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Interaction of diethanolamine with non-rinse chromate treated steel surfaces

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The interactions between diethanolamine (DEA), which is used as a model of an amine cured epoxy resin, and non-rinse chromate treated steel substrates have been investigated by X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS). The saturation coverages of DEA, as determined by XPS adsorption isotherms, were as follows: chromate surface > chromate + colloidal SiO_2 surface > silica surface. The chromate + SiO_2 surface has less capacity for DEA, because its surface is rich in silica and strongly affected by the adsorption characteristics of this material. Three specific interactions between both chromate treated steel surfaces and DEA are proposed on the basis of the XPS and ToF-SIMS data: (i) Brönsted acid–base interaction between the amine of DEA and the hydroxyl functionality of the chromate surface by proton transfer from the OH to the amine, (ii) Lewis acid–base interaction between the amine of DEA and CrO_4^- and/or silanol groups, (iii) dehydration reaction between the alcohol group of DEA and the hydroxyl functionality of the chromate surface.

Introduction

In recent years the use of non-rinse chromate treatments for sheet steel has increased as a method of pre-treatment prior to the application of organic coatings. These pre-treatments are used because they give good adhesion and durability in wet and humid environments. In addition, several variations of non-rinse chromate pretreatments have been developed that give a much higher level of performance. Such variations include the addition of colloidal silica or phosphoric acid. Although the performance and structure of non-rinse chromate pre-treatments have been investigated,[1–3] the interactions between organic coatings and non-rinse chromate pre-treated substrates have yet to be fully investigated. The aim of this paper is to study the specific interactions that occur between a small organic molecule, chosen as an analogue of an amine cured epoxy resin coating or adhesive, and steel treated with two types of chromate coating.

X-Ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS) are valuable tools for the study of the interfacial chemistry of adhesion.[4–7] Several studies[8–14] have investigated interactions of organic resins with inorganic substrates, and it has been shown that acid–base interactions make an important contribution to the forces of adhesion. However, due to the complex nature of commercial resins such as amine cured epoxies, investigation of their interfacial reactions is often difficult. Therefore, most studies have investigated the adsorption of small molecule analogues of the resin using surface analysis methods. Amine cured epoxy resins have characteristic linkages of the type $RR'N–CH_2–CH(OH)R''$.[9] Affrossman *et al.*[15] have used XPS and ToF-SIMS to investigate the interaction between a model compound, an adduct of *n*-propylamine and 1,2-epoxybutane, as an analogue of the more complex $RR'N–CH_2–CH(OH)R''$ molecule, and oxidised and phosphoric acid anodised aluminium substrates.[10] This study suggested that bonding of two types was present at the interface, interactions between the hydroxyl functionality in the substrate and the alcohol group of the model resin, and Brönsted acid–base interactions between the amine group and the hydroxyl functionality. Marsh *et al.*[12] reported an interaction between 1,2-diaminoethane and titanium surfaces. The amine functionality interacts with the hydroxyl functionality of the titanium surface by both Brönsted and Lewis acid–base interactions. These studies provide important indications of the exact nature of interfacial bonds that are responsible for adhesion.

The adsorption of gas or liquid phase species on solid surfaces is conveniently studied by the construction of adsorption isotherms. In the case of liquid phase adsorption, which is directly relevant to adhesion studies, it has been shown that the determination of such isotherms by measuring the amount of material retained, measured by a surface analysis technique such as XPS or ToF-SIMS has much to commend it.[16] It is this approach that will be used in the current work to assess the capacity of different surfaces for a molecule with the same characteristic groups as an amine cured epoxy. XPS and ToF-SIMS will also be used to provide an indication of the nature of the interfacial bonding responsible for the adsorption of these molecules.

The strength of the interaction responsible for adhesion between an organic phase and an inorganic substrate has been explored by Bolger[17] for the case of Brönsted acid–base interactions. He defined a delta parameter:

$$\Delta = \mathrm{IEPS}_{(B)} - \mathrm{p}K_{a(A)} \text{ or } \mathrm{p}K_{a(B)} - \mathrm{IEPS}_{(A)}$$

where IEPS is the isoelectric point of the inorganic substrate, and pK_a is the acid ionisation constant of the polymer. If Δ is negative and large, this indicates that acid–base interactions are negligible. If Δ is large and positive, strong acid–base interactions are likely to exist.

In a recent publication it was shown that that the addition of colloidal SiO_2 to the pre-treatment bath led to the inclusion of the SiO_2 phase within the chromate conversion coating.[3] Both chromate and chromate + SiO_2 coatings were shown, by XPS, to contain a mixture of trivalent and hexavalent chromium: a value of Cr^{6+}/Cr^{3+} of 0.745 was recorded for the chromated surface compared with 0.353 for the chromate + SiO_2 treatment.[3] The adsorption of the two components of a typical epoxy resin, Shell Epikote 828 and an amine curing agent, on these two substrates was studied and it was shown that the capacity of the silica modified surface was greater for both components. This observation was correlated to the adhesion and cathodic delamination resistance of the two systems, the chromate + SiO_2 surface being superior in both respects.[3] In the current work the more fundamental aspects of the adhesion of epoxy resins to the two substrate materials are explored. Diethanolamine (DEA) was employed as an analogue of amine cured epoxy, the adsorption of this

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material, both in terms of the capacity of the solid surfaces for the molecule and identification of the bonds formed, was investigated using XPS and ToF-SIMS.

Experimental

Sample preparation

The non-rinse chromate solution was prepared by adding 0.25 mol ethylene glycol to a 1 mol l^{-1} chromium trioxide solution. The concentration of chromium trioxide was adjusted to 2 wt%. The ethylene glycol acts as a reducing agent, and therefore, the chromate solution was a mixture of hexavalent and trivalent chromium (Cr^{3+}/total Cr = 0.35). The non-rinse chromate–silica solution was prepared by the addition of colloidal silica, (atomic ratio of Si/Cr = 1.4), to the standard solution. In the case of the chromate + SiO_2 treatment, 0.28 mol of SiO_2 was added to 1 mol of the standard solution to give a Si/Cr ratio of 1.4.

The cold rolled steel substrate, 0.8 mm thick, was degreased by dipping in a mild alkaline solution followed by water rinsing. After degreasing the substrate was coated with chromate solution using a roll coater, which resulted in a coating weight of 150 mg Cr m^{-2}. The pre-treated substrates were then oven dried at 140 °C for 3 min. 10 mm diameter discs were punched from the pre-treated steel substrates, to be used in the adsorption study. The silicon substrates were washed in toluene prior to the adsorption study.

Solutions of diethanolamine in ethanol were prepared with concentrations in the range of 0.05–5.0 mol l^{-1}. The adsorption characteristics, as a function of DEA solution concentration, were studied by exposing a coupon of the substrate material to the appropriate solution for 3 h. On removal from solution the sample was washed in ethanol and mounted for analysis by XPS. Adsorption isotherms were constructed from the XPS data by plotting the uptake of DEA (as surface concentration of nitrogen in atom%) as a function of solution concentration. Replicate samples exposed to DEA solutions of 2 mol l^{-1} were examined by ToF-SIMS.

An oxidised silicon wafer was used to assess the capacity of the colloidal silica particles, present in the chromate + SiO_2 pre-treatment for DEA.

Table 1 Surface composition, determined by XPS, of steel treated with chromate solutions

	Surface composition (atom%)				
Treatment solution	C	O	Cr	Si	Cr^{6+}/Cr^{3+}
Chromate	35.0	52.6	12.3	0.0	0.745
Chromate + SiO_2	24.6	52.2	3.5	19.7	0.353

Surface analysis

X-Ray photoelectron spectra were recording by using a VG Scientific ESCALAB Mk II spectrometer using Al-Kα radiation. The analyser was operated in the constant analyser transmission mode at a pass energy of 50 eV for the survey spectra and at 20 eV for high resolution spectra of the core levels of interest. The electron take off angle relative to the sample surface was 45° for all spectra recorded. Quantification and curve fitting, based on the high resolution spectra, was carried out using a VGS 5000S data system based on a DEC PDP 11/73 computer.

ToF-SIMS spectra were acquired using VG Scientific Type 23 system, which is equipped with a two-stage reflectron time of flight analyser and a MIG300PB pulsed liquid metal ion source. Static SIMS conditions were employed using a pulsed 26 keV $^{69}Ga^+$ primary ion beam, rastered over an area of 0.5 × 0.5 mm at 50 frames s^{-1}. Spectra were acquired over a mass range of *m/z* 1–800 in both positive and negative ion modes.

Results and discussion

The XPS spectra acquired from the steel substrates pre-treated with the chromate and chromate + SiO_2 indicated the presence of chromium, oxygen and carbon at the surface. Examination of the chromium core level spectra showed that the chromium consisted of Cr^{3+} and Cr^{6+}. The XPS spectra acquired from the chromate + SiO_2 pre-treated steel also detected silicon. Iron was not detected in any of the pre-treated substrates, which indicates that the chromate and chromate + SiO_2 conversion coatings were continuous and thicker than the analysis depth of XPS (to be expected from a coating weight of 150 mg

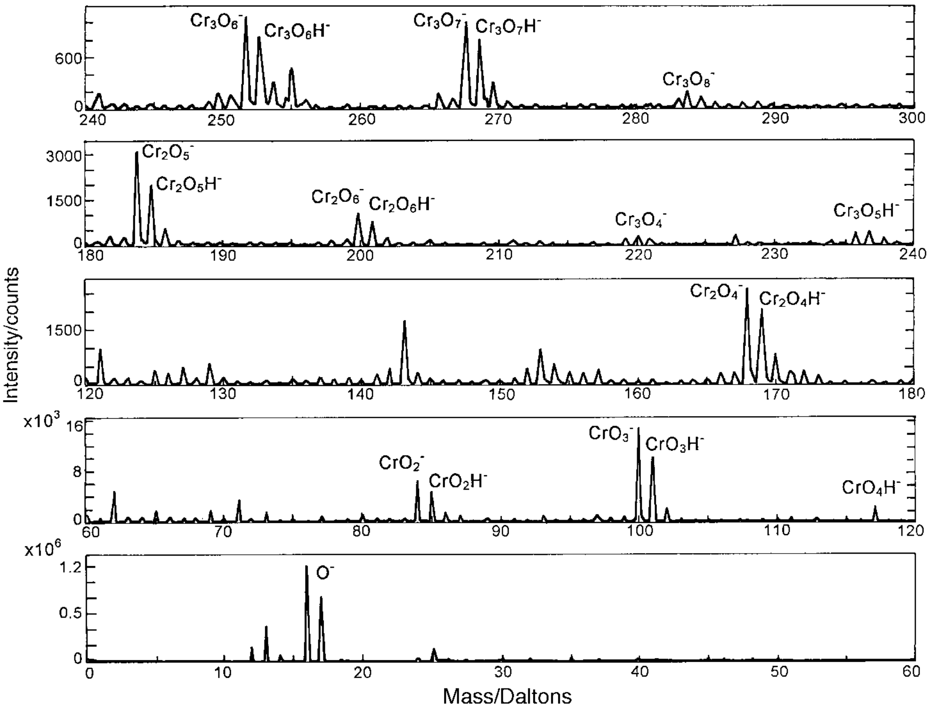


Fig. 1 Negative ToF-SIMS spectrum of chromate treated steel surface.

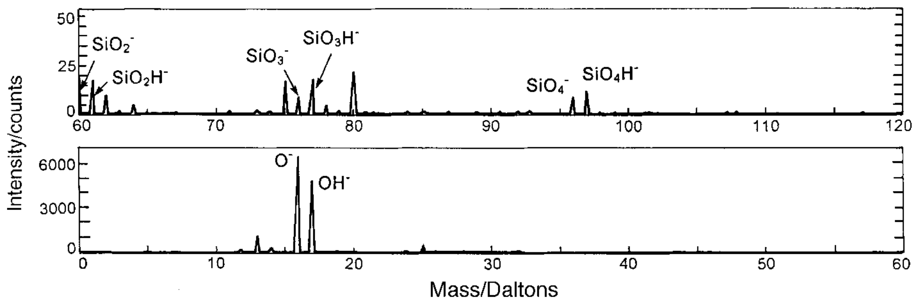


Fig. 2 Negative ToF-SIMS spectrum of oxidised silicon wafer surface.

Cr m^{-2}). The XPS spectra from samples treated in this manner have been discussed in detail elsewhere.[3] The surface compositions of chromate and chromate + SiO_2 pre-treated substrates are presented in Table 1. The Cr/Si atomic ratio from the chromate + SiO_2 pre-treated sample is 5.7 (see Table 1), whereas the Cr/Si atomic ratio of the chromate + SiO_2 solution was 1.4, indicating that the surface of the substrate pre-treated with chromate + SiO_2 is enriched with silicon.

Fig. 1 shows the negative ion ToF-SIMS spectrum of the chromate pre-treated substrate. Ions diagnostic of chromium oxide were observed at $m/z = 84$ and 100, which correspond to CrO_2^- and CrO_3^-, respectively. Ions diagnostic of chromium hydroxide were observed at $m/z = 85$, 101 and 117, corresponding to CrO_2H^-, CrO_3H^-, and CrO_4H^-. This indicates that the chromate pre-treatment forms a conversion coating consisting of chromium oxide and chromium hydroxide. Fig. 2 shows the negative ion ToF-SIMS spectrum of a silicon wafer surface. The ions at $m/z = 60$, 61, 76, and 77 are diagnostic of silicon oxide and silicon hydroxide, SiO_2^-, SiO_2H^-, SiO_3^-, SiO_3H^-, respectively. Fig. 3 shows the negative ion ToF-SIMS spectrum of the chromate + SiO_2 pre-treated substrate. This spectrum contains the ions diagnostic of chromium oxide and hydroxide at $m/z = 84$, 85, 100, 101, and 117, as well as ions diagnostic of silicon oxide and hydroxide at $m/z = 60$, 61, 76, and 77. This shows that the substrate pre-treated with chromate + SiO_2 has a surface consisting of a complex mixture of both silicon and chromium oxides and hydroxide functionalities.

The XPS survey spectra of DEA adsorbed on the chromate and chromate + SiO_2 pre-treated substrates are shown in Fig. 4. The presence of the N 1s peak at approximately 400 eV shows that DEA adsorbed on both surfaces. The amount adsorbed on the oxidised silicon substrate was, however, much lower. Diethanolamine uptake was calculated by using the surface concentration of nitrogen (in atom%) and plotted *versus* solution concentration, which produced the adsorption isotherms shown in Fig. 5. The isotherms in Fig. 5 show that the uptake of DEA varied between the different substrates, and ranked in the following manner: chromate > chromate + SiO_2 > oxidised silicon.

The adsorption of solutes at the solid–liquid interface can often be described by the Langmuir equation. The Langmuir equation assumes that adsorption can not proceed beyond monolayer coverage, that all sites are equivalent, and the ability of a molecule to adsorb onto a given site is independent of the occupation of the neighbouring site. The modified Langmuir equation can be written as follows:

$$\frac{C}{\Gamma}=\frac{1}{b\Gamma_{\mathrm{m}}}+\frac{C}{\Gamma_{\mathrm{m}}}$$

where C is the initial solute concentration (mol l^{-1}), Γ is the uptake measured by XPS (atom%), Γ_m is the saturation coverage of adsorbate on the candidate substrate, and b is a constant. If DEA exhibits Langmuir adsorption a linear relationship should be observed when plotting C/Γ *versus* C. Fig. 6 shows the

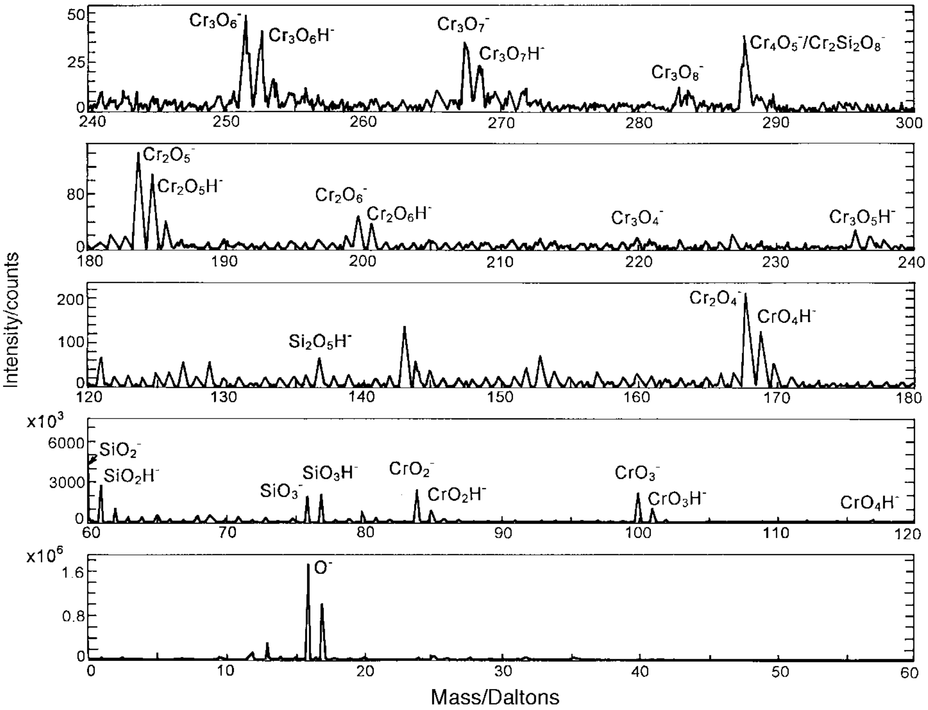


Fig. 3 Negative ToF-SIMS spectrum of chromate + SiO_2 treated steel surface.

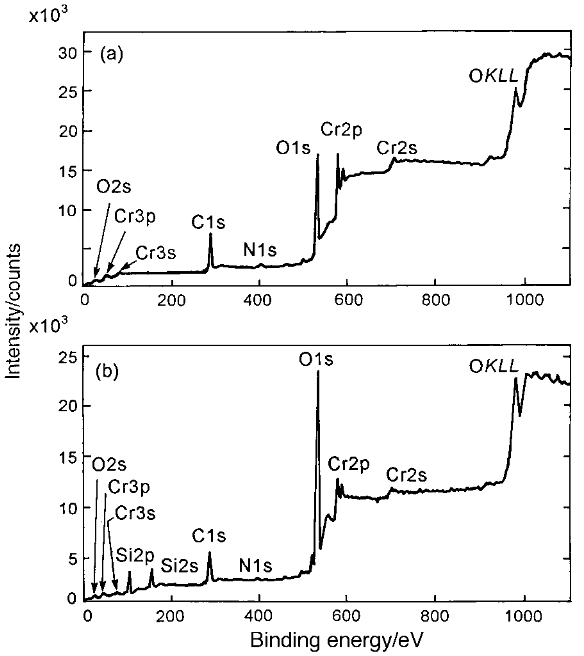


Fig. 4 XPS survey spectra of diethanolamine adsorbed on (a) chromate and (b) chromate + SiO_2 surfaces.

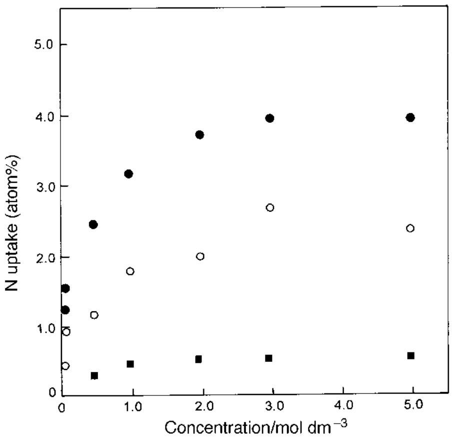


Fig. 5 The adsorption isotherms of diethanolamine on both chromate surfaces and an oxidised silicon wafer surface: (●) chromate surface, (○) chromate + SiO_2 surface, (■) SiO_2 surface.

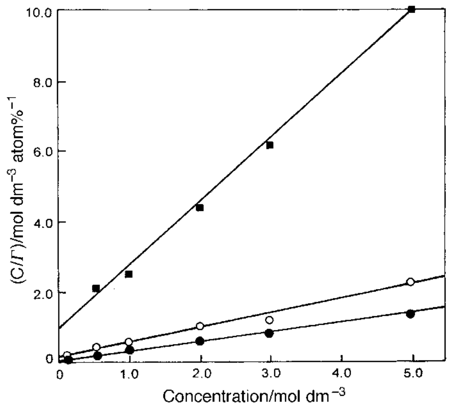


Fig. 6 Langmuir plots for DEA on the three surfaces under investigation: (●) chromate surface, (○) chromate + SiO_2 surface, (■) SiO_2 surface.

Langmuir isotherms for DEA adsorption on the substrates under investigation are linear. The gradient of the Langmuir isotherms is quite simply the reciprocal of Γ_m and thus enables the capacity of the three substrates for DEA to be evaluated. The following values were obtained: $\Gamma_m = 4.1$ for the chromate pre-treated substrate, $\Gamma_m = 2.6$ for chromate + SiO_2, and $\Gamma_m = 0.5$ for oxidised silicon. Thus, the chromate pre-treated substrates have more adsorption sites than the chromate + SiO_2 pre-treated substrates, and oxidised silicon had less sites for adsorption of DEA than either of the chromate pre-treated samples. Thus the capacity of the surfaces for DEA ranks as follows: chromate > chromate + SiO_2 > oxidised silicon.

Fig. 7 and 8 show the positive ion ToF-SIMS spectra of DEA adsorbed on chromate and chromate + SiO_2 substrates compared with the initial surfaces. Ions such as $m/z = 106$ ($HOCH_2CH_2NH_2{}^+CH_2CH_2OH$), $m/z = 88$ ($HOCH_2CH_2$-$NH_2{}^+CH{=}CH_2$) and $m/z = 30$ ($NH_2{}^+{=}CH_2$), confirm the adsorption of DEA on the both chromate surfaces. The $m/z = 106$ fragment is indicative of a Brönsted acid–base interaction at the interface between the amine functionality of DEA and the hydroxyl group of both chromate surfaces, this leads to a protonated species ($M + 1^+$) in the spectrum. This is in contrast to the SIMS spectrum of a thick film of DEA in which the

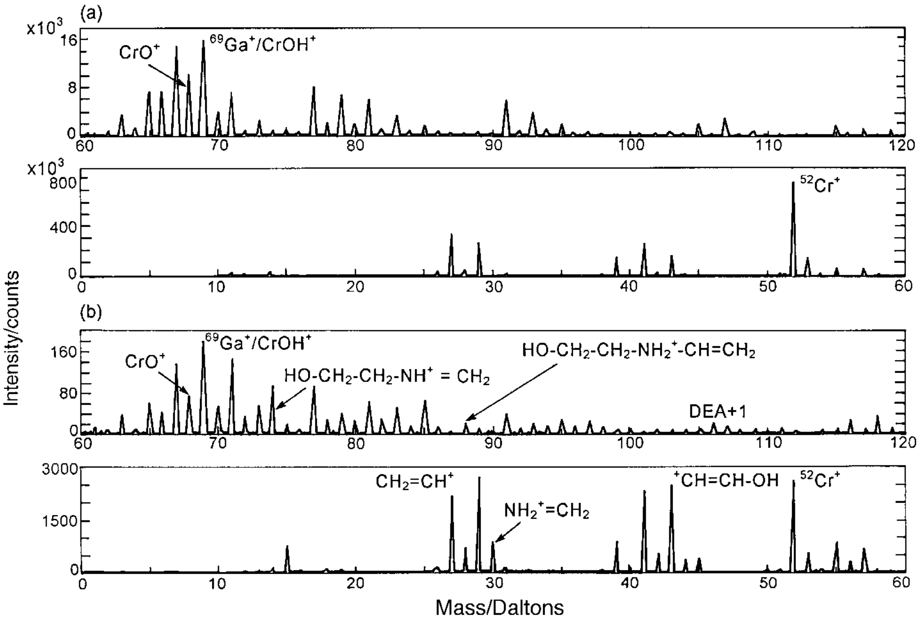


Fig. 7 The positive ToF-SIMS spectra of (a) chromate surface, and (b) diethanolamine adsorbed on the chromate surface from 2 mol l^{-1} solution.

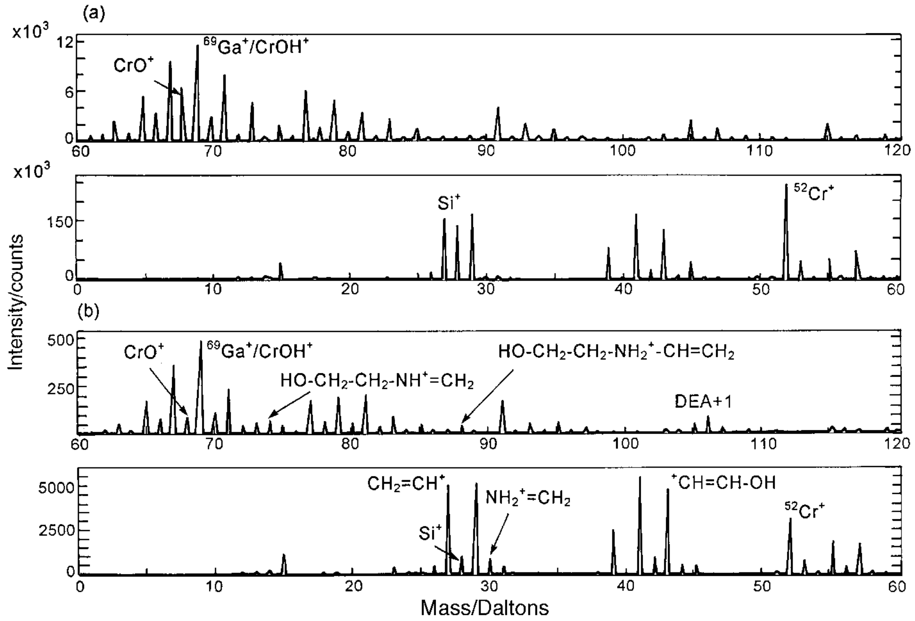
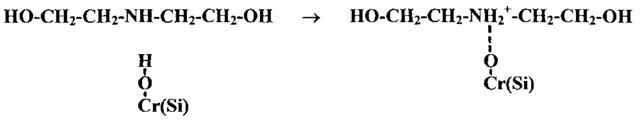


Fig. 8 The positive ion spectra of (a) chromate + SiO_2 surface and (b) diethanolamine adsorbed on the chromate + SiO_2 from 2 mol l^{-1} solution.

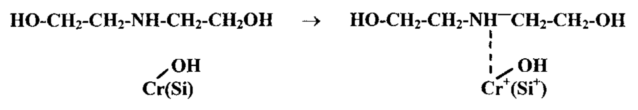
molecular ion ($m/z = 105^+$) is dominant in this region of the spectrum. The interaction leading to the $m/z = 106$ cation is shown schematically in Fig. 9(a). The ion at $m/z = 88$ shows the possibility of the dehydration interaction between the alcohol group of DEA and hydroxyl group of the substrate as shown in Fig. 9(c). These results are strikingly similar to previous work on aluminium and titanium substrates.[11,12] Fig. 10 shows the N 1s high resolution XPS spectrum of DEA adsorbed on the chromate treated substrate, whilst Table 2 shows the peak fitting results of both chromate samples. The N 1s spectrum has two components and it is thought that higher binding energy component is indicative of Brönsted acid–base interaction between hydroxyl functionalities of the chromate and chromate + SiO_2 surfaces and the amine of DEA by proton transfer from the OH group to the amine. The lower binding energy component shows a Lewis acid–base interaction between Cr or Si atoms and the amine group of DEA by electron transfer from Cr or Si atoms (present as chromate ions or silanol groups) to the amine as shown in Fig. 9(b). In this case the amine shows weakly basic behaviour.

Marsh *et al.*[12] reported similar results in their study of the interaction between titanium surface and 1,2-diaminoethane. They concluded that the main interaction is a Brönsted acid–base interaction and that the Lewis acid–base interaction is relatively weak and of secondary importance.

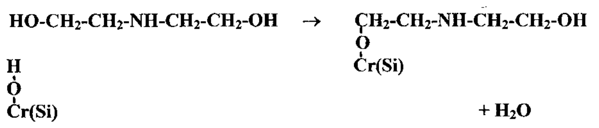
It appears that the reaction between an amine cured epoxy resin and both chromate and chromate + SiO_2 surfaces is almost the same as the interaction with titanium and aluminium surfaces. Fig. 11 shows the positive ToF-SIMS spectrum of DEA adsorbed on oxidised silicon. Fragments such as $m/z = 106$, 88, 30 are observed from DEA adsorbed on this surface. These results are the same as those obtained on both chromate surfaces, and it is thought that the same interactions



(a) Interaction between the amine of DEA and chromate surface as a Brönsted acid-base interaction by transfer of a proton to amine



(b) Interaction between the amine of DEA and chromate surface as a Lewis acid-base interaction by transfer an electron to the amine



(c) Dehydration bonding between an alcohol of DEA and chromate surface

Fig. 9 Proposed interactions of diethanolamine with the chromate layer.

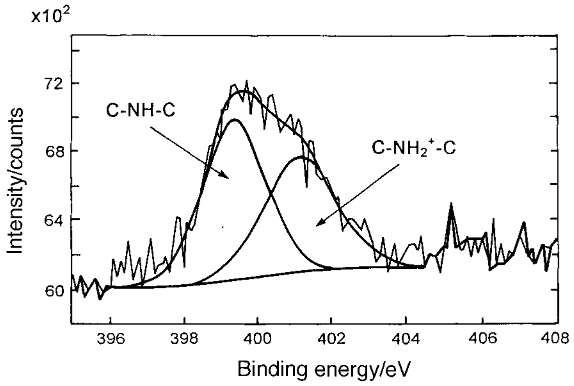


Fig. 10 High resolution XPS N 1s spectrum of diethanolamine adsorbed on the chromate surface from 2 mol l^{-1} solution.

Table 2 Results of peak fitting of N 1s spectra of chromated substrates exposed to a 2 mol dm^{-3} solution of diethanolamine

Treatment solution	Assignment	Binding energy/eV	N 1s Intensity (%)
Chromate	C–NH–C	399.8	65
Chromate	C–NH_2^+–C	401.5	35
Chromate + SiO_2	C–NH–C	399.8	50
Chromate + SiO_2	C–NH_2^+–C	401.5	50

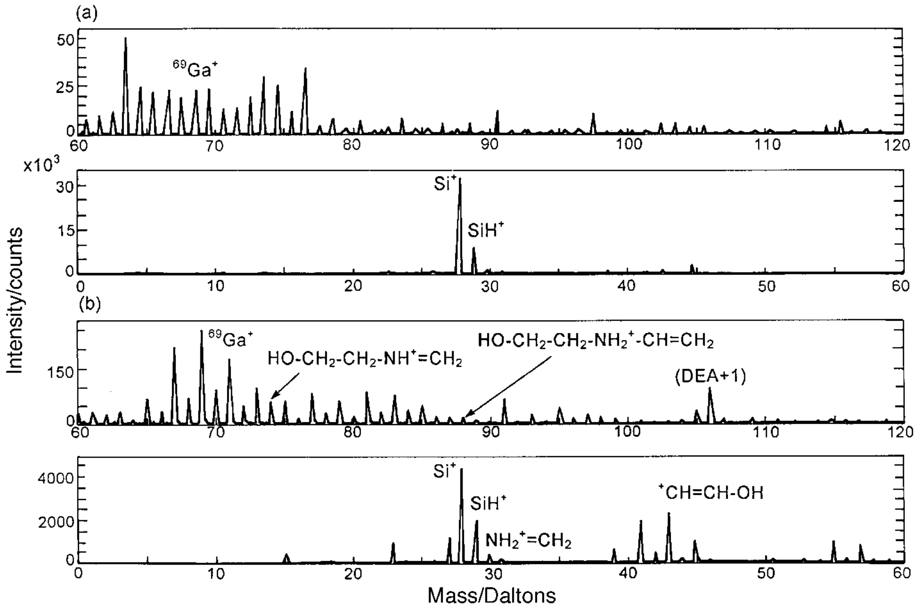


Fig. 11 The positive ion ToF-SIMS spectrum of (a) oxidised silicon wafer surface and (b) diethanolamine adsorbed on the substrate from 2 mol l^{-1} solution.

occur. These surfaces have rather different acid–base properties, however. Data is not available for chromate treated steel or CrO_3, although the isoelectric point (IEPS) of chromium oxide (Cr_2O_3) is reported as ≈ 7 indicating a neutral, and perhaps amphoteric surface. The IEPS of SiO_2 is in the range 1.5–2.0 which shows strongly acid properties as a result of the presence of surface silanol groups. The ionisation constant (pK_a) of DEA is reported as ≈ 11. So, the strength of acid–base interaction between the acidic amine and the substrate components, based on Bolger's equation, are as follows:

$$\Delta_{(\text{DEA and chromium oxide})}=4,\ \Delta_{(\text{DEA and SiO}_2)}=9.$$

Acid–base interaction between SiO_2 and the amine is stronger than that between chromium oxide and the amine. Therefore, although the chromate + SiO_2 surface has less adsorption sites than the chromate surface, the bonds between the substrate and the DEA molecules are stronger. This observation is completely consistent with the observed durability of epoxy coatings on the two chromate pre-treatments.[3] This provides an excellent example of the two features that are important in the design of durable interfaces; not only the number of bonds that can, potentially, be formed but also the strength of the specific interactions formed at the interface.

Conclusions

In this study, XPS and ToF-SIMS were used in order to investigate the interaction between both chromate and chromate + SiO_2 surfaces and diethanolamine, which was employed as a model of an amine cured epoxy resin. On the basis of XPS adsorption isotherms of DEA on both chromate substrates and an oxidised silicon substrate, the capacity of the three surfaces ranks as follows:

$$\text{chromate surface} > \text{chromate} + SiO_2 \text{ surface} > SiO_2 \text{ surface}$$

The chromate + SiO_2 surface has a lower aeric density of adsorption sites for DEA than the plain chromate treatment because its surface is rich in SiO_2 and strongly affected by the adsorption characteristics of this material, which has about an eighth of the capacity of the chromate surface for DEA.

There are three kinds of interaction at the adsorption interface between non-rinse chromate surfaces and diethanolamine, which can be identified as follows: (i) A Brönsted acid–base interaction between amine groups of DEA and hydroxyl groups of the chromate surface by proton transfer from the OH group to the amine of DEA. (ii) A Lewis acid–base interaction between the amine of DEA and Cr or Si atoms by electron transfer to the amine functionality of DEA. (iii) A dehydration reaction between the alcohol groups of DEA and the OH functionalities of the chromate surface.

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