

THE EFFECT OF SUBSTRATE MINOR COMPOSITIONAL DIFFERENCES ON THE CORROSION PERFORMANCE OF COATED STEELS

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Abstract—Cabinet tests with wet and dry cycles were undertaken to investigate the effect of small differences in the composition of steels provided by two different manufacturers on their corrosion behaviour when coated and exposed to controlled atmospheres inside a cabinet. A clear alkyd lacquer was chosen as the coating in order to facilitate the monitoring of the corrosion features. Scribed panels were exposed to two aggressive atmospheres. The first environment simulated the effect of industrial atmospheres (Prohesion test). The second environment was made up of a solution which was 10 times more concentrated than the acidic rain of Manchester. In the Prohesion test, the corrosion characteristics of the coated steels obtained from different manufacturers showed distinct differences which seemed to be related to the microstructural characteristics of the various steels, mainly their inclusion content. However, the results from the acid rain test did not distinguish the various coated specimens in terms of their corrosion behaviour. The Prohesion test was more corrosive than the acid rain test. This indicates that the degree of corrosivity of the environment influences the ranking of coated specimens in relation to their corrosion performance.

INTRODUCTION

THE NATURE of the metallic substrate contributes significantly to the anti-corrosive properties exhibited by an organically coated system. Tomashov and co-workers¹ testing the electrochemical behaviour of coated surfaces of platinum, copper and iron found that film deterioration increased with increasing reactivity of the base metal. Work by Walter² on painted samples of steel, galvanised steel, Zn/55% Al coated steel and aluminium also showed that the corrosion performance of the painted metal was directly related to the corrosion resistance of the bare metal. In addition to the reactivity of the metal, the substrate may also influence the protective life of a coating via the type of corrosion product formed,³ nature of the adhesive bond at the interface^{4,5} and its catalytic properties for the oxygen reduction reaction which is a critical step in the cathodic delamination of a film.⁶ This work investigates the effect of small variations in the composition of steels when coated and exposed to controlled corrosive atmospheres inside a cabinet.

It is well known that although salt spray tests are widely used to evaluate the protective properties of organic coatings, they often lack correlation with paint performance observed in real situations.⁷ This seems to be particularly true when industrial atmospheres are of concern.^{8,9} Several modifications have been suggested but most of these also have been proved inappropriate for testing organic coatings, since they do not reproduce the modes of coating failure usually found in long-term atmospheric exposure.¹⁰ A solution consisting of 3.25% wt ammonium sulphate and 0.25% wt sodium chloride was recommended by some authors,^{9,11,12} and this was observed to yield improved correlations with long-term outdoor exposures in

industrial environments. Timmins¹³ suggested that the dilution of the above mentioned solution would be even more effective. The test procedure adopted by Timmins,¹³ also named 'Prohesion' test, describes a philosophy which means protection by adhesion and implies that adhesion failure precedes corrosion. This test solution has been reported as providing an approximate simulation of atmospheric attack on steel.¹¹ Recently, research carried out by the atmospheric corrosion group at UMIST revealed that a test solution which is 10 times more concentrated than the rain of an industrial urban area like Manchester could provide a more suitable simulation environment of corrosion attack in an industrial atmosphere.¹⁴

Despite the lack of correlation in many cases with outdoor exposure trials, cabinet tests may provide little or no mechanistic information. However, cabinet tests remain in widespread use simply because they provide a rapid means of comparing different paint systems. In this study the corrosion performance of two types of coated steels, mild steel and weathering steel, was evaluated by two different cabinet tests.

EXPERIMENTAL METHOD

The surface of four steels, two mild steels (MS) and two weathering steels (WS), was prepared by grinding with silicon carbide paper up to grade 1200, degreasing in trichloroethylene, rinsing in de-ionised water and finally hot-air dried. A clear alkyd coating was subsequently applied by flood spinning. Dry film thicknesses in the range 24–30 μm were obtained. The coating was then scratched through to the base steel (scribe marked) to determine whether the resistance of the organic film to undercutting differed with the steel substrates used.

Two cabinet tests were used. The first involved the exposure of the coated panels to an intermittent wet/dry cycle corresponding to 1-h wet, 1-h dry in a test cabinet. The cabinet was heated to 35°C during drying and cooled naturally during the wet cycle (mist). The solution used in this test consisted of a mixture of 0.35% $(\text{NH}_4)_2\text{SO}_4$ + 0.05% NaCl. The test was continued until corrosion had spread over most of the surface. The second test employed an aggressive solution simulating the acid rain of Manchester, 10 times more concentrated. The composition of the artificial acid rain solution was arrived at after various analysis of the Mancunian rain at UMIST,¹⁴ and is given in Table 1. The pH of the artificial acid rain was adjusted to 3.5 with NaHCO_3 . The wet-dry conditions applied in this test consisted of spraying the solution for 2 h followed by a 1 h drying period. The temperature inside the cabinet was maintained at approximately 22°C. For reasons of reproducibility four specimens of each substrate were used in each test. X-Ray photoelectron spectroscopy (XPS) was carried out on the scribed and disbonded areas of the specimens, after removal of the coating from the substrate. The coating was peeled off with a tape, being easily removed from the disbonded areas next to the scribed region. The XPS analysis was carried out in a V.G. Scientific ESCALAB MK 1 using Al K_{α} radiation (1486.6 eV).

EXPERIMENTAL RESULTS AND DISCUSSION

The chemical composition of the steels studied was obtained by emission spectroscopy analysis and is presented in Table 2.

TABLE 1. COMPOSITION OF ACID RAIN SOLUTION¹⁴

Constituent	Concentration (mg l^{-1})
H_2SO_4 (98%)	31.85
$(\text{NH}_4)_2\text{SO}_4$	46.20
Na_2SO_4	31.95
HNO_3	15.75
NaNO_3	21.25
NaCl	84.83

Steel types 1 and 2 were supplied by different manufacturers. The main differences between the two steel types was that WS was higher in Cu and included Cr compared with MS. The microstructure of the various steels used in this work was analysed by Optical Metallography and Scanning Electron Microscopy. Type 2 steels had more inclusions than type 1 steels.

Visual observation of specimens

The corrosion features of the various scribed specimens were followed by visual observation with increasing exposure time. In the Prohesion test, differences were observed between the corrosion performance of two groups of steels. These differences were evident from the early days of exposure. For each group of steels with similar corrosion behaviour there was a mild steel type (MS) and a weathering steel type (WS). Undercutting and delamination at the scratch was observed on the coated steels MS 1 and WS 1 after only 1 day exposure. On the other hand, only slight undercutting at the scratch was produced by the two other steels, MS 2 and WS 2. In the following days, the difference in performance of the coated steels was even more pronounced. After 10 days exposure to the wet-dry cycle the coating on the specimens corresponding to the substrates MS 1 and WS 1 had lifted from the substrate at the areas surrounding the scribe mark and large volumes of liquid had accumulated underneath the coating. The adhesion in the area surrounding the scribe was completely lost. Conversely, coating adherence to the substrates MS 2 and WS 2 was still maintained in the regions away from the scribe at the same exposure time (Fig. 1).

It is evident from the observations made that the modes of degradation produced were similar in the cases of the steels MS 1 and WS 1, but the deterioration characteristics of these specimens showed some differences from the two other steels used. The high reproducibility obtained for the four specimens of each substrate tested, validates these results. One possible explanation for the improved corrosion performance of the MS 2 and WS 2 steels in terms of the degree of delamination observed is that the cathodic reaction on these steels could have mostly occurred on the exposed metal at the scratch. The likely reason for this could have been the larger content of inclusions of MnS or mixed, MnS+oxide, in these steels. These types of inclusions would favour the cathodic reaction on their surface.¹⁵ Consequently less delamination would occur for these steels at the areas away from the scratch. The

TABLE 2. ELEMENTAL COMPOSITION OF STEELS STUDIED

Steel	MS 1	WS 1	MS 2	WS 2
C	0.058	0.076	0.20	0.11
Si	0.012	0.36	0.04	0.47
Mn	0.24	0.36	0.67	0.78
S	0.012	0.009	0.028	0.010
P	0.011	0.093	0.011	0.013
Cr	—	0.88	—	0.50
Ni	0.02	0.013	0.016	0.02
Cu	0.03	0.28	0.01	0.32
Fe	balance	balance	balance	balance

evaluation of inclusion content was carried out on optical micrographs. It was found that the steel MS 2 presented a much larger, approximately 2–4 times, content of inclusions than the other steels. The steel WS 2 ranked second in inclusion content and had approximately 1.5–2 times more inclusions than the other steels.

In this work the presence of carboxylated species at the interface detected by surface analysis techniques, indicated the attack of the polymer by the alkaline environment, due to reduction of oxygen, as one of the causes of the disbondment. The degree of delamination as indicated by this work seemed to be dependent on the nature of the steel surface. The largest degree of delamination was produced by the specimens corresponding to the MS 1 steel substrate, while the steel WS 2 exhibited optimum cathodic delamination resistance. Various explanations have been given in the literature to the cause of cathodic delamination.^{15–18} In the case of the coating used in this work, delamination may occur as a consequence of the saponification of the reactive ester groups present in the coating resin leading to the breakage of the adhesive bond at the coating–substrate interface. It is also possible that other mechanisms such as the dissolution of the oxide film at the interface might have an effect on the process of delamination. Filiform corrosion was commonly observed on the MS 2 and WS 2 steels in the region of the scribe. In the case of the other steels, however, this type of corrosion was not normally found. The substantial loss of coating adherence as a result of delamination in the case of the MS 1 and WS 1 steels could be the probable reason for the lack of filiform corrosion. Since one of the causes of filiform corrosion is differential aeration, this condition would be favoured in the case of the MS 2 and WS 2 steels which had more adherent corrosion products.

XPS analysis of specimens exposed to 0.35 wt% (NH₄)₂SO₄ + 0.05 wt% NaCl

XPS analysis was carried out on the specimens corresponding to the substrates MS 1 and WS 1 after 10 days exposure inside the cabinet, and after 15 days for the substrates MS 2 and WS 2. The analysis was carried out at the coating interface on the scribed and heavily corroded region and also on the disbonded one. The results obtained from this analysis showed that the substrate with the largest and smallest concentration of corrosive species at the interface corresponded to the MS 1 and WS 2 steels, respectively. Those were also the steels which presented the lowest and highest corrosion resistance, respectively. Figure 2 shows the XPS spectrum relative to the oxygen 1s electron shell (0 1s) at the coating interface of the four steels analysed. It can be seen that the (0 1s) spectrum corresponding to the WS 2 substrate shows larger concentration of oxide oxygen species, O²⁻, in comparison to the hydroxyl species, OH⁻. However, for the other substrates the proportion of OH⁻ was higher than that of O²⁻ species, and this proportion seemed to have increased in the following order: MS 1, WS 1 and MS 2. This indicates that the OH⁻ concentration in the coating interface seems to be directly related to the corrosion characteristics of the system.

Specimens exposed to artificial acid rain solution

The scribed specimens tested in the artificial acid rain were maintained inside the cabinet for 35 days. The development of corrosion features on the various specimens used was followed with time. It was evident from this test that similar corrosion features developed around the scribe mark of the coating on the various steel substrates used. The corrosion characteristics corresponded to blisters beside the

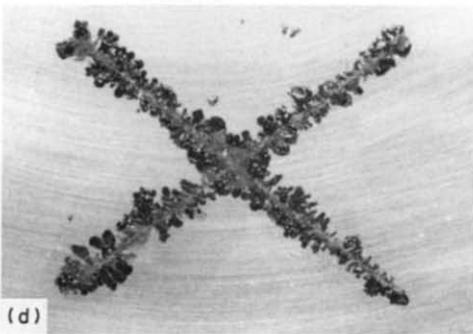
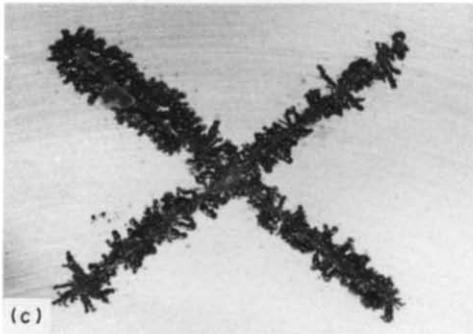
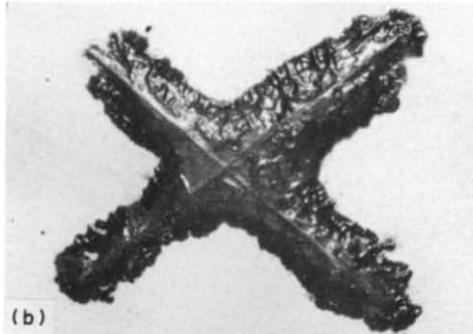
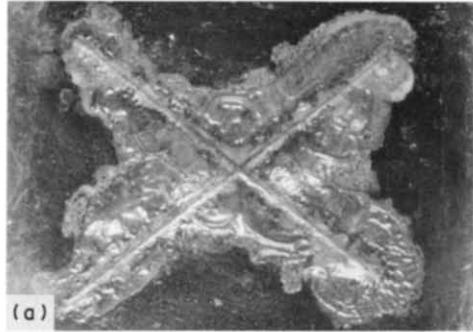


FIG. 1. Scribed specimens exposed in cabinet (Prohesion test) for 10 days: (a) MS1 (b) WS1, (c) MS2, (d) WS2.

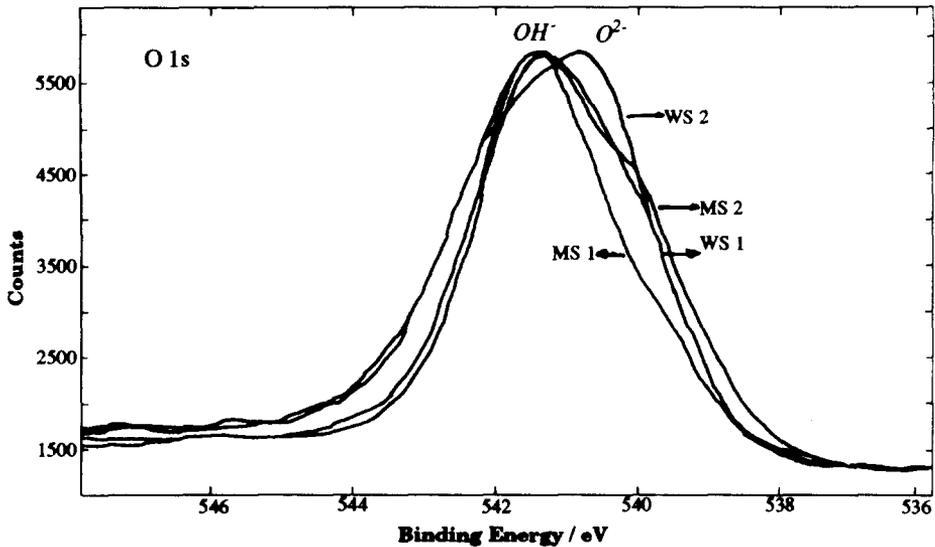


FIG. 2. O 1s XPS spectrum at the coating interface of the four steels analysed.

scribe filled with black and/or brown loose corrosion products and volumes of liquid. The significant observation of this experiment was that the various steels tested could not be differentiated throughout the whole testing period under the conditions used. This indicates that the conditions of an accelerated test are of major importance in ranking different coated substrates with respect to their corrosion properties.

The main difference between the two tests carried out in the cabinet was the chemical nature of the environment. The composition of the solutions differed with respect to ion concentration and pH. In the Prohesion test the medium had an ionic concentration of approximately 0.4% wt and a pH of around 5.6; whereas for the artificial acid rain solution the concentration of ions was nearly 0.023% wt and the pH was approximately 3.5. Considering that during the dry cycle the concentration of ions of the two media becomes concentrated and at the saturation point eventually achieve a similar concentration, it seems that the difference in the ionic concentration between both environments could not have significantly influenced the results obtained. On the other hand, the distinct pHs of the two atmospheres, one corresponding to a nearly neutral medium and the other being of an acidic nature, could account for the different type of response produced. It is possible that in the acidic environment used, the sulphide inclusions were dissolved more rapidly than in neutral media. As a consequence of this attack, the inclusions played an insignificant role on the overall corrosion of the steel substrate. Another possible explanation for the reduced delamination found at the low pH atmosphere is that the evolution of hydrogen could have become the dominant reaction resulting in less alkaline conditions at the interface.

CONCLUSIONS

Clear differences were found in the corrosion deterioration of the various coated steels tested in the Prohesion cabinet. This difference seemed to depend on the inclusion content of the steel substrate rather than the variation in alloying elements.

However, no distinction was seen when the same steels were tested in the artificial acid rain solution. The finding of this work sheds further light on the importance of the specific conditions employed in accelerated tests and used to rank coated systems in terms of their corrosion characteristics. Work is in progress to determine the correlation between the performance of the various coated substrates in these accelerated tests and outdoor exposure.

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