Paint by numbers

by Tom von Moltke, Roelf Sandenbergh and Pheladi Mohlala

Poor and acceptable paint adhesion is often experienced on steel substrates produced under seemingly identical industrial conditions. This problem recently caused havoc when the paint identifying the content of steel containers peeled off. Research into this phenomenon revealed that it is possible to change a substrate displaying poor paint adhesion to one displaying acceptable paint adhesion, but only once the steel surface had been tested and the surface chemically treated. To ensure acceptable paint adhesion to steel surfaces for industrial purposes, it was necessary to determine and understand the mechanism causing this phenomenon.

Background

In Figure 1, an X-ray Photo-electron Survey (XPS) spectrum shows the typical surface composition of the steel substrate of a container before painting. Only iron (Fe), oxygen (O) and carbon (C) were detected for surfaces displaying poor or acceptable adhesion. Poor paint adhesion therefore did not occur as a result of surface contamination.

Surface species

The results of paint adhesion tests obtained on surfaces displaying poor and acceptable adhesion are shown in Figure 2. In both cases the samples were painted by dipping them in the alkyd paint, letting them drip dry, followed by a curing step at 120°C for 15 minutes. After the samples had cooled to room temperature, they were placed in a temperature controlled water bath at 40°C for 24 hours. The samples were then removed from the water, dried with a paper towel and a cross-hatched pattern was cut through the organic coating to the steel substrate. Adhesive tape was then applied over the cross-hatched pattern and pulled off to test the adhesion of the paint to the substrate. Paint adhesion was either proper (no paint came off) or poor (all the paint was removed). All paint tests were evaluated against paint adhesion tests performed simultaneously on so-called standard paint test samples for this specific paint system. These standard paint test samples were produced by etching the surface in a commercially available inhibited hydrochloric acid to remove all rust from the surface, rinsing under running tap water to determine whether the surface is oily, and finally rinsing in alcohol and drying with hot air to prevent flash rusting. These samples were painted, cured and tested using the same process as industrial samples. If poor adhesion was observed on the standard samples, the test was repeated.

To explain the variation in adhesion between the two surfaces, the surface species found in each case were identified. The XPS Fe 2p3 peaks obtained from the two surfaces did not display any obvious differences, as was expected because the cationic XPS peaks in general do not display unambiguous species information. From the anionic oxygen 1S XPS peaks, however, a major difference was observed between the peaks obtained from the two surfaces. In Figures 3 (a) and (b), deconvoluted oxygen 1S peaks are shown. In both cases three peaks could be fitted to the oxygen 1S peaks. The binding energies of these three peaks were found to be at approximately 530.1 eV, 531.5 eV and 533.0 eV, respectively. According to the acceptable XPS binding energy databases and the fact that the only cation present on the surface was iron (Fe), these three oxygen species were attributed to $Fe(OOH)$, $Fe(OH)_2$ and adsorbed water, respectively. Comparing the peak area of $Fe(OH)_2$ species to that of the $Fe(OOH)$ species (from the deconvoluted peak areas), the results for the different surfaces could be summarised, as shown in Table 1. It was found that in all cases where proper adhesion was displayed, the $(OH)_2:(OOH)$ ratio was approximately 1:1. In the cases where poor adhesion was experienced, the ratio was approximately 4.5:1. Because these samples were produced industrially, it was essential that the cause of this phenomenon was established and corrected.

The cause of the variation in the $Fe(OH)_2$ to $Fe(OOH)$ peak ratio

It was noted that the $Fe(OH)_2:Fe(OOH)$ peak ratio obtained from the standard paint adhesion sample was also approximately 1:1. When the equations describing the chemical preparation of the standard paint adhesion samples were evaluated, it became obvious that the only way to obtain more $Fe(OH)_2$ than $Fe(OOH)$ on the surface of the standard paint adhesion samples would be to remove the dissolved oxygen from the rinsing water.

This can be achieved by purging pure argon gas through the chemical solutions under laboratory conditions. Standard paint adhesion samples were then prepared in the aerated and de-aerated solutions, their surface compositions determined and paint adhesion characteristics determined. Not only did
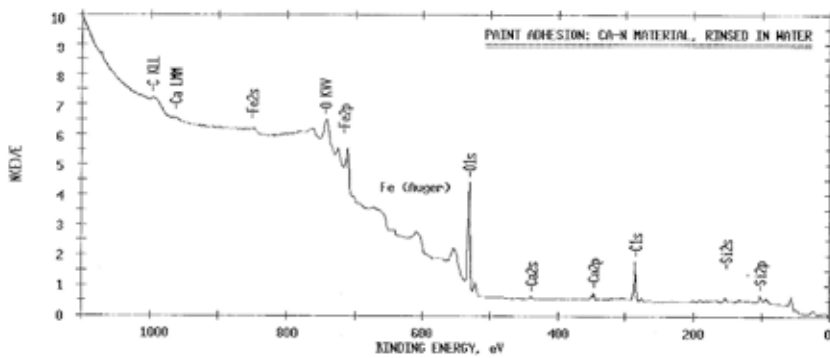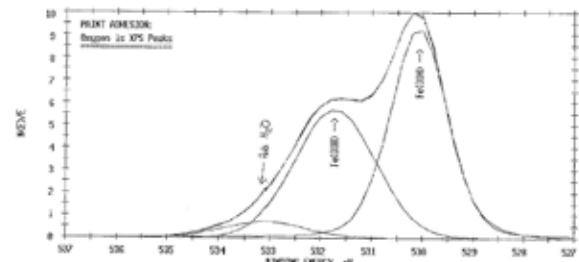
→ 1. A typical XPS survey spectrum of a steel surface. The calcium originates from the industrial water and the Si from the industrial cleaner.

→ 2. Typical paint adhesion test results showing perfect adhesion on the standard and rinsed steel surface and no adhesion on the as-received surface.
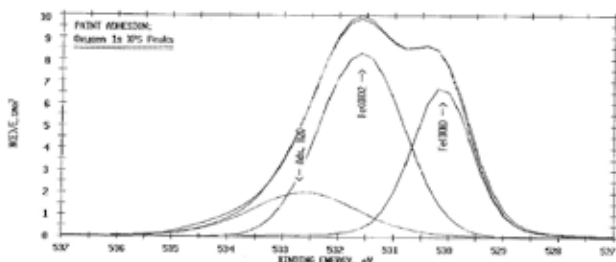

(a)

(b)

→ 3. (a) An oxygen 1S XPS peak from a surface showing poor paint adhesion. Note the relative Fe(OH)$_2$ and Fe(OOH) peak areas.
(b) An oxygen 1S XPS peak obtained from a steel surface showing good adhesion. Note the Fe(OH)$_2$ and Fe(OOH) peak areas are approximately the same size.

Table 1. The relative peak areas for all three peaks identified under the oxygen 1S XPS peak obtained from good and poor paint adhesion substrates are shown. Compare the Fe(OH)$_2$: Fe(OOH) ratios between the good and poor adhesion surfaces

Binding energy (eV)	CA-N (Rinse)	CA-N (Rinse)	Paint Std. Ox. Free	Paint Std. Normal	Chemical species
	Poor	Good	Poor	Good	
533.0	12.8	8.1	11.4	6.0	H_2O
531.5	70.9	49.4	72.0	48.44	$Fe(OH)_2$
530.1	16.3	42.5	16.6	45.8	$Fe(OOH)$
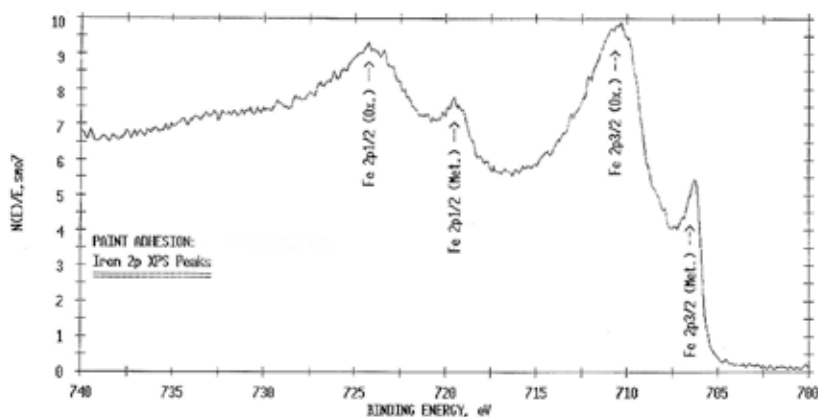
→ *4. An Fe 2p XPS peak obtained from a surface showing good paint adhesion. Note the peak originating from the steel substrate indicating a layer of less than three mono layers.*

the surface species of the aerated and de-aerated samples compare perfectly to those of the species found on the industrial samples displaying proper and poor adhesion, respectively, but the paint adhesion test also perfectly simulated proper and poor adhesion. It was determined that in the industrial process, the steel sheet enters the rinse tank with a surface temperature of about 200°C. This gives rise to water temperature of about 80°C under normal operating conditions, effectively removing most of the dissolved oxygen from the water and therefore resulting in the higher Fe(OH)$_2$ surface concentration, with increasingly poor adhesion as more and more steel was processed.

Another question that needed to be answered was how it was possible to change the oxide species by changing the dissolved oxygen at room temperature and if it was indeed logical to characterise the surface species as oxides when they exist in one or two mono layers. The thickness of the surface species could be deduced from the surface sensitivity of XPS and the fact that the metallic Fe was visible on the Fe 2p3 XPS peak shown in Figure 4. To determine if the product was really an oxide, the steel samples were placed on a heat stage in ultra high vacuum and heated to 300°C. Figures 5 (a), (b) and (c) show the XPS survey spectra of such a surface before heating, after heating and after exposure to atmosphere at room temperature. It is obvious that after heat treatment, the "oxide layer" disappeared. The high resolution Fe 2p3 XPS peak also indicated a metallic substrate with no indication of an oxide from the peak shape. It is not possible for iron oxides to dissociate under these temperature conditions. The only possible surface layer that could fit these characteristics is a surface layer of chemisorbed water. It would also explain the incorporation of the dissolved oxygen and the fact that the layer is only one to two mono layers thick.

The adhesion mechanism

The results indicated that, although XPS results indicated "Fe(OH)$_2$" and "Fe(OOH)" as oxide species, it is a pseudo oxide surface. Nonetheless, these two states of the surface, "(OH)$_2$":"(OOH)" ratio of ~4.5 :1

and ~1:1 do influence the adhesion characteristics drastically. In order to explain the adhesion loss, or better still, to prevent adhesion loss, the mechanism of adhesion in this case needed to be established. It was shown that mechanical interlocking was not the way the paint adhered to the surface. The only mechanism left was chemical adhesion. From the literature a mechanism was found whereby the surface is characterised as either a Lewis acid or a Lewis base. For paint to adhere to a Lewis acid surface, it should have a Lewis base character. All that was needed now was to establish if the two surfaces displaying either proper or poor adhesion, could be characterised as a Lewis acid and Lewis base, respectively. The paint supplier indicated that the paint used had a Lewis base character.

The use of probe molecules to determine surface characteristics

Boric acid trimethyl ester (BATE) has one empty p-orbital and can therefore act as a Lewis acid, that is, the molecule would accept an electron pair. It is therefore possible to determine if a surface is a Lewis base. If the surface retains this probe molecule, one can safely classify the surface as having a Lewis base character. The steel surface displaying poor adhesion properties with the alkyd paint classified as a Lewis base paint, should display a Lewis acid character if the Lewis acid-base theory holds for this paint system.
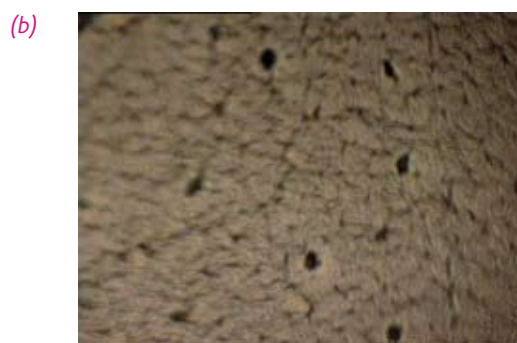
Steels displaying poor and proper adhesion characteristics, respectively a Lewis base surface and a Lewis acid surface, were then immersed in the BATE solution for 30 seconds and left to dry for 10 minutes in an inert atmosphere. In Figure 6 the FTIR (Fourier Transform Infra Red) spectra obtained from these two surfaces are shown (from the PhD work of Mohlala). It is evident from the spectra that significantly more BATE was retained by the Lewis base surface. The SEM (Scanning Electron Microscope) images obtained from these two surfaces are shown in Figure 7 and the difference in surface morphology is clear. The Lewis acid surface retained its typical metallic morphology while the Lewis base surface

(a)

(b)

(c)
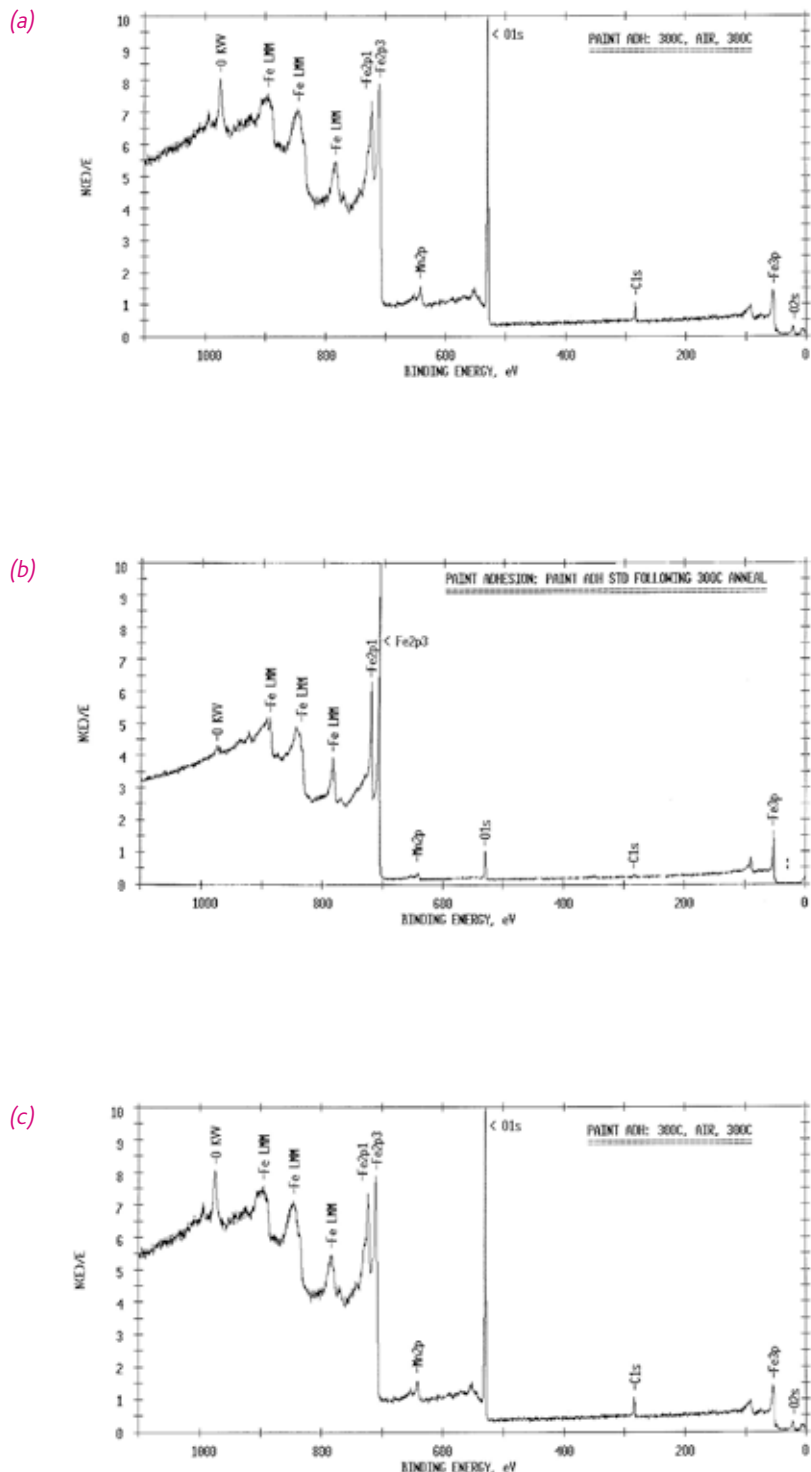
→ 5. In the above three XPS survey spectra, the steel surface composition is shown (a) as received, (b) following 300°C exposure for 10 minutes and (c) following air exposure at room temperature. Note the disappearance of the oxygen peak in Figure 5 (b).
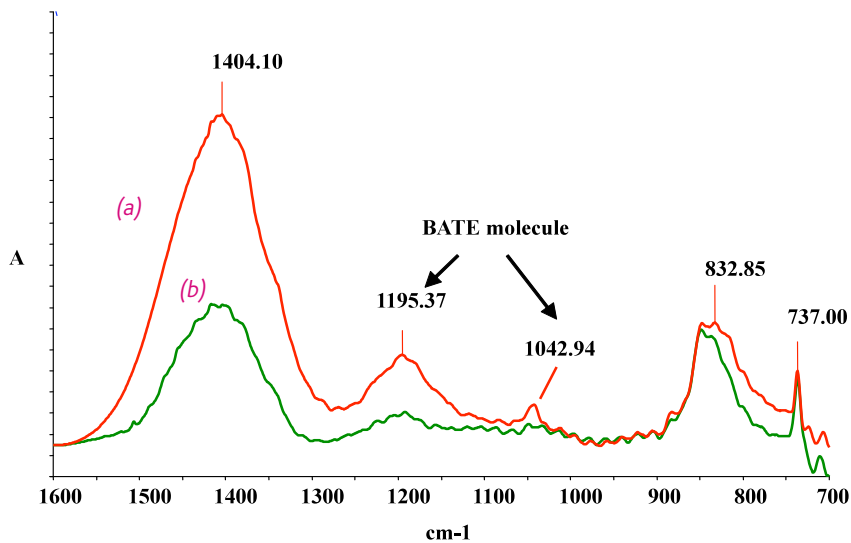
→ 6. FTIR spectrum showing (a) high BATE molecule adhesion on Lewis base surface and (b) very low adhesion on Lewis acid surface.

clearly displays the adsorbed BATE coverage.

This study therefore showed that a surface layer, which consists of only a chemisorbed water layer of one or two mono layers thick, can drastically alter the paint adhesion results by the incorporation or not of dissolved oxygen in the adsorbed water layer. It was also clearly demonstrated that the Lewis acid-base classification of these surfaces could explain the paint adhesion characteristic. A Lewis base paint requires a Lewis acid substrate, or vice versa, to display proper paint-substrate adhesion. By changing either the Lewis character of the adsorbed layer or that of the paint used, poor adhesion could effectively be overcome and proper adhesion ensured. ☻

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(a)

(b)

→ 7.
(a) SEM secondary electron image showing clean steel surface, no probe molecule adhesion.
(b) SEM secondary electron image showing the surface after probe.