

Effect of Surface Preparation on Protective Efficiency of Organic Coatings

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Abstract

Surface preparation of metal prior to painting is one of the key factors in order to ensure consequent protective properties of coating. This is mainly done to produce effective adhesion between the coating and substrate. Interfacial adhesion can be improved through two general mechanisms; electrostatic bonds and mechanical interlocking. Electrostatic bonds between the polar coating and metal substrate can be improved by removing any significant (eg millscale) oxide layer and impurities. Surface roughening enhances the mechanical interlocking of paint within the surface irregularities. In general surface preparation of any kind is believed to improve the adhesion and consequent protection afforded by organic coatings. However recent findings have shown that the electrochemical properties of oxide film play an important role and also vary by the preparation method.

In the present study 5 methods of surface preparation are applied to mild steel and the resulting surface has been characterized using various electrochemical techniques. Scanning vibrating electrode technique (SVET) has been used to characterize the metal surface. Metal surfaces are then coated with different coating systems and exposed to corrosive environment. Anti-corrosive properties were examined as a function of time. DC resistance method was used as the basic method for electrochemical resistance measurement. The mechanical wet and dry adhesion strength has been examined using pull-off adhesion method. Results have indicated that surface geometry governs the electrochemical activity of metal. Also it is suggested that surface activation without providing effective metal-coating bonds promotes corrosion. Theories of this breakdown mechanism are tentatively advanced.

Keywords: surface preparation, anti-corrosive coating, adhesion, DC resistance measurement

1. Introduction

Previous work in our laboratory (1) showed that the type of surface preparation of the steel prior to coating had a dramatic effect on the subsequent corrosion protection afforded in immersion tests and in salt spray testing. Particularly water jetting led to better performance. It is generally accepted that factors such as removal of impurities and introducing surface roughness to steel to obtain better adhesion through the mechanical interlocking of polymeric structure and the metal surface play

a part. However it was postulated that the ease of breakdown of the oxide film is also critically important and varies between surface preparations. This was investigated in recently reported work (2) where 5 different surface preparation methods (abrasive blasting, water-jetting, abrasion, acid pickling and degreasing) were applied to the mild steel surface and each resultant surface was characterised using electrochemical methods. Scanning vibrating electrode technique (SVET) detected anodic and cathodic sites on the surface and also determined the intensity of electrochemical activity at these sites. Scanning electron microscope (SEM) together with energy dispersive X-ray spectroscopy (EDX) was used to characterise the surface structure and its chemical composition. Changes in open circuit potential were monitored during the time of exposure to electrolyte in order to investigate the general surface activity. This work showed that the type of surface preparation greatly affects the reactivity of the surface. (A fuller set of references relating to this type of work can be found in the paper (2)). Some of SVET and EIS results from this previous work are given here although they are presented differently. Then new results from organically coated samples with the same five surface preparations are given. Differences both between the electrochemical properties (DC resistance) and the wet adhesion of coated samples have been investigated.

2. Experimental

2.1 Surface preparation methods:

The steel surface has been treated by means of 1) Degreasing the as received panel with iso-propanol, 2) wet abrasive (garnet) blasting at 10K psi, 3) UHP (ultra high pressure) water-jetting at 40K psi, 4) acid pickling in 20%w. hydrochloric acid for 100 sec followed by rinsing with distilled water and 5) abraded surface with 180 grit emery to remove the existing oxide layer and to introduce the surface roughness. Standard steel Q-panel was used for degreasing, abrasion and acid pickling treatments and wet abrasive garnet blasting (abrasive blasting) and hydro-blasting (water-jetting) were applied on the low carbon steel plates provided by Rentajet Group Ltd. All samples were placed in desiccator right away after preparation.

2.2 Coating application

A solvent based short-oil alkyd and 2-k polyurethane varnish were used to coat the steel surfaces. Two coats were applied by spray to give a system with a final dft of about 120 μm .

2.3 Evaluation techniques

- SVET experiments on bare metal surfaces were performed using a SVET machine made by the University of Swansea, Department of Material Science. The test area was approx. 10mm \times 10mm and the rest of surface was masked in order to avoid interference. All surfaces were assumed flat and so the 4 points height scan method was employed to adjust the 150 μm distance between the vibrating probe and the metal surface. Measurement's resolution was 200 μm between each 2 consecutive

measured points. The current density map of the surface has been produced using the data of surface potential map as the initial outcome.

- EIS on bare metal surfaces was done using ACM GillAC potentiostat with 20 mV voltage perturbation around OCP in frequency range of 10 kHz-10 mHz. The provided software by ACM was employed to fit appropriate equivalent electrical circuit and calculate the charge transfer resistance value.
- DC resistance measurements on coated surfaces were performed using the Keithley 610C solid-state electrometer.
- Adhesion strength of coated surfaces was measured using an automatic Pull-off adhesion tester model AT-A at 100 psi/s rate with 20mm dolly size
- The electrochemical experiments on bare metal surfaces were conducted in the 0.001 M NaCl solution at RT (18-22 °C). The electrochemical experiments on coated metal surfaces were done with PVC cells affixed to the surface exposing 11.4cm² filled with 0.5M NaCl

3. Results and discussion

3.1 Uncoated steel surface

The corrosion current density has been locally mapped and illustrated in figures 2-6.

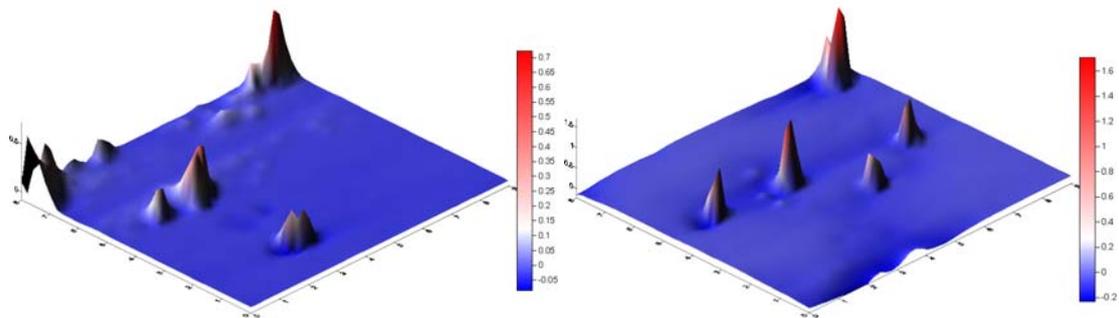


Figure 1: Current density map of the As received mild steel surface after 5 min (left) and 2 hrs (right) immersion in 0.001 M NaCl

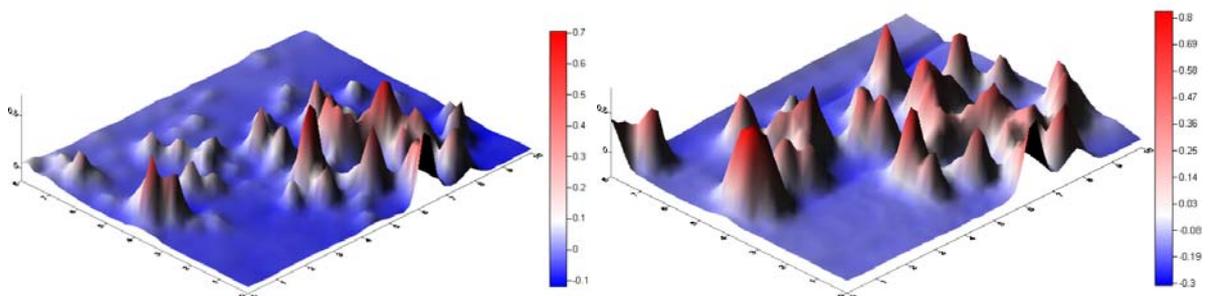


Figure 2: Current density map of the water jetted (hydroblasted) mild steel surface after 5 min (left) and 2 hrs (right) immersion in 0.001 M NaCl

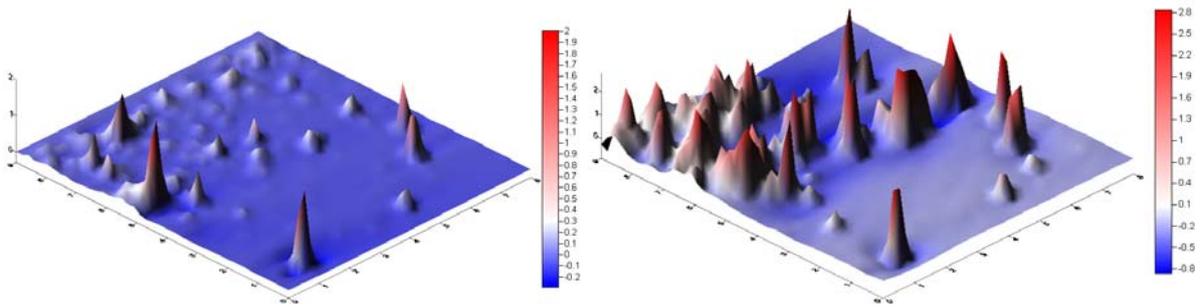


Figure 3: Current density map of the abraded mild steel surface after 5 min (left) and 2 hrs (right) immersion in 0.001 M NaCl

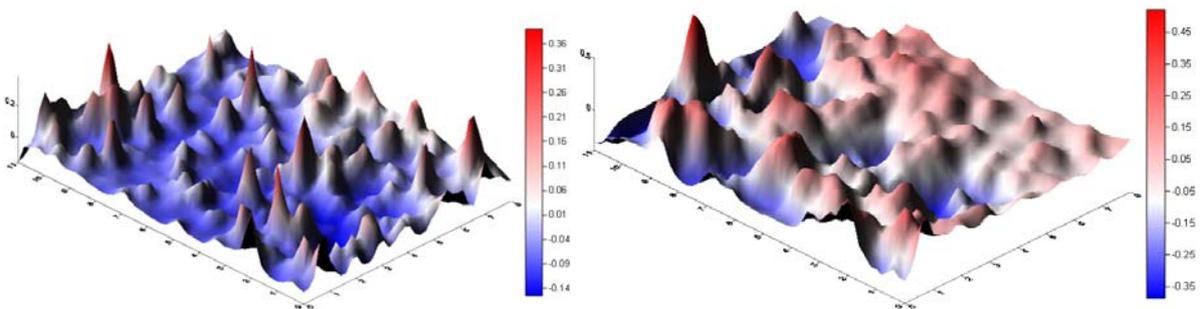


Figure 4: Current density map of the abrasive blasted mild steel surface after 5 min (left) and 2 hrs (right) immersion in 0.001 M NaCl

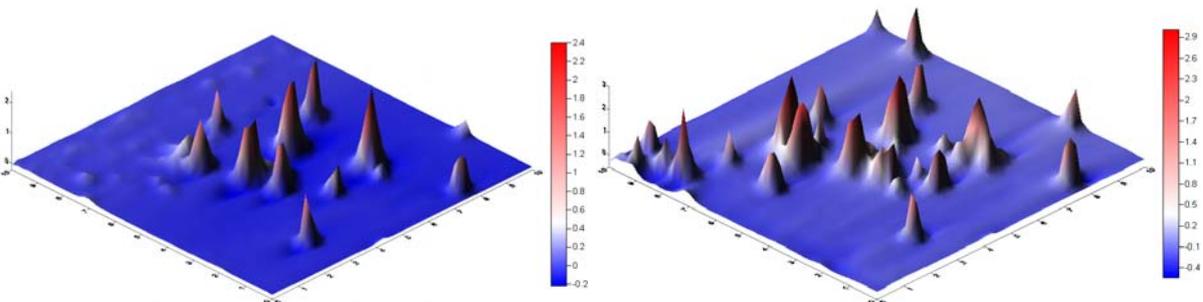


Figure 5: Current density map of the acid pickled mild steel surface after 5 min (left) and 2 hrs (right) immersions in 0.001 M NaCl

In all cases the surface has become more anodic after 2 hr contact with electrolyte in comparison with 5 min immersion. This is probably due to the corrosion product deposition on the surface limiting the surface access to oxygen. Consequently these areas turn into anodic sites with a drop of potential resulting in an overall potential shift toward more noble potential. As can be seen from the images, the number of initial anodic sites plays a key role in the long term anodic/cathodic activity and it varies by the surface preparation method. Comparison between different surface treatments reveals that the surface roughness has a significant effect on the number

of initial anodic sites. According to the profilometry results (not presented here) the surfaces can be ordered by their roughness values as follows:

As received Q-panel = acid pickled > emery abraded >> UHP hydroblast > wet abrasive blast

Apart from the effect of surface profile, the type and structure of the pre-existing oxide film seems to play an important role in long term activity of surface. This was discussed in the previous work (2) and it was showed that the oxide film on the acid pickled surface breaks down easier than the oxide film on the as received Q-panel. This explains the higher anodic activity of acid pickled surface; this in spite of the fact that it has a similar surface profile to the as received Q-panel.

The results from an EIS examination after 2 hour contact with 1mM NaCl solution is shown in figure 6. The Table 1 shows values for charge transfer resistance and double layer capacitance

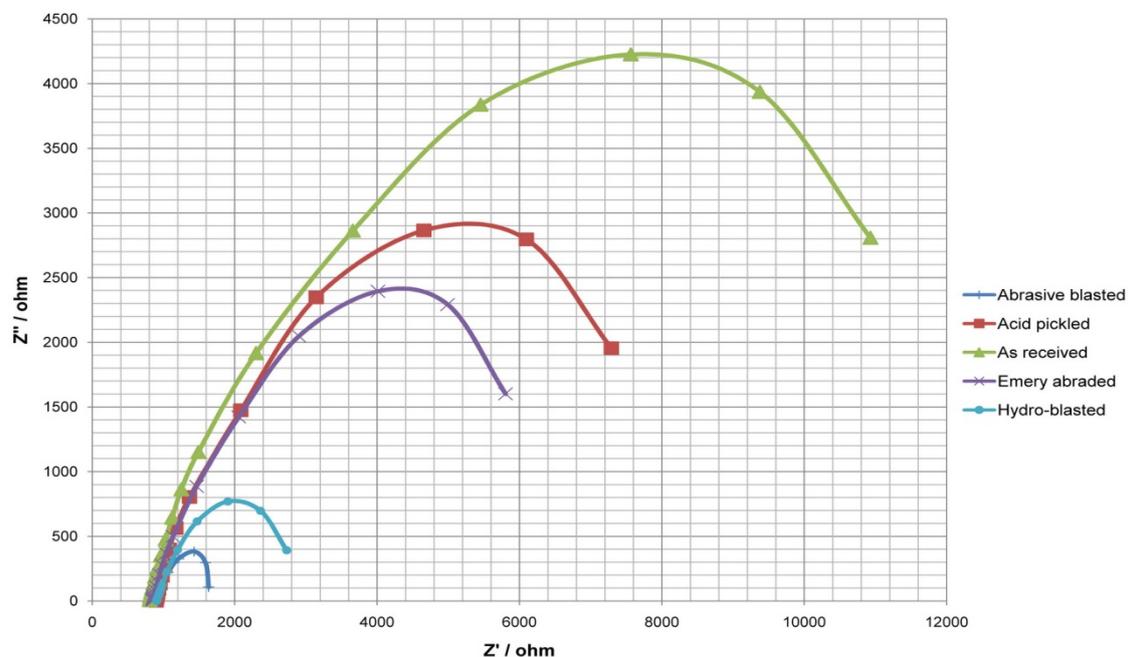


Figure 6. Nyquist plots after 2 hr contact with 1mM NaCl

Table 1. Charge transfer resistance and double layer capacitance values after 2 hrs contact with 1mM NaCl

	Abrasive blasted	Acid pickled	As received	Abraded	Hydro-blasted
R_{ct} ohm-cm ²	739.1	5988	9143	4737	1683
C_{dl} F/cm ²	0.002929	0.0001617	0.0001248	0.0002531	0.001539

Comparing the R_{ct} results with SVET results shows that there is an inverse relation between charge transfer resistance and surface activity. This indicates the greater ease of corrosion reactions on a more anodically active surface, although it has to be considered that introducing higher surface profile provides larger specific surface which may increase the apparent charge transfer resistance regardless of the type and structure of oxide layer. Table 1 provides electrical double layer capacitance of above surfaces. With regard to the equation $C = \epsilon_0 \epsilon_r A / l$ which expresses relation

between Dielectric constant, surface area and capacitance, higher capacitance of rougher surfaces can be reflected by their larger surface area and/or type of the oxide film.

It is traditionally believed that introducing higher surface profile enhances corrosion protection efficiency where the surface is coated by a polymeric coating. This has been considered as a result of increased adhesion strength between coating and substrate due to improved mechanical interlocking of polymeric coating into surface irregularities. This work seems to throw doubt on this assumption.

3.2 Alkyd coated steel surface

Further work has gone on to look at the different surface preparations when organically coated. The figures 7 and 8 show the change in the DC resistance of the five different surface preparations over a period of seventy five to one hundred days when coated with either an alkyd paint (fig 7) or an alkyd varnish (fig 8).

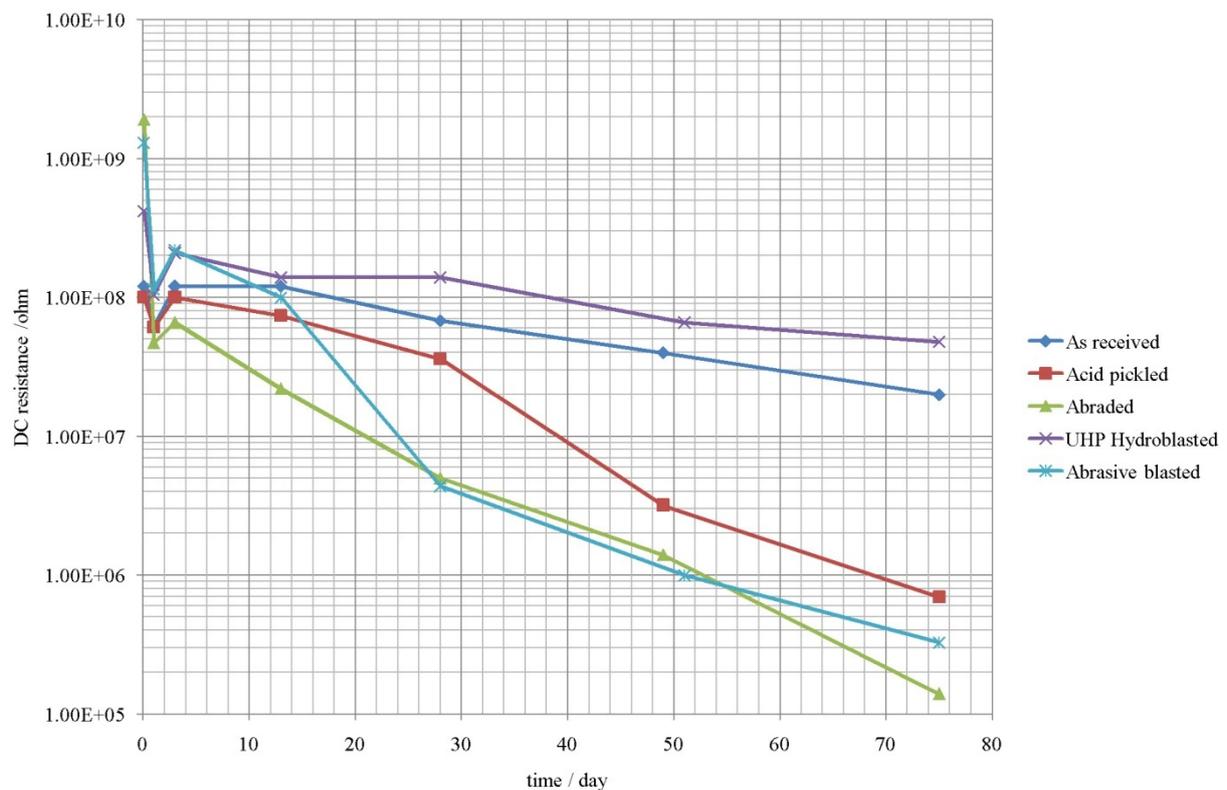


Figure 7. DC resistance of Alkyd paint in 0.5 M NaCl

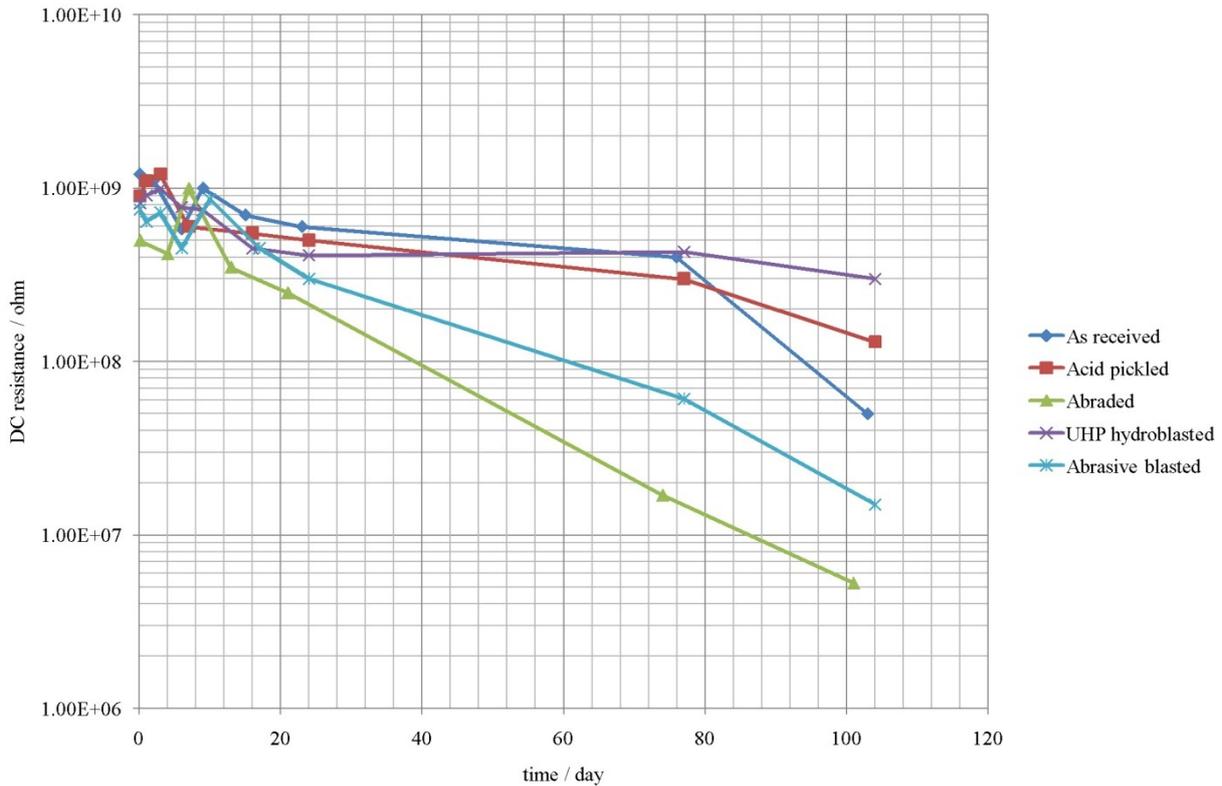


Figure 8. DC resistance of Alkyd varnish in 0.5 M NaCl

Fluctuation can be seen during the first 10-15 days of immersion which is probably due to the pore plugging process where the pathways are not opened up enough yet to let the corrosion product out. Soluble anodic reaction products while travelling through ionic pathways may meet oxygen and turn into insoluble oxide forms. Consequently the ionic resistance increases temporarily until chloride ions dissolve the oxide and open the micro-capillary. As the corrosion proceeds, delamination happens and the wet surface spreads beneath the coating. This occurs because of the hydrolysis of polymer bonds and/or dissolution of pre-existed oxide film on substrate. Consequently a larger fraction of the substrate will be exposed to electrolyte which drastically reduces ionic resistance and protection level.

With both pigmented and unpigmented coating systems the abraded Q-panel and abrasive blasted steel panel show the most remarkable deterioration. After 75 days the ionic resistance has dropped by about 4 orders of magnitude on abrasive blasted and abraded surfaces coated with alkyd paint. This was despite the fact that both systems were highest in protection at the very early time of exposure to corrosive media. Within 24 hrs of contact with the electrolyte, their ionic resistance has dropped down by about 1.5 orders of magnitude. It should be noted that both uncoated surfaces were quite active as observed by SVET. This suggests that although surface activation might be beneficial for making stronger electrostatic bonds with polar groups of polymeric coating but on the other hand it can provide stronger driving force for the polar water molecules to adsorb on the metal surface. With an oxide film sensitive to chloride and alkali, electrolyte spreads quicker at the interface and the protective efficiency reduces.

Despite the high surface activity of UHP hydro-blasted steel surface, evidenced by SVET, it shows relatively consistent protection when coated by either paint or varnish systems. This can be reflected by the passiveness of the pre-existed oxide

film in presence of alkaline condition. In general these results agree with work done previously on alkyd and vinyl painted surfaces (1)

Further work was done looking at the effect of the different surface finishes on the wet and dry adhesion of the coating. Figures 9 and 10 illustrate the mechanical wet adhesion strength of the coating systems.

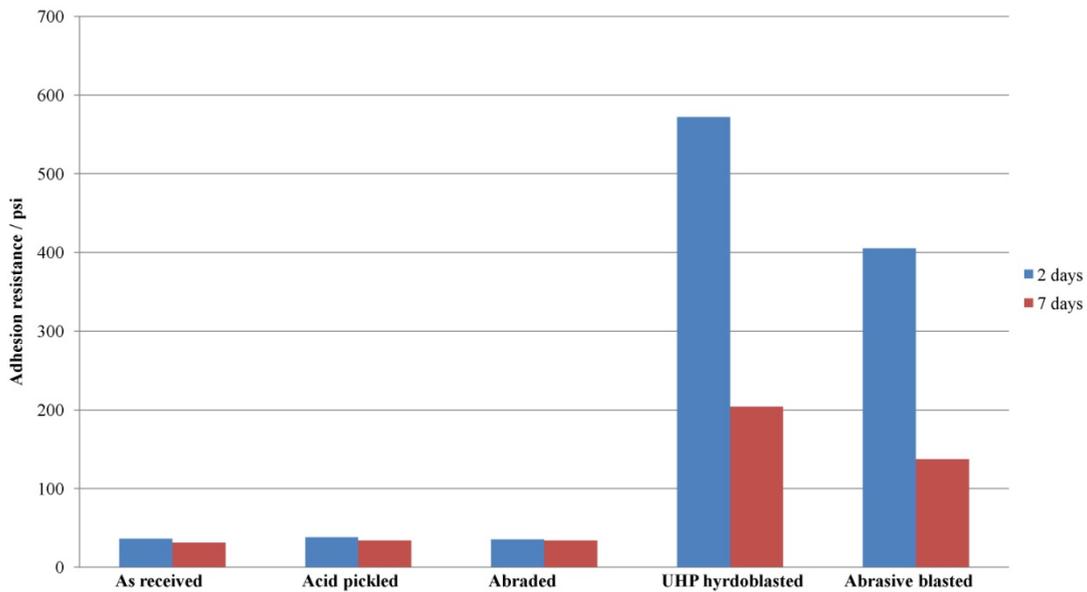


Figure 9. Wet adhesion of Alkyd paint in 0.5 M NaCl after 2 and 7 days contact

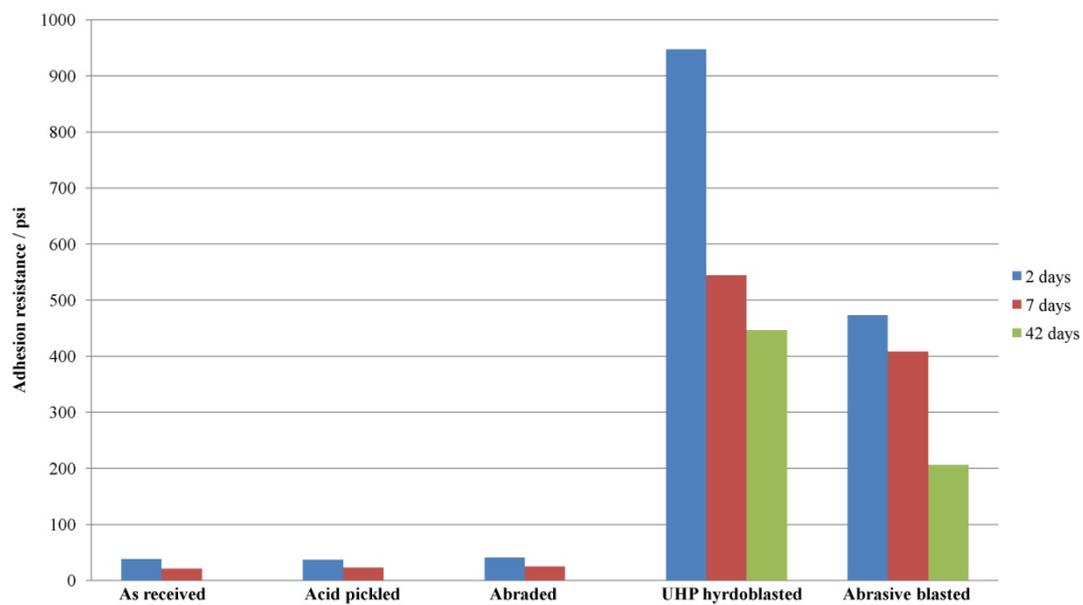


Figure 10. Wet Adhesion of Alkyd varnish in 0.5 M NaCl after 2, 7 and 42 days

These results show that there is not much difference between the wet adhesion of the as received, acid pickled and abraded samples. They are all low and also all are somewhat lower after 7 days compared with 2 days. The results for the UHP hydroblasted and the abrasive blasted (garnet entrained in water at 10 kpsi) samples are much higher with hydro-blasted giving higher adhesion than abrasive blasted.

These again show a drop between two days and seven days. They continue to show a reduction in adhesion up to 42 days with the higher adhesion of the hydroblasted (water jetted) samples compared with the abrasive blasted being maintained.

4. Conclusions

The two main factors that “received wisdom“ say determine the protectiveness of a coating system are surface profile and adhesion. The results presented here strongly suggest that other factors play at least as important, and quite possibly a more important part than these two. Certainly the surface reactivity of the surface appears to be a controlling factor. The implications of the work suggest that variables like cleanliness and oxide integrity (ease of dissolution of the oxide film) play an important role. The adhesion results are quite startling and further data and analysis of these will be presented in a later paper.

Acknowledgements

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