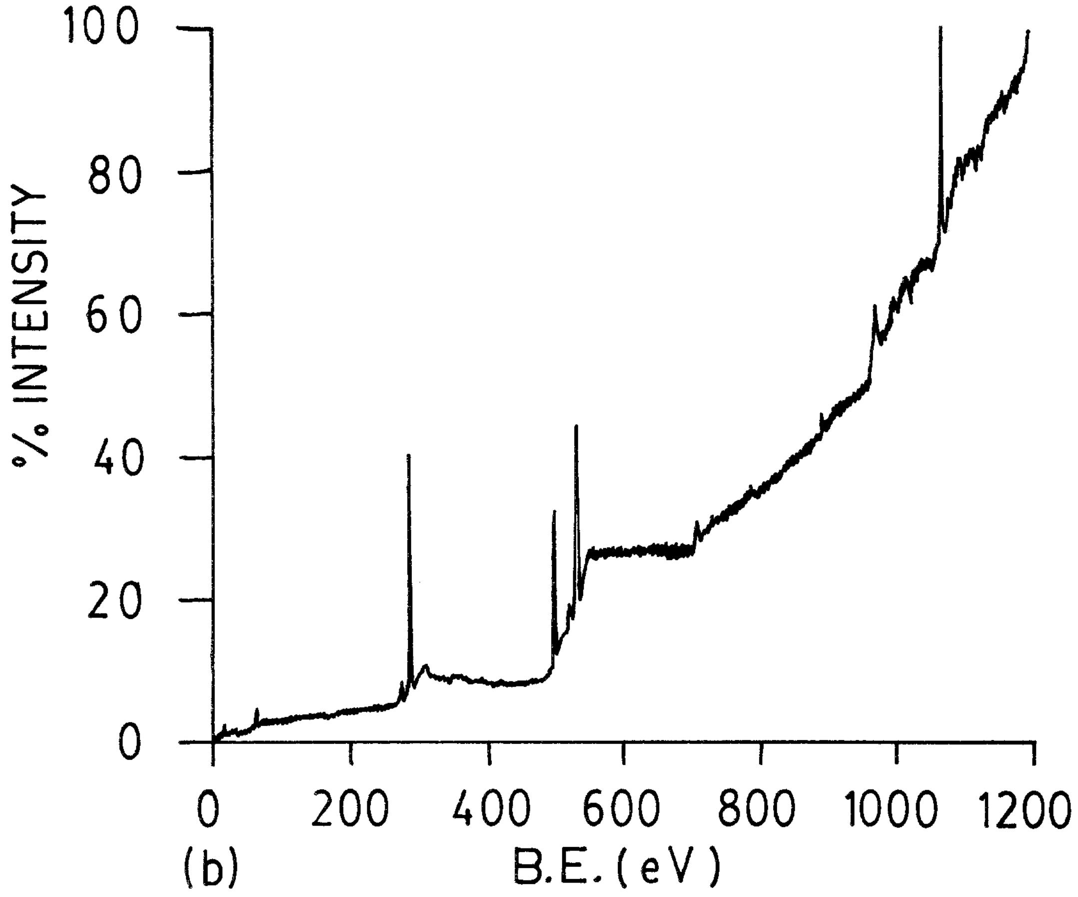

Figure 10 Continued.

The fact that the oxide is only reduced in localized patches indicates that oxide reduction is not a necessary pre-cursor for cathodic disbondment to occur, but may occur after disbondment has taken place as a result of a high pH generated at the edge of the disbondment crevice. The XPS results (Section 3.2) indicate a thickening of the oxide once disbondment has been accomplished.

4. Discussion

The cohesive failure of the polybutadiene steel couple by shear loading indicates a well made joint, that is, one in which there is no barrier to adherend/adherate interaction which may act as a path of least resistance for failure. Bikerman refers to such zones as weak boundary layers (WBLs) [15]. The cohesive failure of such an interface can be predicted from surface free energy concepts [16], however such calculations are only pertinent to systems where adhesion is attributed to dispersion or van de Waals forces. In the case of polybutadiene on steel it is apparent that the highly stable nature of the interphase region is due to direct chemical bonding between the two materials.

Using XPS it has been shown that this interphase region is recognised by the appearance of divalent iron in the spectrum, seen both as a broadening on the low binding energy side of the peak and a "filling-in" on the high binding energy side due to the Fe^{2+} satellite, as observed on studies of oxide standards [17]. This has been observed both when the interphase is approached through the oxide, and when it is observed directly after incomplete crosslinking of the polymer. The inability to remove all the polymer after the latter experiment lends further credance to the notion of an interphase zone formed by the reaction between the two components.

Studies by infrared spectroscopy have shown that crosslinking of polybutadiene resins occurs by an oxidative mechanism [13, 14]. This process will also lead to the reduction of the trivalent iron at the substrate/coating interface and bring about the formation of a well defined chemical boundary

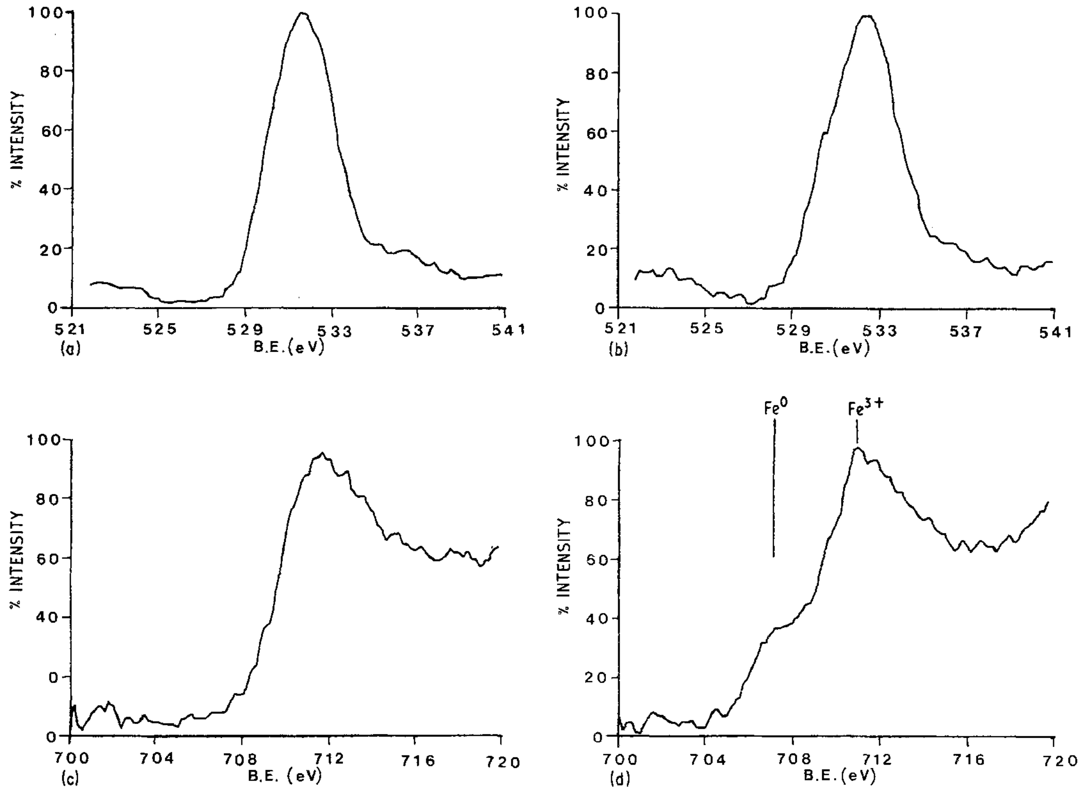

Figure 11 High resolution XPS spectra of (a) Type II failure, O1s, (b) Type I failure, O1s, (c) Type II failure, Fe2p3/2, (d) Type II failure, close to disbondment front, Fe2p3/2.

layer, analogous to that encountered with silane adhesion promoters, employed in some coatings applications. Although it has not been possible to completely define the chemistry of this interphase compound, the most characteristic feature is the presence of ferrous iron. It is envisaged that in its simplest form the interphase will consist of an aliphatic iron salt such as an iron carboxylate (FeCOOR).

Although when polybutadiene is mechanically delaminated from a steel surface the failure is clearly cohesive with a considerable overlayer of polymer remaining on the steel surface, the situation is rather more complex when failure is brought about by cathodic polarization. In this case two types of failure are observed which can be identified both visually and spectroscopically.

In the zone nearest to the exposed metal on the cathodically polarized panels the failure is described as Type II. Here there is complete segregation between the organic material and the metal oxide surface. The polymer surface from this disbondment zone shows a small amount of iron and it is concluded that the interphase zone remains attached to the polymer film. This conclusion is reinforced by the finding that the surface composition of the polymer specimen from the Type II failure region is very similar to the composition of the substrate surfaces of the Type I failure, both showing the low levels of iron which are associated with the interphase material. The

TABLE IV Contamination levels on mild steel before and after cathodic protection

Pre-treatment	Cathodic protection	(at %)				
		C	O	Fe	Na	Cl
Emery	No	31.1	53.1	15.8	0	0
Emery	Yes	51.3	39.6	8.4	0.05	0.6
Alkali clean	No	63.5	34.2	2.1	0	0
Alkali clean	Yes	59.6	36.2	3.8	0.03	0.4

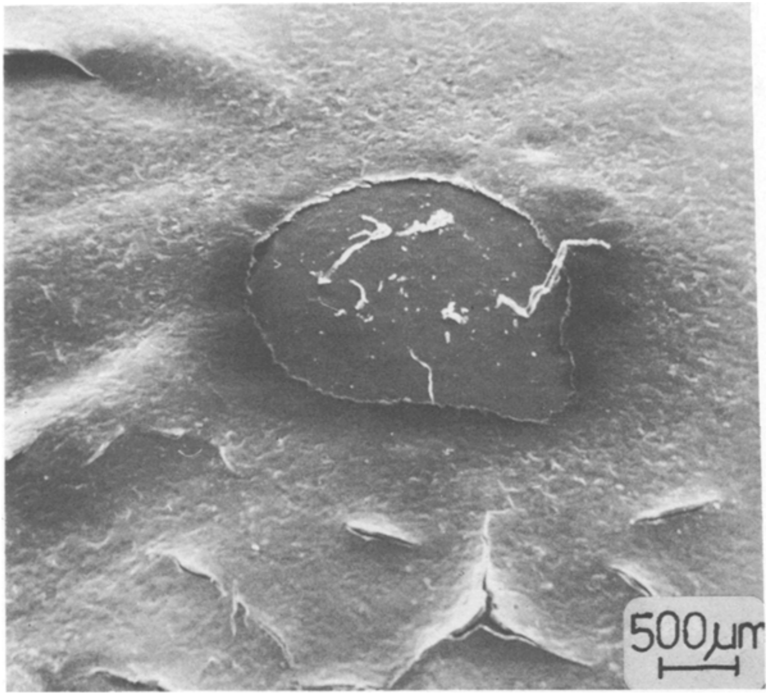

Figure 12 Scanning electron micrograph of stripped oxide/polymer film showing disbondment halo.

absence of iron on the polymer surface of the Type I failure (Table III) indicates that the interphase zone remains adhering to the substrate while the near interphase polymer is attacked and weakened sufficiently to render peeling back of the coating a simple matter. Thus the interphase zone appears to segregate either to the polymer surface (Type II) or to the metal substrate (Type I) depending on the mechanism of failure.

Both types of failure are associated with the

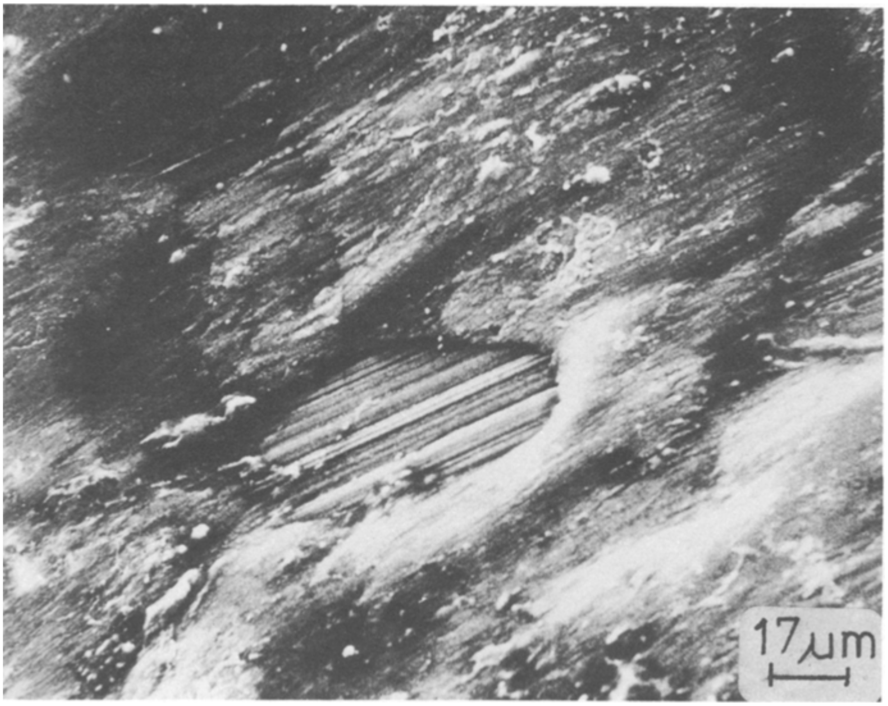

Figure 13 Scanning electron micrograph showing elliptical region of reduced oxide in disbondment halo.

underfilm alkalinity confirmed by the excess of sodium ions over chloride since in the exposure of unpolarized, oxidized steel to sodium chloride solution it is usual to record an excess of chloride ions [18].

The clean metal surface characteristic of the Type II failure is the result of the attack of the interphase region adjacent to the metal oxide. The pH reached at the edge of the disbondment zone is certainly high enough for hydrolysis of the FeCOOR salt proposed. The pH at the edge of the disbondment crevice may be even higher since the reduction of iron oxide occurs in this vicinity. Thermodynamic considerations predict oxide reduction at a pH greater than about 13.5 [19] and values of this order have been recorded using underfilm pH probes on model systems [20, 21]. Away from the disbondment front the pH is probably lower since oxide film thickening takes place in this region, as illustrated by the lack of metallic iron in the spectrum from the near defect surface of the ten day exposure panel, and both specimens of the fifteen day test panel. The sodium ion concentration is then similar to that found in Type I failure and it seems likely that this failure mode occurs at a lower pH value than does Type II.

The two zones of alkalinity associated with Type I and Type II failure may, in fact, result from different diffusion paths for the sodium ion. Type I failure occurring as a result of downward diffusion of the cation via conducting pathways in the film, (as described by Leidhesier and Kendig [5]) reaching the interphase zone but not penetrating it, and weakening the near interphase polymer by a build up of sodium and hydroxyl ions at this point. For the Type II failure lateral diffusion of the ions can take place from the initiating defect and are able to attack the interphase zone directly leading to failure at the oxide/interphase region, the resulting metal surface being very clean and relatively free of organics, the interphase zone segregating with the polymer.

For the specimens at rest potential considerable rusting is seen at the exposed metal; this region being anodic to the coated metal surface. As the Type II disbondment proceeds, (which it does only slowly; approx 1 mm in 10 days), the area of the anode is increased and rusting becomes evident even under the polymer film. This aspect of cathodic disbondment has been illustrated by other investigators visually, and by using electrical measurements [5].

It is relevant at this point to compare the results of this investigation with that of other workers who have studied the same resin/substrate system. By far the most extensive investigations have been carried out by Leidheiser and co-workers. Initially they were concerned with permeation of the coating by water and ionic species and using an impedance technique developed a comprehensive model of coatings failure in terms of the developement of surface anodic (rusting) and cathodic (blistering) sites [4, 5]. They propose attack of the polymer due to high pH levels at the cathodic sites and we have been able to show directly that the alkalinity at the interface makes an important contribution to the durability and mode of failure of the coating/substrate bond. The question of bond disruption has been more recently investigated for cathodically polarized systems [7, 8] and the authors tentatively propose failure at the coating/substrate interface: the Type II failure reported in the present study.

XPS has been employed by other workers to define the locus of failure of cathodically polarized polybutadiene on steel [14]. These authors showed evidence of a cohesive failure of the coating, close to, but not at, the metal oxide surface, once again an excess of alkali cations in the surface assay indicating that underfilm cathodic conditions prevail. This is the failure mode designated Type I in the present work. Evidence of the presence of a reacted zone separating the loci of failure by Type I and Type II modes has been obtained by a model study in which emission Mössbauer spectroscopy was used to study polybutadiene on cobalt. This showed that a significant amount of interfacial Co(III) was converted to Co(II) by the process of stoving at 200° C in air [22], and is in complete accord with our findings.

5. Conclusions

When polybutadiene bonds to mild steel it does so by the formation of a discrete chemical interphase region identified by the presence of divalent iron in the XPS spectrum. The formation of this zone is associated with the role of polybutadiene as a reducing agent for iron oxide.

If fracture of the polybutadiene/steel system is brought about by mechanical loading the failure is cohesive, a considerable overlayer (in surface analysis terms) of polymer remaining on the metal surface.

When the coated steel is exposed to saline solution the rate of delamination is slow and the exposed metal is anodic to the coated substrate. Notwithstanding this the adhering polymer is severely weakened by the underfilm alkalinity and can be peeled back leaving a residue of polymer on the substrate surface. This is Type I failure, the near interphase polymer is attacked but on peeling back the polymer the interphase zone remains adhering to the substrate.

In the case of cathodically polarized panels a two stage failure process is observed. Delamination is rapid and can be visually identified by blister formation. Outside this region the near interphase polymer is weakened as described above. Within the disbondment zone Type II failure is observed in which the interphase zone itself is attacked. The exposed metal surface is very clean, metallic iron is present in the spectrum due to oxide reduction and the interphase zone segregates with the polymer coating.

Oxide reduction takes place at the advancing edge of the disbondment crevice, but the random nature of this process makes it unlikely to be an important factor when considering cathodic disbondment of this system. As the disbondment front advances, so oxide thickening takes place.

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