Rust Converter with Improved Adhesion for Topcoats

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Abstract

Surface preparation before application of protective coatings to badly maintained aging industrial facilities is particularly challenging on constructions that, for a variety of reasons, may be unsuitable for abrasive or water blasting. Rust converters applied to hand/power tool cleaned surfaces, which together with topcoats, offer corrosion protective characteristics matching those of blasted specimen, are of imminent technological and economical interest. This paper investigates the performance of VpCI CorrVerter on, corroded specimens cut from an aged, heavily rusted industrial construction that was exposed to coastal atmosphere. The rusted surface of specimens was characterized by: metallographic, SEM/EDS, XRD, surface chlorides and surface roughness measurements. Manually cleaned rusted plates were treated with conventional tannin and phosphoric acid based converters and the VpCI CorrVreter. Plates were subsequently coated with alkyd, epoxy and polyurethane coatings. Measurement of the impedance of the coatings was carried out by electrochemical impedance spectroscopy. Adhesion of coatings was measured by pull-off" and cross-cut techniques. Performance of rust converters was rated by comparison to the hand tool cleaned specimen without rust converters and to the Sa 2 ½ sandblasted specimen.

Keywords
rust converter; surface preparation; protective coating; electrochemical impedance spectroscopy;

Introduction

Degradation of industrial structures due to ageing-related mechanisms is becoming a key issue at a worldwide scale. [1-4]. The 'ageing' label is generally applied when structure displays a level of wear or obsolescence that raises the prospect of failure. Corrosion is considered one of the most important factors leading to age-related structural degradation. In particular, localized corrosion is dangerous as it may be accompanied by a corrosion failure such as loss of containment or braking of the metallic parts.

There are multiple benefits that arise from effective corrosion management because through successful corrosion management, very old industrial structures can be kept fit for purpose, never to reach a failed state [3, 4].

Protective coatings are the most widespread method of corrosion protection. In particular, they are the main means of corrosion protection of carbon steel, the most ubiquitous engineering metallic material. Besides acting as a barrier, to prevent the physical contact between the metal surface and the corrosive environment, protective coatings act as a resistive layer that diminish the flow of current in the corrosion cells. The electrical resistance of protective coatings may be taken as an indicator of the coating protective ability [5]. High quality coatings are excellent electrical insulators and typically have the electrical resistivity greater than 10^9 Ohm cm^2. Good quality coatings have resistivity between 10^8 and 10^9 Ohm cm^2, fair quality coatings have resistivity between $10^{6.5}$ and 10^8 Ohm cm^2 and poor coatings have resistivity lower than $10^{6.5}$ Ohm cm^2.

The performance of protective coatings applied to steel is significantly affected by the state of the steel surface immediately prior to painting. From a practical standpoint, Sa 2 ½ surface cleanness grade, rated according to ISO 8501-1 [6], is probably the best quality surface preparation that can be expected to today for existing facility maintenance work. However, abrasive blast cleaning is not always applicable to in service facilities.

Rust converters have been investigated in order to address the challenges of paint application to rusted surfaces in the past [7-14]. In the present study, the effectiveness of three types of rust converters to enhance the protective abilities of coatings applied to hand tool cleaned, heavily rusted surfaces, are explored.

Experimental

Two ASTM A283-03 grade C steel plates, approximately 1 m x 1m in dimensions, cut out from the same structure and of identical appearance, were used for tests. One of the plates was sandblasted. The appearance of the plate, a) before and b) after sandblasting, is shown in Figure 1. The nominal thickness of the plates was 7.5 mm.

The surface of specimens was characterized by: metallographic, Scanning electron microscopy and Energy dispersive X-ray spectroscopy (SEM/EDS), X-ray diffraction (XRD), surface chlorides and surface roughness measurements.

Metallographic test was done on microscope OLYMPUS BX51 following sample preparation by: encapsulating the sample in epoxy resin, polishing it with alumina suspensions of particle sizes 1, 0.3 and 0.05 µm and etching it with nital solution.

SEM and EDS were done on FEG QUANTA 250 SEM FEI microscope.

XRD analysis has been performed on corrosion products, removed from the plate and ground into powder. The XRD apparatus used was Philips PW 1830 HT generator, Ni filtered CuKα radiation tube, PW 1050 vertical goniometer with step scanning motor, proportional counter, PW3710 control electronics and system software. Analysis was made using characteristic radiation of copper cathodes to scan the samples between 5° and 80°, Kα lines.

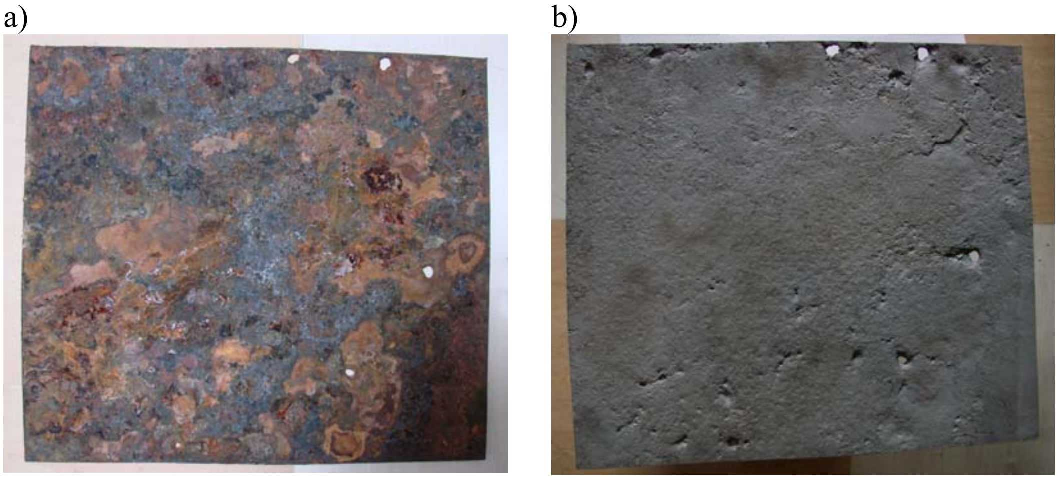

Figure 1. Specimen appearance before and after sandblasting.

Chlorides at the surface were measured, before and after sandblasting, by taking a sample using Bresle patch according to ISO 8502-6 [15], and measuring chloride content in the retrieved electrolyte by Oakton chloride selective electrode and Oakton PCD650 meter.

DeFelsco PosiTector 6000 with SPG probe was used for measuring surface roughness.
One sandblasted and one as received plate, were cut into 10 cm x 15 cm samples. Rusted samples were hand tool cleaned. VpCI CorrVerter and two commercial converters, one tannin based and one phosphoric acid based, were applied to the surface of the specimens according to the instructions of the rust converter manufacturers. The plates were further coated with one layer of epoxy, polyurethane and alkyd coatings, 100 μm in thickness. Coating was done by conventional air spraying, by professional applicators. The specimens prior to impedance measurements are shown in Figure 2,

Figure 2. Specimens with applied rust converters and polymer coatings prior to EIS measurements.

The investigated combinations of substrate, rust converter and polymer coating are given in Table 1.

Table 1. Combinations of substrate, rust converter and polymer coatings investigated.

System abbreviation	Substrate	Rust converter	Polymer
EPPJ	Steel sandblasted to Sa 2 ½	-	epoxy
EPHR	Hand tool cleaned steel	-	epoxy
EPKOHR	Hand tool cleaned steel	VpCI CorrVerter	epoxy
EPTNHR	Hand tool cleaned steel	tannin	epoxy
EPFOHR	Hand tool cleaned steel	phosphate	epoxy
ALKOHR	Hand tool cleaned steel	VpCI CorrVerter	alkyd
POKOHR	Hand tool cleaned steel	VpCI CorrVerter	polyurethane

Electrochemical impedance spectroscopy was measured using a press-on cell, 1.5 cm in diameter. Reference electrode, Ag/AgCl electrode, also acted as a counter electrode, due to the very low currents generated during the measurements. The amplitude of AC signal was 50 mV. Two electrode systems for measuring coating impedance have been explained else ware [16]. The measurements were done at form 10^{-4} to 10^{-2} Hz. The value of impedance at 10^{-1} Hz was extracted as it may be considered indicative for coating quality [5]. The electrolyte was 3.5% NaCl solution prepared with analytical grade NaCl and double distilled water. Impedance was measured by Palm Sens 3, Potentiostat/Galvanostat/Impedance Analyzer. Faraday's cage was used to avoid noise generated by the electrical appliances in the environment. The experimental setup is shown in Figure 3.

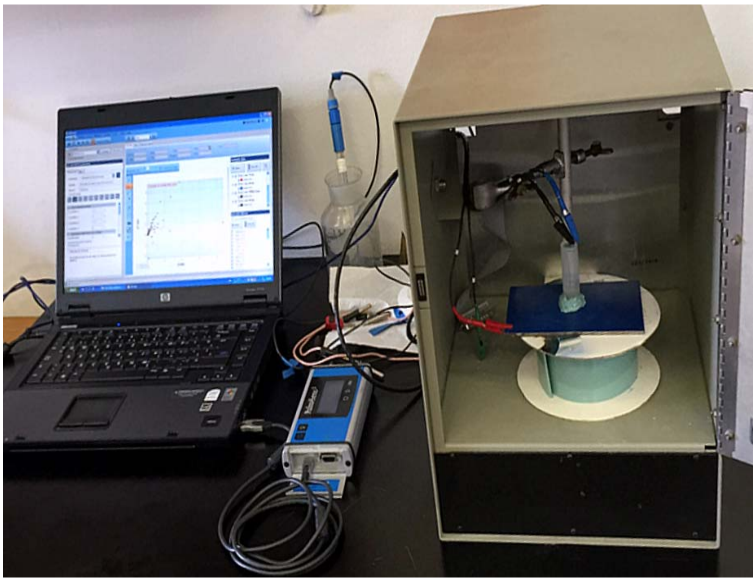

Figure 3. Experimental setup for EIS measurements on coatings.

Adhesion was measured using Elcometer 108 Hydraulic Adhesion Tester and Elcometer 107 Cross Hatch Cutter.

Results and discussion

The rusted plates used in this study show, both, general and localized corrosion. Metallographic analysis has been conducted in order to reveal the cause of localized corrosion that was not expected to happen on steel plates exposed to uniformly corrosive environment.

Figure 4. Microscopic image of the metallographic sample prepared from the investigated steel plate.

Figure 4 shows a microscopic image of the metallographic sample prepared from the investigated steel plate. It is readily observed that the steel has ferrite- pearlite microstructure with visible inclusions. Inclusions were further studied by SEM/EDS. Figure 5 a shows the morphology of an inclusion and Figure 5 b, its EDS map.

a) b)

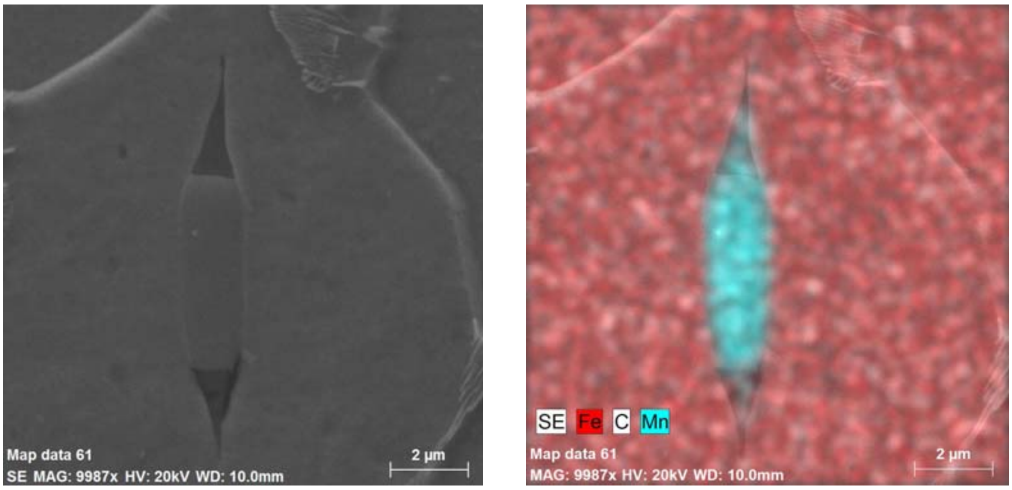

Figure 5. SEM image and EDS map of MnS inclusion at the investigated steel plate surface.

Apparently, relatively high S content in ASTM A283-03 grade C steel has led to formation of MnS inclusions. Localized defects in the lattice of the immediate surroundings of MnS inclusions are known to generate anodic sites, which initiate excessive iron dissolution [17]. The resulting excess Fe^{+2}/Fe^{+3} draws excess Cl^- into the region, and Fe^{+2}/Fe^{+3} hydrolysis acidifies these areas locally, which spurs more corrosion, which in turn dissolves the MnS inclusions. This has been a probable cause of macroscopic pitting observed at the specimen.
The XRD analysis (Figure 6) of the two types of corrosion products, firmly adherent black and loosely adherent brown-green, has shown that these were magnetite (Fe_3O_4) and a mixture of lepidocrocite (γ-FeOOH) and siderite ($FeCO_3$), respectively. The observed rust composition confirms with the process of abiotic corrosion [18].
Some of the surface cleaning methods, including hand tool cleaning, are unable to remove inner hard black scale but only remove loose top-scale. Besides the adherent scale that is not removed by hand tool cleaning, pitted surface presents an additional challenge for successful coating application. The recommended surface roughness of the abrasive blasted surfaces is 35-75 μm [19]. Surface roughness of the hand tool cleaned surfaces is not well defined. Still, the measurement on hand tool cleaned surface, shown in Figure 7 a, is indicative of surface that would be highly problematic for successful paint application and would warrant stripe coating. For comparison, measurement of surface roughness on sand blasted specimen is given in Figure 7 b.
Very high salt content equal to 3369 ppm was measured in the rust sample. Also, at the sandblasted, the measured value of 55.6 mg m^{-2} of Cl^- remained well above the required level of 25 mg m^{-2} of Cl^- [19].

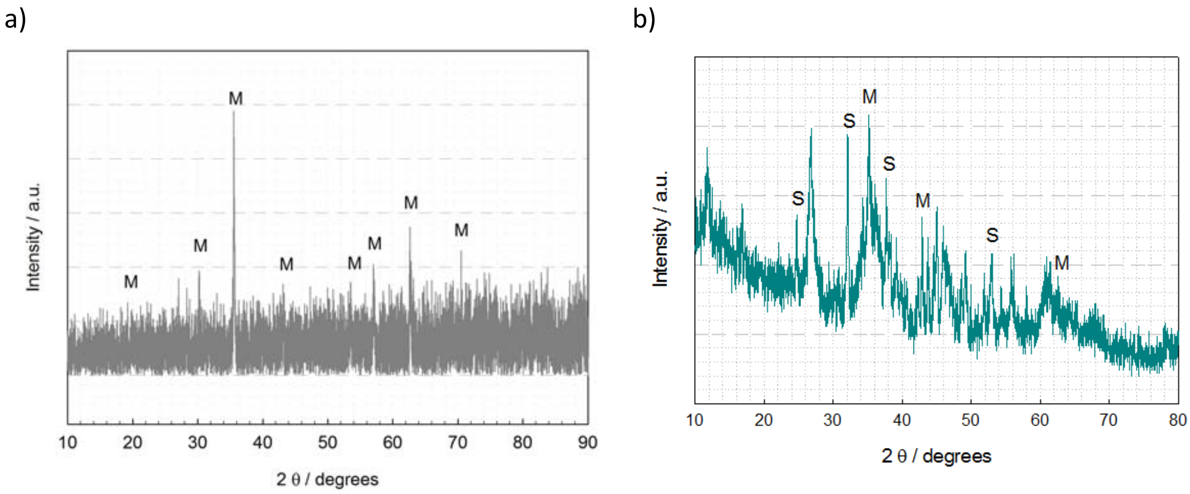

Figure 6. XRD spectra of black and brown-green corrosion product samples removed from the investigated rusted steel plates.

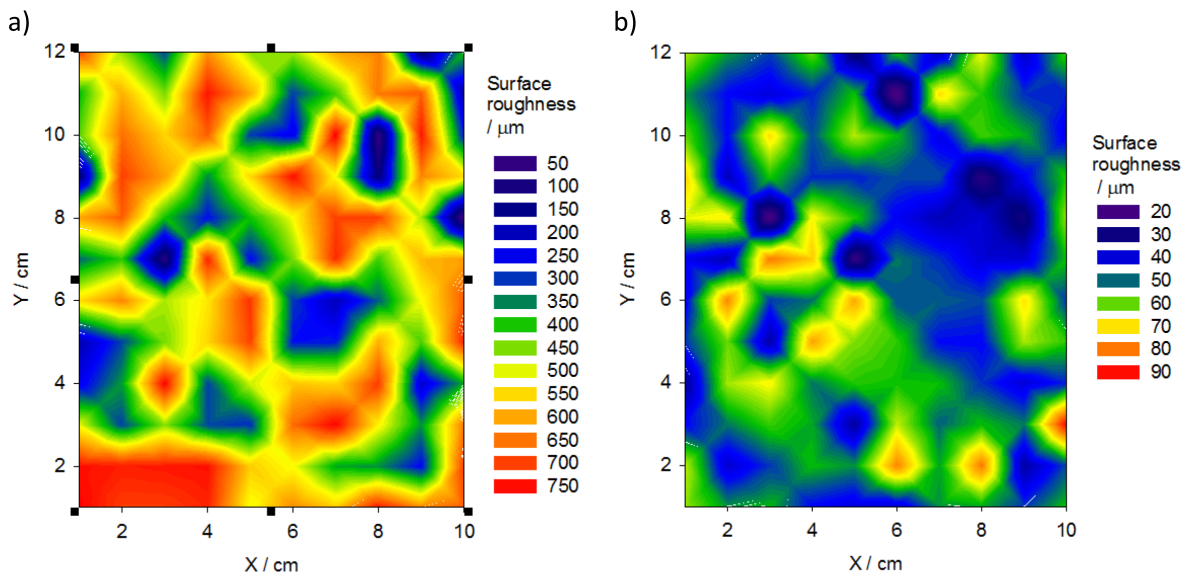

Figure 7. Surface roughness of specimen: a) before and b) after sand blasting.

In order to address the challenges of painting pitted, salt laden, hand tool cleaned surfaces, the systems given in Table 1 were chosen for rust converter testing by EIS measurements. The values of impedances at 0.1 Hz were extracted from impedance spectra (shown in Figures 8 and 9) and are presented in Figures 10 and 11, for various times of exposure of coatings to the 3.5% NaCl solution.

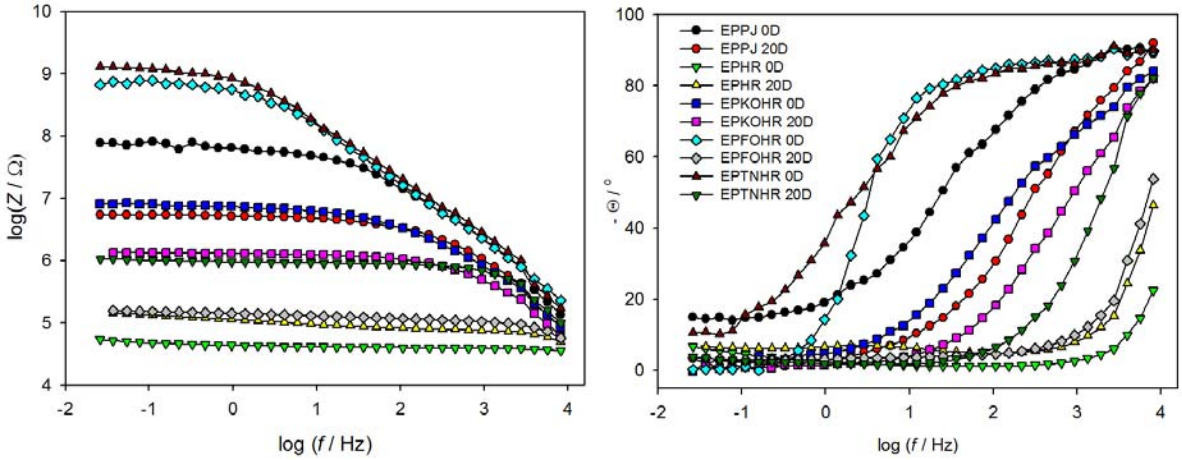

Figure 8. Bode plots of epoxy coated specimens, immediately after exposure to 3.5% NaCl electrolyte and after 20 days of exposure.

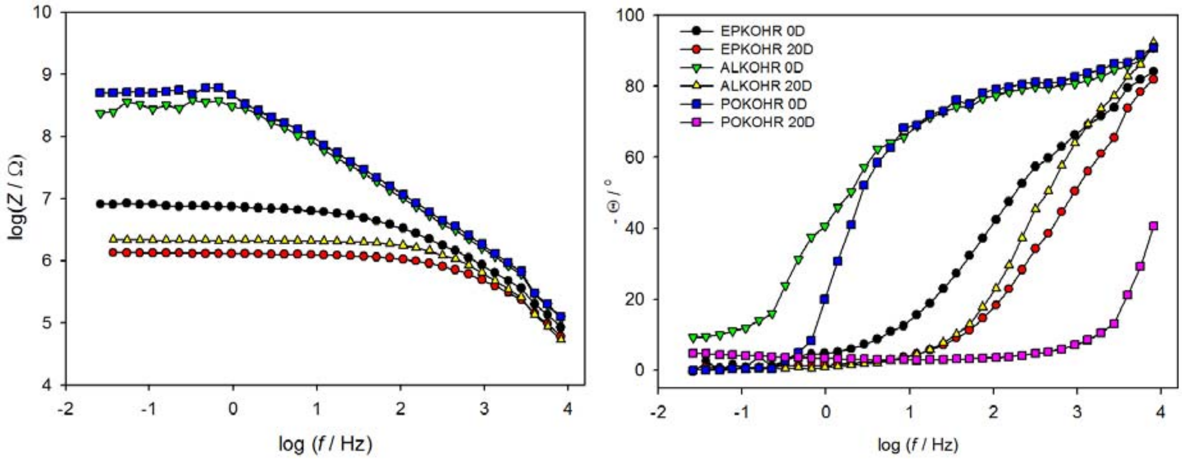

Figure 9. Bode plots of epoxy, alkyd and polyurethane coatings, on hand tool cleaned surface with VpCI CorrVerter, immediately after exposure to 3.5% NaCl electrolyte and after 20 days of exposure.

Figure 10 shows comparison of coating impedances at 0,1 Hz, for epoxy coated systems. It should be noted that the impedances are fairly low due to the fact that the coatings have been applied in a single 100 mm layer. This is also reflected on phase angle plots, that start at approximately -90^{o} and rise to almost 0, at low frequencies. One-coat system has been chosen to reflect the protective ability of the rust converter, more than the coating itself.

Epoxy coating applied to the sand blasted surface shows the highest final value of impedance after 20 days of exposure, approximately equal to 10^7 Ω cm^2. Epoxy applied to the rusted hand tool cleaned surface shows impedance approximately equal to $10^{5.5}$ Ω cm^2. Similar impedance is observed for epoxy applied to the rusted surface treated with phosphate converter. Tannin and VpCI CorrVerter treated surfaces show impedances between those attained for the hand tool cleaned and sand blasted surfaces, showing that these two treatments improve the protective ability of the coating applied to tightly adhering rust. In particular, for VpCI CorrVerter, the result is closer to that of the sand blasted surface than that of the hand tool cleaned one.

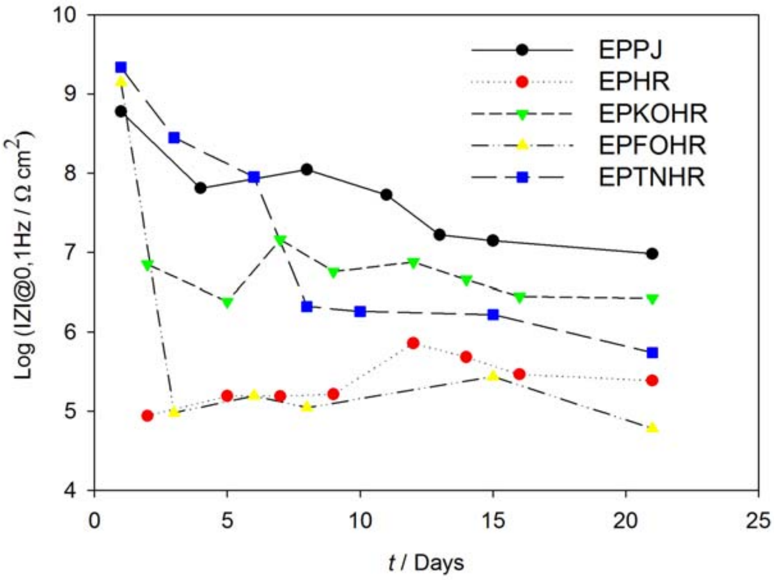

Figure 10. Time dependence of coating impedance at 0.1 Hz for epoxy coating systems combined with various rust converters and substrates.

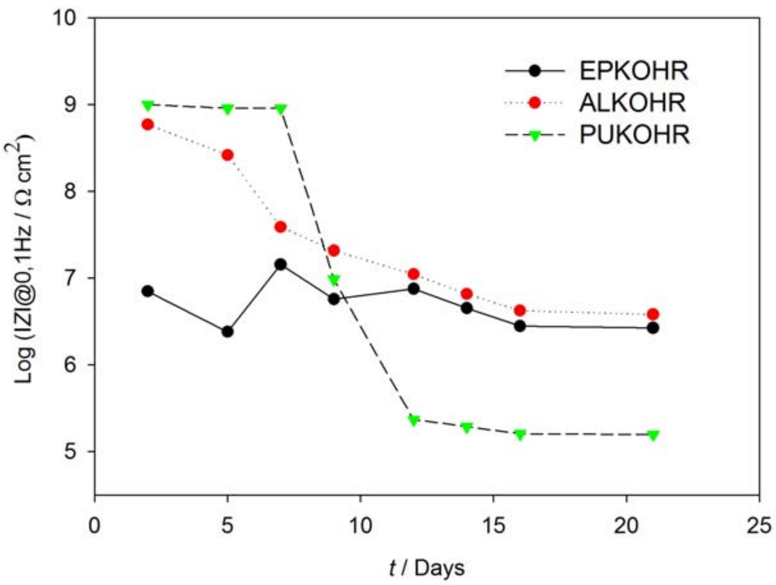

Figure 11. Time dependence of coating impedance at 0.1 Hz for various coating systems combined with CorrVerter and rusted hand tool cleaned substrate.

Figure 11 show that a similar behaviour is to be expected for alkyd coatings applied to hand tool cleaned steel treated by VpCI CorrVerter, while the polyurethane coating showed a sudden decline in protective ability after 1 week of exposure. It should, however be noted that in the case of VpCI CorrVerter, which is the only of the three investigated converters that has a resin base and therefore is more viscous than the tannin and phosphoric based formulations. Hence, the results not only reflect the protective ability of the converter, but also the thoroughness of application to the substrate of problematic geometry, similarly as for the coating. A detailed specification for each type of rust converter application is required for attaining their beneficial influence on coating protective ability.

Measurements of coating adhesion by pull-off technique proved to be problematic on all coated substrates that were previously hand tool due to inability to seal the dollies firmly to the surface of the coating because of the surface irregularity.

As an alternative, a cross-cut test was done in the case of various coating types in combination with VpCI CorrVerter that yielded results relevant to the one-layer coating adhesion to the rust layer. The results shown in Figure 12 show good adhesion that can be rated as 0 according to ISO 2409 standard [20].

a) b) c)

Figure 12. Cross-cut test results for epoxy, alkyd and polyurethane coatings on hand tool cleaned rusted surface treated by VpCI CorrVerter.

Conclusions

Various combinations of substrate, rust converters and polymer coatings have confirmed beneficial influence of VpCI CorrVerter and tannin type converter on overall system protective ability. For phosphate converter, the improvement over converter untreated surface was not observed.
VpCI CorrVerter applied to hand tool cleaned steel covered with epoxy and alkyd coatings, yielded results closest to that obtained in the case of epoxy applied to Sa 2 ½ sand blasted surface. All three types of coatings investigated, epoxy, alkyd and polyurethane, applied over the VpCI CorrVerter layer, adhered well to the hand tool cleaned substrate.
Extremely high degree of surface roughness may significantly reduce the efficiency of rust converter and coating application. A detailed specification, based on laboratory trials and practical observations, describing appropriate technique of rust converter and coating application, is imminent for attaining their synergistic protective ability.

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