The use of surface analytical techniques to characterize steel surfaces for organic coatings

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Synopsis

Steel is a highly versatile material due to its low cost and good mechanical properties, but typically needs some or other form of corrosion protection due to its tendency to corrode when exposed to atmospheric conditions. In the case of organic coatings, the corrosion protection and functionality of the final product is critically dependent on the adhesion of the coating to the surface of the steel. In this work the effect of contaminants and the nature of the surface layers present on industrial steel products are investigated by means of paint adhesion tests, Auger electron spectroscopy (AES), and X-ray Photoelectron spectroscopy (XPS). It was found that the presence of sodium species on the surface is very detrimental to paint adhesion under wet conditions, while satisfactory adhesion may be obtained even in the presence of silicon and carbon residues. It was also found that the nature of the Fe-O layer, formed under wet conditions is labile and different from that formed in dry air, and that subtle changes in process conditions, such as changing the oxygen content of the quench water, may change the adhesion of paint to the surface of the steel. Lewis acid-base interactions are discussed as a mechanism that may determine the bonding between the steel and polymer coating.

Introduction

In the low-cost steel packaging industry, organic coatings are used not only for decorative purposes but also for labeling the contents of low-cost steel containers. In such cases the purpose of the organic layer used in the labelling is not so much corrosion protection as such, but the prevention of such corrosion as may compromise the bonding to the steel surface and the functionality of the label. It is interesting to note that the surface condition of the steel used for such low-cost, mass-produced items, may indeed be more critical than that used for more sophisticated applications, where further extensive surface preparation is typically done prior to the application of organic coatings. This often frustrates the steel producer as subtle process variations may give rise to the rejection of a low margin product. One of the aims of this paper is to indicate how surface analytical techniques may be used to identify process conditions that may compromise the quality of the product and also to develop more robust processes.

Steel is a highly versatile material due to its low cost and good mechanical properties, but typically needs some or other form of corrosion protection due to its tendency to corrode when exposed to atmospheric conditions. The nature of the protective coating applied is typically dictated by the intended usage and ranges from relatively low-cost decorative coatings for packaging applications to sophisticated multiple layer coatings for long-term protection. However, for all applications it is critical that the coating adheres to the steel surface to be functional and to afford the intended corrosion protection to the steel.

The bonding of organic coatings to the steel surface is due to Lifschitz-van der Waals dispersive (LW) forces, Lewis Acid-Base (AB) interactions between the coating polymer and the metal surface, and to keying with the surface profile. AB interactions are usually dominant and account for the majority of the bonding achieved[1]. Although the bonding strength of a coating to steel is typically much higher than that indicated by the thermo-dynamic work of adhesion, as supplied by LW and AB interactions, these forces are a necessary requirement for bonding and in their absence very little bonding is achieved[2]. The dominance of the AB interactions in polymer adhesion to steel implies that the AB nature of the steel surface and of the polymer will be critical to the bonding process.

It is, of course, an oversimplification to consider the bonding interface as that between the bulk polymer and the bulk steel; it would indeed be more appropriate to rather think of the bonding region as an interphase with oxide-covered steel on the one side and a

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polymer with properties different from that of the bulk polymer on the other[3]. It is thus clear that the properties of the steel surface play a critical role in the bonding achieved with a polymeric coating[4].

The bonding of the polymer to the surface of the steel is also critical for corrosion protection. Corrosion is an electrochemical process in which the anodic sites, where metal dissolution occurs, are coupled to the cathodic sites, where the reduction of dissolved oxygen typically occurs, by electron conduction through the metal and ionic conduction through the electrolyte on the surface of the metal[5]. Corrosion is generally favoured by increased spatial separation of the anodic and cathodic sites on the metal, as this makes the retardation of the anodic process by the deposition of corrosion products on the anodic sites less likely. Spatial separation is favoured by the presence of anions such as chloride and sulphate, which not only increase the mobility of the metal cations by preventing their precipitation close to the dissolution site, but also increase the conductivity of the solution.

An organic coating decreases the corrosion of the steel substrate by separating the environment from the steel surface, though be it mainly for ionic species and not for water and oxygen, which readily pass through most organic coatings[6]. If the bond with the substrate is maintained, the resistance of the ionic conduction path between anodic and cathodic sites on the metal is increased substantially, as conduction now has to occur through the rather tortuous conduction paths through defects or weak points in the coating or along the interface between the coating and the steel. The corrosion protection afforded by organic coatings is largely the result of this increase in the resistance of the ionic conduction path[7].

Surface contamination in the form of carbon, residue of lubrication oils or salts deposited by the evaporation of residual process water could seriously jeopardize the integrity of the bond between the steel and the polymer by interfering with the bonding itself, or by compromising the bond during subsequent exposure to the environment[8]. Separation of the polymer from the steel surface may, for instance, be caused by the osmotic pressure generated by the movement of water through the polymer, which acts as a semi-permeable membrane[6], at salt residues on the steel surface. The separation of the coating from the substrate would of course then allow corrosion of the steel substrate in the usual way with ionic conduction through the electrolyte on the surface.

It is therefore obvious that the nature of the steel surface and contaminants present on the steel surface play a critical role in determining the functionality of a specific organic coating applied to such surfaces[4]. From a practical point of view, it is indeed critical to establish the nature and source of the contaminants on steel surfaces as well as the chemical characteristics of the surface due to the effect of these on the adhesion of organic coatings.

Experimental

To determine the as-received paintability of steel sheet processed via a continuous cleaning and annealing line, the paint adhesion of the industrially prepared steel sheet was compared to that obtained on paint adhesion standard samples prepared under laboratory conditions. These standards were prepared from the same material using alkaline cleaning to remove any organic contaminants, inhibited hydrochloric pickling to remove any existing oxide layer, tap water rinsing at room temperature, and a final alcohol rinse followed by forced hot air drying.

The paint used in the investigation was a urea modified alkyd paint, typically used as a low-cost labelling paint on steel surfaces. Both types of samples were dip painted, cured at 120°C for 10 minutes and exposed to water at 40°C for 24 hours before adhesion testing.

The adhesion tests were done according to an ASTM testing procedure[9], and entailed drying the water off the surface of the samples with a paper towel on removal from the water bath, cutting a cross-hatched pattern through the paint down to the steel surface, fixing a 25 mm wide piece of 3M clear tape over this area, and pulling it off. The level of adhesion was then indicated on an eight-point scale by the area of the paint removed from the surface of the steel. On the eight point scale zero indicated perfect adhesion and seven no adhesion. If any of the paint adhesion standard samples failed to attain perfect adhesion, i.e. some paint was removed by the adhesion test, it was interpreted as unreliable data and the test was repeated.

The continuous cleaning and annealing line of which the steel was investigated, consists of an electrolytic alkaline cleaning and rinsing section followed by a high temperature (~ 700°C) annealing section and finally a quench, drying and coiling section. The alkaline cleaner used in this case was sodium meta-silicate, a typical high density cleaner.

The XPS analyses were made using a PHI spectrometer (model 5400) equipped with an Mg/Al dual anode source and a small area analyser with PSD detector. An achromatic Mg Kα X-ray (1253.6 eV) source was operated at either 400 W or 450 W and 15 kV. Survey spectra were obtained at a take off angles of 45°C while angle resolved spectra were obtained for take-off angles between 20 and 90°. Data analysis was performed using PHI XPS software (version 2.0). AES analyses were performed in a PHI 600 spectrometer using a primary electron beam of 2×10^{-6} ampere at 10 kV. In both cases the vacuum in the spectrometer chambers was better than 6×10^{-9} torr.

The XPS peaks were identified by assuming the carbon 1s peak to be at 284.6 eV and by using the NIST XPS peak binding energy database. The XPS angle-resolved analysis technique makes it possible to determine differences in chemical species in the outer surface compared to the species from the deeper lying layer. In Figure 1 the reaction volumes producing the XPS signal are indicated at low and high take-off angles, illustrating the difference in signal resulting from different take-off angles.

Results and discussion

Residual salts

Although care is taken to reduce the amount of residual water left on the metal after aqueous processing by the use of surfactants and high pressure air wipers, some water, together with its salt contents, inevitably remains on the surface of the steel and is deposited in the form of salt

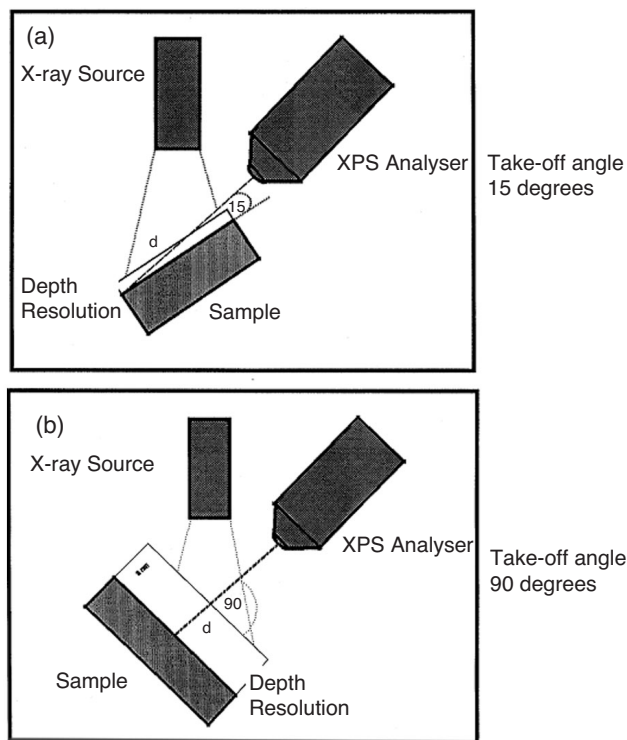# The use of surface analytical techniques to characterize steel surfaces

Figure 1—Schematic illustration of the photoelectron sample detected from a surface layer by the XPS analyser as a function of the take-off angle used
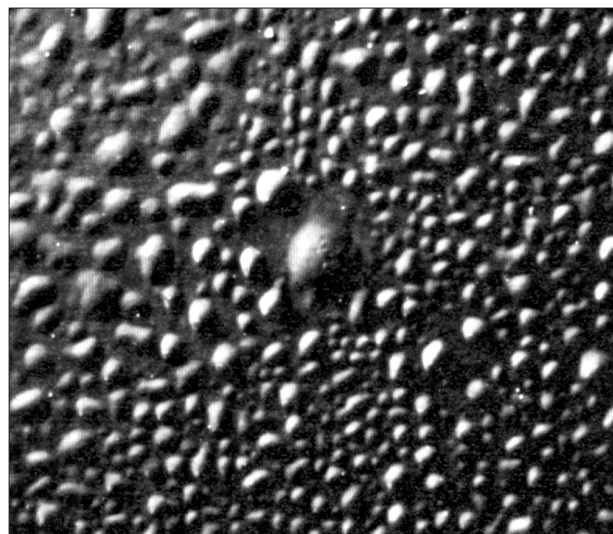

Figure 2—Light micrograph of a painted steel sample after 24 hours exposure to water at 40°C, magnification 50X. The surface displays typical osmotic blistering due to salt residue on the steel surface prior to painting

Figure 3—XPS spectrum obtained from a steel surface below an osmotic blister indicating the presence of the sodium and silica due to sodium silicate cleaner residues

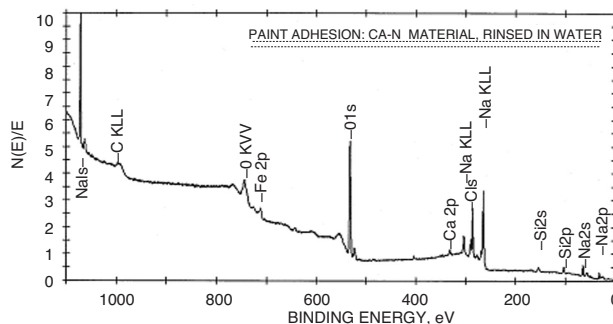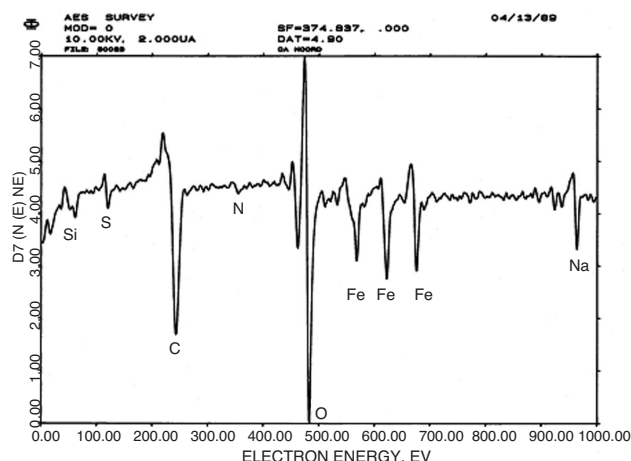

Figure 4—AES spectrum obtained from a steel surface below an osmotic blister indicating the presence of the sodium and silica due to sodium silicate cleaner residues. Also note the relatively large carbon (C) peak indicating surface carbon contamination

crystals when the water evaporates. In the continuous annealing and cleaning line, steps should be taken to limit the retention of cleaning agent residues on the surface. Although total removal of residues would be difficult, if not impossible, it is vitally important to ensure that the rinsing and brush actions, which follow the cleaning section, are effective.

When a salt residue on steel is over-coated with an organic polymer and is then exposed to an aqueous environment, the movement of water through the semi-permeable polymer membrane[8] generates an osmotic pressure underneath the coating, which invariably results in the separation of the coating from the substrate. This condition is typified by the appearance of so called osmotic blisters on the surface of the coating, of which an example is shown in Figure 2.

XPS and AES analyses were used to establish the cause of the osmotic blistering by analysing the surface of the steel underneath the blister. The results of such survey analyses are shown in Figures 3 and 4. Although the amounts were too small to use SEM techniques[10], it was possible to establish from the XPS peaks for Si 2p at 99.3 eV and Na 1s at 1071.8 eV[11] and from the Auger spectrum showing silicon at 96 eV and sodium at 996 eV[12], that sodium silicate residues caused the osmotic blistering.

To determine preventative actions, it is also important to determine which element is involved in the osmotic blistering, either sodium, possibly present as a sodium oxide, or the silicon, possibly as a silicate, following the annealing of the steel. It is relatively easy to remove the sodium from the surface, but not the silicon, for which acidic etching is

required, which is not possible in this case. To identify the element involved, the sample was subjected to a water rinse followed by forced air drying, prior to painting. This only left the silicates as contaminant on the surface, as shown in the XPS survey in Figure 5.

To determine the influence of sodium on the blistering, the sodium silicate contaminated sample was air oxidized at 300°C for 60 minutes. The air oxidation caused iron oxides to coat the silicates due to the fast cationic diffusion of iron. This is not possible for sodium due to its large atomic radius as shown by the XPS survey in Figure 6.

In Figure 7 the results of the paint adhesion tests done on these samples are shown, with the black areas indicative of surfaces where the paint was removed. It was found that the paint adhesion was so poor after water exposure that the complete painted layer was removed and the eight point ASTM test yielded only good adhesion or no adhesion at all. The osmotic blistering obtained in the case of the sodium on the surface is indicative of the higher water solubility of the sodium oxide compared to that of the silicon oxide.

Carbonaceous contamination

In this study no correlation was found between the surface carbon detected on the steel surfaces, as for example indicated by the Auger peak height at 275 eV in Figure 4, and paint adhesion results obtained for this paint system. Although the surface compositions were always checked, no excessive carbon contamination was ever detected and the influence within this range of surface carbon was not specifically investigated. The low level of carbon residues found is due to the annealing cycle in the process, which should remove any residual rolling lubrication from the surface. Moreover, cleaner surfaces do not necessarily result in better adhesion, as will become obvious later.

Type of oxide on the steel

It was found that even after steps were taken to minimize the cleaning residue on the surface to a level where these elements were either just detectable or below the detection limit, poor paint adhesion persisted on the industrial surfaces, although osmotic blistering was not detectable any more. When the elemental surface composition of this

ESCA SURVEY 7/5/89 ANGLE= 45 deg ACQ TIME=14.68 min
FILE: f05A1 CA-noord: Na waterspoel op lyn, C243294
SCALE FACTOR=56.825 k c/s, OFFSET= 13.642 k c/s PASS ENERGY= 89.450 eV Mg 400 W
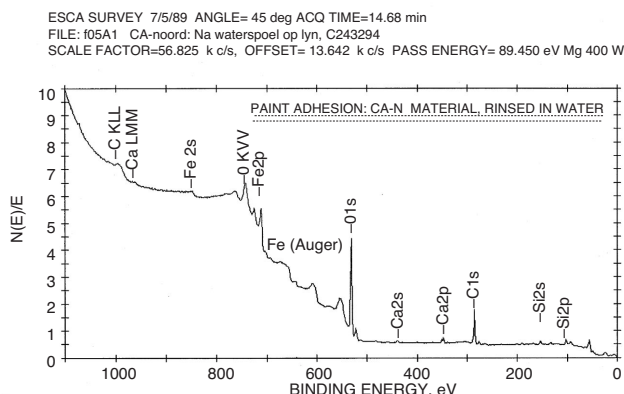

Figure 5—XPS spectrum of a steel surface, initially contaminated with sodium silicate residues and then rinsed in water, showing only the presence of silicon (Si at 99 eV).

material was compared to that of material collected directly after a maintenance shutdown or the paint adhesion standard samples, no elemental differences could be detected on normal XPS and AES surveys. Only when the shape of the oxygen 1s high resolution XPS peak, obtained from the industrial surface giving poor paint adhesion (Figure 8), was compared to the oxygen 1s XPS peak obtained from the paint

ESCA SURVEY 3/5/89 ANGLE= 45 deg ACQ TIME=14.67 min
FILE: f1581 Verfbaarheid: HCl, ortosilikaat doop, pks 300C 1h
SCALE FACTOR=55.224 k c/s, OFFSET= 1.053 k c/s PASS ENERGY= 44.750 eV Mg 400 W
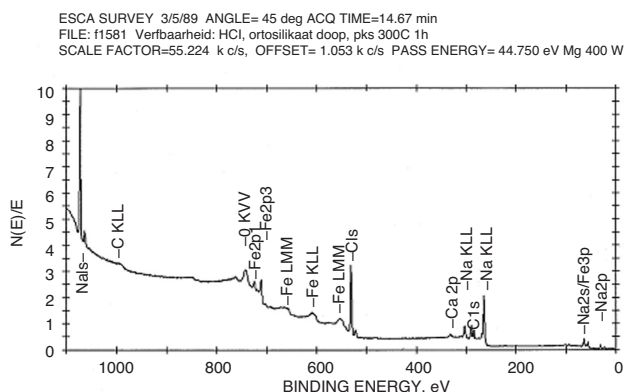

Figure 6—XPS spectrum of a steel surface contaminated with sodium silicate after heating in air for 60 minutes at 300°C showing only the presence of sodium (Na at 1071.8eV)

Figure 7—Paint adhesion test results obtained on painted steel samples, prepared from steels initially contaminated with sodium silicate residues, and then selectively removing either the silicon, by oxidation of the steel at 250°C in air to cover the silicon with iron oxide, or removing the sodium by water rinsing, painting and exposure to water at 40°C for 24 h. The results obtained with the standard sample are also shown for comparative purposes. Paint adhesion was either good or very poor

ESCA CURVE FIT 4/4/89 ANGLE= 45 deg ACQ TIME=3.35 min
FILE: Curve_Fit Verfbaarheid: CA-noord, droog temper grof, Pvdb, anan 2
SCALE FACTOR=3.526 k c/s, OFFSET= 0.000 k c/s PASS ENERGY = 17.00 eV Mg 400 W

Figure 8—High-resolution XPS 1s oxygen peak obtained on a steel surface showing poor paint adhesion. Note the relative areas of the three deconvoluted peaks representing H_2O, $Fe(OH)_2$ and $Fe(OOH)$ respectively
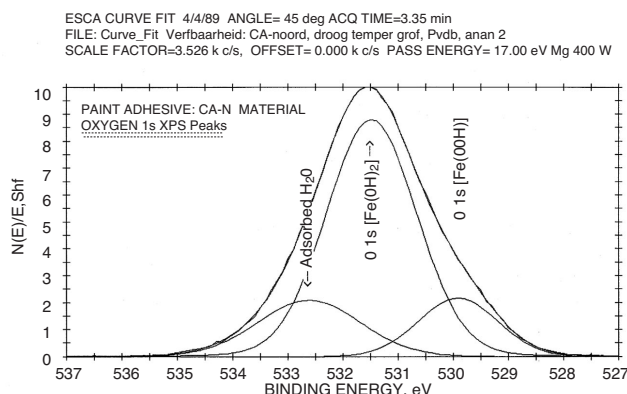
ESCA CURVE FIT 2/13/89 ANGLE= 45 deg ACQ TIME=3.35 min
FILE: Curve_Fit Verfbaarheid: CA-noord soos ontvang van PvdB, DT
SCALE FACTOR=0.734 k c/s, OFFSET= 0.000 k c/s PASS ENERGY = 17.900 eV Mg 400 W
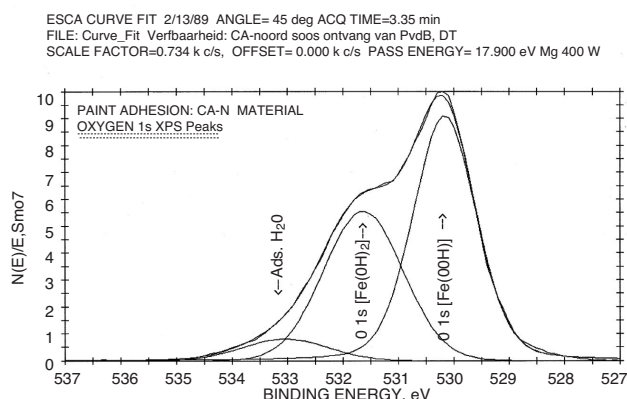

Figure 9—High-resolution XPS 1s oxygen peak obtained on a steel surface showing good paint adhesion. Note the relatively higher contribution of the $Fe(OOH)$ peak

adhesion standard sample, giving good paint adhesion (Figure 9), a noticeable difference was apparent. On deconvolution of these high-resolution oxygen 1s XPS peaks, three chemical species were identified. These species were identified as adsorbed water (H_2O) at ~ 533 eV, $Fe(OH)_2$ at ~ 531.5 eV and $Fe(OOH)$ at ~ 530 eV. An approximate relationship, as shown in Table I, was determined between the $Fe(OH)_2$ and $Fe(OOH)$ peaks. From the paint adhesion data it was found that good adhesion could be associated with the ratio of $Fe(OH)_2$ and $Fe(OOH)$ species on the surface

of the steel. It is further interesting to note that only two ratios of $Fe(OH)_2$ to $Fe(OOH)$ species were found, namely ~ 1:1, which resulted in acceptable adhesion, and ~ 5: 1, which resulted in poor adhesion, with no intermediate values. This seems to indicate that only two atomic packing configurations are possible under these conditions and also explains why either perfect adhesion or no adhesion at all was found.

To evaluate this further, paint adhesion standard samples were prepared by removing the dissolved oxygen in the acid, as well as in the rinse water, through nitrogen sparging, using the chamber schematically shown in Figure 10. The high resolution oxygen 1s XPS peaks from the steel prepared in either the oxygen depleted or normal solutions, respectively, are shown in Figures 11 and 12. From these it is clear that the oxygen content of the solutions did influence the iron species present on the surface with $Fe(OH)_2$ as the dominant species in the absence of oxygen. The ratios of the $Fe(OH)_2$ to $Fe(OOH)$ peaks were again ~1:1 or ~5:1, for the aerated and de-aerated conditions respectively. Paint adhesion tests done on these samples confirmed the correlation of poor paint adhesion associated with an abundance of $Fe(OH)_2$ species on the surface. Because the $Fe(OH)_2$ can be characterized as a Lewis base (electron donor) and the $Fe(OOH)$ as a Lewis acid (electron acceptor),
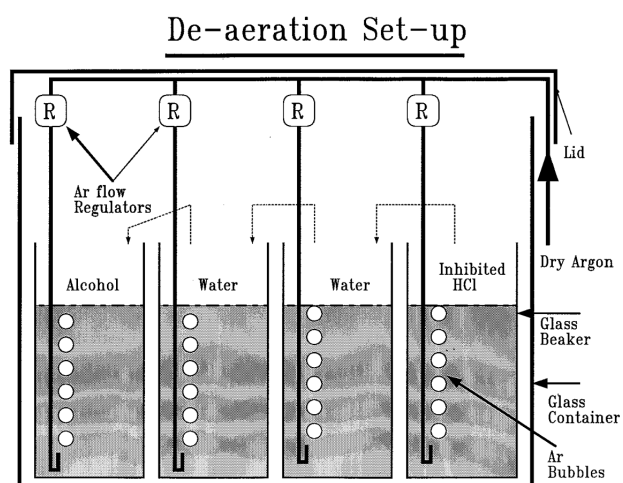
De-aeration Set-up

Figure 10—Experimental set-up used for the preparation of paint adhesion standards. Note the facility to strip oxygen from the solutions by nitrogen gas sparging and the hood to provide a protective atmosphere for the transferring of the sample from the one solution to the other

Table I

Estimated contributions of the surface oxygen species to the XPS 1s high resolution oxygen peak on steel as a function of the preparation method. Determined by deconvolution of the oxygen 1s peaks obtained, using the average of 20 analyses on each sample and using the relative contribution of the areas under the specific peaks to determine the contribution of each species

Binding energy (eV)	Chemical surface species	Industrial poor adhesion	Industrial good adhesion	Paint Std. oxygen depleted poor adhesion	Paint Std. normal oxygen, good adhesion
533.0	H_2O	12	10	11.4	10
531.5	$Fe(OH)_2$	70	49	72.0	48
530.1	$Fe(OOH)$	15	43	16.1	45
Ratio	$Fe(OH)_2/Fe(OOH)$	4.7	1.1	4.5	1.1

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ESCA CURVE FIT 9/16/91 ANGLE= 70 deg ACQ TIME=6.70 min
FILE: Curve_Fit Verfbaarheid: Byt in Hibitex, Suurstofvrye H2O, Droog
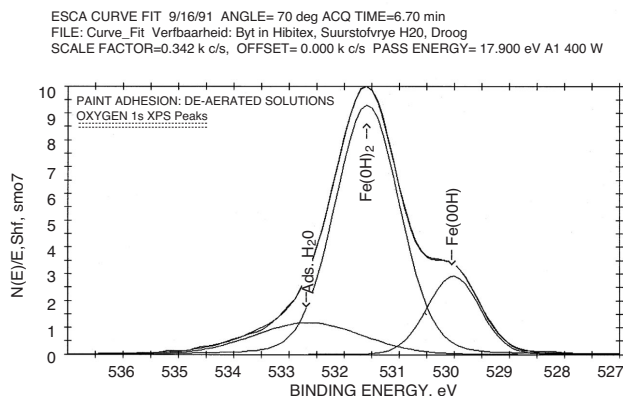SCALE FACTOR=0.342 k c/s, OFFSET= 0.000 k c/s PASS ENERGY= 17.900 eV A1 400 W

Figure 11—XPS high-resolution 1s peak of oxygen obtained in an angle resolved analysis with a take-off angle of 70° on a paint adhesion standard surface prepared in solutions from which the oxygen was stripped. Note the relatively smaller contribution of the Fe(OOH) peak

ESCA CURVE FIT 9/2/91 ANGLE= 70 deg ACQ TIME=6.70 min
FILE: Curve_Fit Verfbaarheid: CA-Noord, na HC1-ets, Waterspoel, A1k
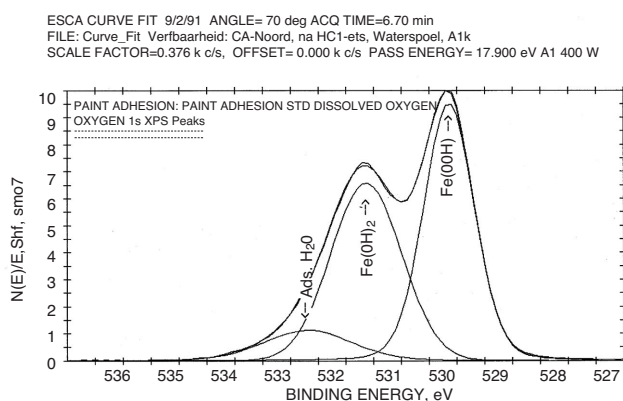SCALE FACTOR=0.376 k c/s, OFFSET= 0.000 k c/s PASS ENERGY= 17.900 eV A1 400 W

Figure 12—XPS high-resolution 1s peak of oxygen on a paint adhesion standard surface prepared in solutions with a normal oxygen content obtained in an angle resolved analysis with a take-off angle of 70°. Note the larger contribution of the Fe(OOH) peak

it seems to confirm the overriding influence of the Lewis acid-base bonding at the interface on paint adhesion[13–15].

The nature of the oxide on the steel prepared under the oxidizing conditions was further characterized using angle resolved XPS analyses of the oxygen 1s and iron 2p peaks of which the results are shown in Figures 13 and 14. The angle resolved montage obtained on the iron 2p peaks indicate that, as expected, the broad peak associated with an Fe-O species seems to be on top of the metallic iron; this is indicated by the larger Fe2p1/2(Ox) and Fe2p3/2(Ox) peaks obtained at the lower take-off angle, where a volume closer to the surface is sampled, as well as the higher Fe2p1/2(Met) peak at the higher take of angle, where less of a volume closer to the surface is sampled. The fact that the angle resolved montage, obtained on the oxygen 1s peak, indicates that the Fe(II) or Fe(OH)$_2$ species are found on the outside of the Fe-O layer can thus be accepted as such. This indicates that the Fe-O layer found on the surface of the wet prepared steel via an aqueous treatment process, differs from the Fe-O layers produced under dry conditions, where the Fe(III) species were found on the outside of the layer.

By heat-treating such wet produced oxide layers at 300°C for 15 minutes in an ultra high vacuum, it was found that the Fe-O layer completely disappeared and the remaining surface resembled a freshly Ar-etched surface, as indicated by the reduction in the oxygen peaks in the XPS surveys shown in Figures 15 and 16. Leaving this heat treated surface in the vacuum for some hours to cool down to room temperature and then exposing it to air at room temperature for a short time, created a surface Fe-O layer of similar thickness as the wet produced layer indicated by the XPS survey shown in Figure 17. However, this oxide could not be removed by using the same heat treatment under vacuum at 300°C for up to an hour.

It was also established that surfaces created under dry conditions at room temperature or by oxidizing at 250°C for 15 minutes in air, both showed a Fe(II):Fe(III) ratio of ~ 1:1 and both displayed excellent paint adhesion.

It must be stressed that although the two species were identified as Fe(OH)$_2$ and Fe(OOH), photoelectrons originating from oxygen atoms or ions on the steel surface were analysed and these identifications are done from the binding energy values of the photoelectrons. It does not necessarily imply that the stoichiometric iron oxide species were present on the surface of the steel.

ESCA MUTIPLEX 11/12/91 EL=01 REG 1 ANGLE= 80 deg ACQ TIME=6.68 min
FILE: f12A4 Verfbaarheid: Verf Std, Voor verf, voor 300C, T0A=80 deg
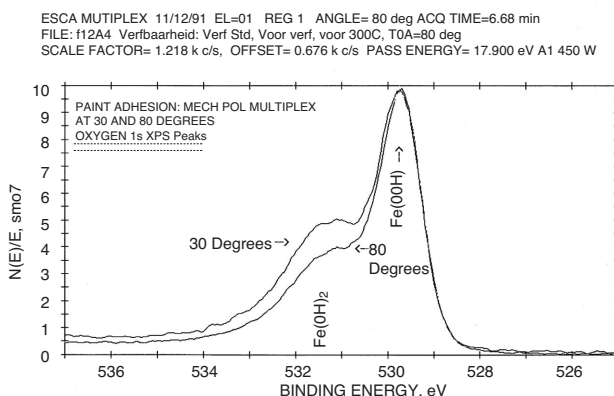SCALE FACTOR= 1.218 k c/s, OFFSET= 0.676 k c/s PASS ENERGY= 17.900 eV A1 450 W

Figure 13—Oxygen 1s angle resolved peaks obtained on a clean paint standard steel surface showing the higher OH component at the low take-off angle, indicating a higher concentration of the Fe(OH)$_2$ species on the outer surface

ESCA MUTIPLEX 11/12/91 EL=Fe1 REG 2 ANGLE= 80 deg ACQ TIME=13.35 min
FILE: f12A4 Verfbaarheid: Verf Std, Voor verf, voor 300C, T0A=80 deg
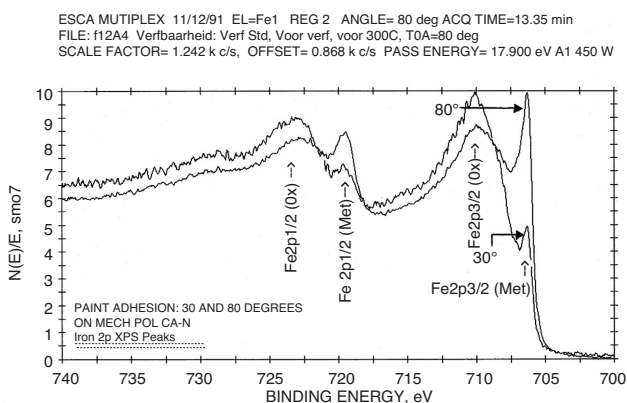SCALE FACTOR= 1.242 k c/s, OFFSET= 0.868 k c/s PASS ENERGY= 17.900 eV A1 450 W

Figure 14—Iron 2p angle resolved peaks obtained on a clean steel paint adhesion standard surface showing the excess oxygen component of the layer on the steel surface. Note the lower metallic peak at the low take-off angle due to the longer path length through the oxide

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ESCA SURVEY 11/7/91   ANGLE= 70 deg   ACQ TIME=7.34 min
FILE: f07B01 Verfbaarheid: Verf Std, voor verf, voor 300C, verhitting
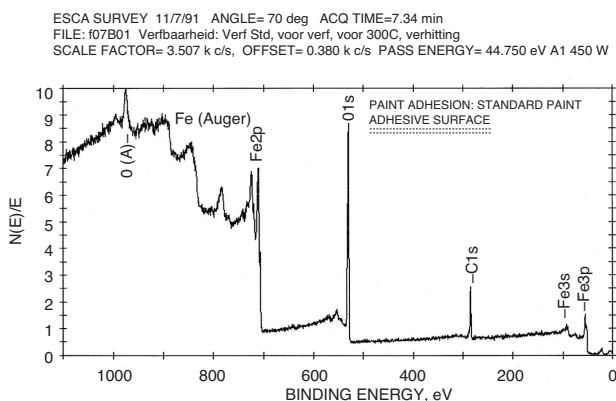SCALE FACTOR= 3.507 k c/s, OFFSET= 0.380 k c/s PASS ENERGY= 44.750 eV A1 450 W

Figure 15—XPS angle resolved spectrum obtained at a take-off angle of 70° on a paint standard clean steel surface before heat treatment under vacuum. Note the height of the oxygen peak

ESCA SURVEY 11/6/91   ANGLE= 70 deg   ACQ TIME=14.67 min
FILE: f06A4 MPOL in water, na 300C, verhitting
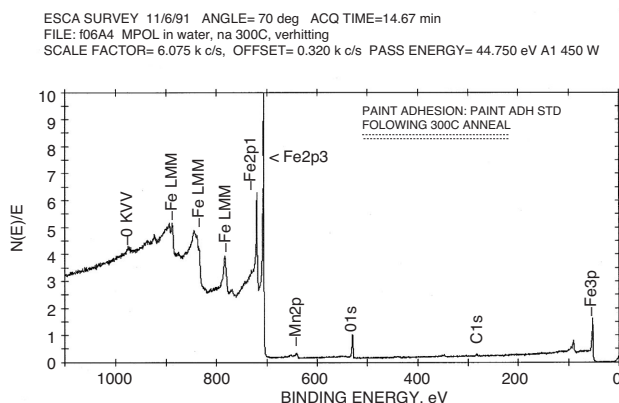SCALE FACTOR= 6.075 k c/s, OFFSET= 0.320 k c/s PASS ENERGY= 44.750 eV A1 450 W

Figure 16—XPS angle resolved spectrum obtained at a take-off angle of 70° on a paint standard clean steel surface following a heat treatment of 15 minutes at 300°C in the ultra high vacuum. Note the near total removal of the oxygen

ESCA SURVEY 11/11/91   ANGLE= 70 deg   ACQ TIME=5.87 min
FILE: f07B08 Verfbaarheid: Na verhit 300C, Na 0ks verdwyn, na lug
SCALE FACTOR= 5.178 k c/s, OFFSET= 0.175 k c/s PASS ENERGY= 44.750 eV A1 450 W
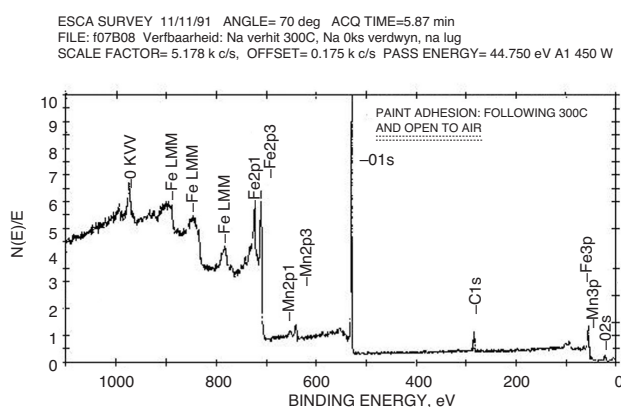
Figure 17—XPS angle resolved spectrum obtained at a take-off angle of 70° on the vacuum heat treated steel surface after exposure to air at room temperature. This XPS spectrum is similar to the one obtained on the paint adhesion standard steel, but in this case the oxygen could not be removed by subsequent heat treatments in the ultra high vacuum

Once it was established that the steel with the higher Fe(III) species concentration on the outer oxide layer gave better paint adhesion results, the quest was to delineate the conditions under which such an oxide could consistently be produced on an industrial plant. It was shown that the temperature of the water in the quench tank following the annealing furnace, changed from room temperature after a maintenance start-up to approximately 90°C after a couple of coils has been processed. This caused the oxygen content of the water to drop to a low value, causing the oxygen depleted surface layer with an Fe(II):Fe(III) ratio of ~ 5:1 and the corresponding poor paint adhesion. To rectify this, an acetic acid spray was introduced between the last two quench tanks. The presence of the acid changed the surface composition from an Fe(II) to an Fe(III) type surface and therefore to a surface displaying good paint adhesion.

Conclusions

In this work it has been shown that the availability of the sophisticated surface analysis techniques to characterize industrially produced steel surfaces can contribute significantly to the development of production route control measures to ensure consistent functional properties of steel products as well as to elucidate the mechanisms responsible for good paint adhesion. These techniques seem to be essential to ensure an understanding of paint adhesion failure analysis and quality control on process lines producing such materials.

It was shown that the nature of the 'oxide layers' produced under wet conditions is significantly different from that produced under dry conditions[16]. The nature of the surfaces, produced under wet conditions, could be altered by changing the dissolved oxygen in the process solutions. An oxide with Fe(II) dominating on the outer surface formed on steel in contact with water containing little oxygen, while on oxide with Fe(III) dominating on the outer surface formed in oxygen saturated water.

It was also found that the wet produced oxides could be totally removed under vacuum at slightly elevated temperatures. The term oxide layer in these cases could be misleading and it seemed that the Fe-O layer formed under wet conditions more closely resembled a layer of chemisorbed water. This would explain the fact that depleting the process solutions of oxygen also depleted the surface layer of oxygen and also the disappearance of the layer under vacuum at elevated temperatures. It is well known that the rate of removing adsorbed water from surfaces of high vacuum chambers can be increased by baking the system at temperatures above 220°C for times up to 24 hours.

Work is currently underway to further investigate the contribution of Lewis acid-base interactions to the bonding of organic coatings to steel surfaces.

Acknowledgements

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