A Comparison of the Long-Term Outdoor Performance of Two Modern Paint Coating Systems and a Traditional Lead-based Paint Applied to Historic Wrought Iron

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Abstract

A real time 5-year outdoor study compares the performance of three paint systems (traditional oil based; acrylic; epoxy resin) applied to naturally corroded wrought iron, with their surfaces prepared to Swedish Standard Sa2.5 or Steel Surface Preparation Standard ST3. Interim data at 2 years reports on gloss, colour change, pull-off testing and EIS measurements. Traditional oil-based paint exhibited significant visual change; a modified alkyl paint underwent minor but visually undetectable changes and an epoxy/acrylic coating remained unchanged. The oxide layer in ST3 controlled adherence of the coatings.

Keywords

Protective coatings; wrought iron; electrochemical impedance spectroscopy; colourimetry; pull-off; gloss

1. Introduction

1.1 Conservation of historic ironwork

Wrought iron corrodes readily in the atmosphere to produce permeable, non-protective corrosion products that laminate and spall, a process enhanced by regular wet and dry climate events (Hoerlé et al. 2004). Coatings are commonly used to control corrosion but since their limited lifespan makes this a costly process, research aims to identify the best performing coatings to support cost benefit decisions. Decision-making in selection of coatings, surface preparation methods and application protocols within heritage is mostly based on best practice and well-established techniques (Blackney and Martin 1998). Quantitative evidence of coating performance is more often found in commercial or industrial research. Unfortunately, rationales and acceptable methods and outcomes in these sectors are often governed by different ethical and aesthetic decision-making processes when compared to historic contexts.

Conservation practices for coating historic iron may use commercial standards alongside methodologies such as flame cleaning, where variable control lies with the individual (Emmerson et al. 2019). This does not align with the needs of coating manufacturers. Many coatings used commercially have performance characteristics that require adherence to defined standards to guarantee their service life. These normally involve specified surface preparation and coating application methods, as well as defining the necessary environmental parameters for successful coating application. Fulfilling much of this guidance within historic contexts is difficult, due to the corroded nature of the material, limitations imposed by differing ethical and aesthetic standards and the cash poor state of the sector.

Ethical constraints and numerous variables make designing experimental research to replicate the reality of conservation practice difficult to achieve and compromises may need to be sought. A major advance would be to identify the ‘weak link(s)’ in the variable chain; essentially identifying which variable(s) dictates coating performance the most and, if possible, developing this to provide a rank order. This would facilitate informed decisions when balancing factors like ethics and aesthetics against longevity and cost benefit.

While real time testing and a representative sample set are essential factors to underpin quantitative prediction of coating lifespan, this can only offer an indication of coating performance in the environment adopted for the test procedure. Some quantitative methods such as EIS (Cano et al. 2010) can provide useful comparative data but this cannot be extrapolated to provide predictive insight into service life performance, due to the essential but unrealistic test conditions and an absence of real time testing. Visual change, sometimes scaled according to international standards, is useful but the qualitative data this produces may limit insight into the relative extent of failure and the precise prediction of coating performance.

Following the concept of assigning value to both quantitative and qualitative indicators of performance, the study reported here employs a mixture of quantitative and qualitative assessment techniques to produce an integrated insight into coating performance. Real time testing of historic wrought iron, with surfaces prepared by two commonly used techniques within historic wrought iron preservation, is used to study the performance of three coatings that represent traditional and modern approaches within the sector. A single pack oil-based alkyd and a two-pack epoxy resin/acrylic urethane are compared with a lead-based, linseed oil system traditionally used for the long-term protection of iron. Their performance is assessed using a range of criteria including their longevity, ease of use, reversibility and health and safety issues. Hopefully, the results will allow a reasoned assessment of their performance, so that the conservator can make informed choices about the materials and methods to use when painting historic ironwork.

1.2 Aims and objectives

Aim:

- To determine the long-term, real-time performance of two modern protective coating systems and one traditional system for exterior ironwork.

Objectives:

- To coat samples of historic iron and control samples of glass with one of three coating systems.
- To assess qualitatively the application of the coatings to historic wrought iron relative to conservation practices.
- To expose the coated samples to outdoor conditions for a period of 5 years.
- To assess the visual and protective properties of the coating systems by colorimetry, gloss measurement, pull-off testing, electrochemical impedance spectroscopy and oxygen consumption at 12-month intervals throughout the study period.

This preliminary paper reports the results of the first 24 months of outdoor exposure of the samples. Oxygen consumption method and results are not reported as it is too early for meaningful data to be presented.

2. Method

2.1 Sample material

Samples were produced from two rolled wrought iron sheets from a 19th century gasometer. Although wrought iron is inhomogeneous by nature (Dillmann et al. 2004), taking samples from just two rolled plates minimised the risk of compositional differences. The sheets had thicknesses of 4mm and 6mm and were cut using a hydraulic guillotine to avoid microstructural changes from heat-generating cutting processes. Corrosion during exterior exposure has generated corrosion products including magnetite, goethite and lepidocrocite on the surface as identified by x-ray diffraction (Emmerson et al. 2019).

2.2 Surface preparation

The samples were prepared to two levels of cleanliness prior to coating (Table 1). 96 samples were cleaned to Swedish Standard Sa2.5 (ISO 8501.1:2007) using abrasive blast cleaning to achieve a near white blast cleaned surface (Joint Surface Preparation Standard SSPC-SP10). 144 samples were cleaned to a Steel Surface Preparation Standard ST3 (ISO 8501.1:2007), achieved by thorough hand and power tool cleaning to leave the metal surface with a sheen appearance. Control samples of float glass cut to the same dimensions, oil gilded and coated in the same manner as the wrought iron samples allow for examination of changes in the coatings over time independent of the wrought iron substrate.

Table 1. Details of all samples as prepared for the range of analysis techniques.

Figure 1. Sample surfaces uncleaned, cleaned to Sa2.5 and ST3 and following application of the three coating systems.

2.3 Coating

Sample coupons were brush painted with one of the three paint systems chosen (Table 2).

Table 2. Details of the coating systems as applied to the samples.

2.4 Characterisation of coatings as applied

Following application, the coating thickness, gloss, and colorimetry measurements were recorded for each coating. A control sample of coating systems is stored in the dark throughout the test period to allow for comparison with samples undergoing outdoor exposure.

2.5 Outdoor exposure

Samples are mounted between strips of extruded ‘H’ section PVC fixed to a stainless-steel frame angled at 60^{o} to the horizontal (Figure 2). Each sample frame is fixed off the ground in a south-facing direction. The samples are exposed in a location whose conditions are between a low (C2) and medium (C3) risk environment category (BS EN ISO 12944-2) on the edge of a small inland town. Onset HOBO data loggers record air temperature, relative humidity (RH), surface wetness, and cumulative light exposure in real time throughout the outdoor sample exposure period. This data will be collated to relate weather patterns to coating performance.

Figure 2. Samples mounted on their exposure frame with the environmental monitoring equipment fitted.

2.6 Assessment of coating performance

Coating performance, both protective and aesthetic, is assessed annually using oxygen consumption in a fixed relative humidity (RH), electrical impedance spectroscopy (EIS), pull-off adhesion testing, colorimetry, gloss measurement and digital photography. As EIS and pull-off testing are destructive techniques, these samples (Table 1) are not returned to outdoor exposure. Oxygen consumption samples are returned to outdoor exposure after measurement being remeasured each year.

2.6.1 Electrical impedance spectroscopy

Electrical impedance spectroscopy (EIS) can be used to characterise the behaviour of an electrical system by applying a small electrical excitation signal (sinusoidal voltage) to the system and measuring the response (current) created (Orazem, Tribollet 2017). The frequency of the signal is varied, and the resulting responses can be analysed using electrical methods (Cogger and Evans 1999). EIS has been used as a tool to test varying coating types since the mid 20th century and has recently been applied to the field of heritage science (Amirudin, Thierry 1995; Cano, Lafuente, Bastidas 2010; Barat et al. 2019). EIS spectra are produced either showing the impedance Z (the ratio of voltage over current), and phase angle Φ, known as a Bode Plot, or in polar coordinates with real and imaginary elements (Nyquist Plot). These plots provide information on the performance of a coating with impedance values reducing as a coating begins to fail.

One corner of each EIS sample was tapped with an M4 thread to fit an electrical connection post. The sample was placed on a Gamry Instruments PTC1 Paint Test Cell (Figure 3). The cell was filled with 40ml of electrolyte before a graphite counter electrode and saturated calomel reference electrode were inserted into the top. The circuit was completed by connecting the sample terminal to form the working electrode. Synthetic rain was chosen as the electrolyte to match the real time exposure environment more closely. This was developed for the assessment of copper alloys and steels in outdoor environments (Letardi et al. 2016). It contains several soluble salts and is used at a 10x concentration. The analysis was carried out using an Amtek/Princeton Applied Research Parstat 3000a Potentiostat/Galvanostat instrument with the acquired data being processed using Rhd Instruments RelaxIS 3 Impedance Analysis software.

Figure 3. Painted coupon mounted in the test cell.

2.6.2 Pull-off adhesion testing

Adhesion of the coating systems was examined by pull-off testing according to BS ISO 4624:2016. This measures the force required to pull-off a specified diameter of coating using hydraulic pressure. The technique records the highest pressure required to detach all or part of the paint coating from the substrate surface. Coatings might fail at the substrate surface or within/between coating layers.

Each test area was lightly cleaned and abraded using a 3M Scotchbrite pad (7447) before degreasing with industrial methylated spirits. A 20mm aluminium dolly was bonded to the paint surface at each test site using Araldite 2021-1, a two-part methacrylate adhesive. Eight dollies were adhered to each sample and left for 24 hours for the resin bond to form fully. The test area was separated from the surrounding adhesive using a cutting tool (Figure 4) and adhesion tested using a Deflesko Positest AT-A Pull-off Adhesion tester.

Figure 4. A 150mm x 150mm sample coupon being prepared for pull-off measurements.

2.6.3 Colorimetry

To assess colour change, 36 colorimeter measurements were made on each large sample using a Konica-Minolta CM700d portable sphere-type spectrophotometer every 12 months (Figure 5). Results are processed using Konica Minolta SpectraMagic NX software. Colorimetry measurements are compared with the previous measurement 12 months before and with the control samples stored in the dark.

Figure 5. The Konica-Minolta CM700D Colourimeter instrument and a sample with overlaid template.

2.6.4 Gloss

The gloss of a surface relates to its level of reflectivity and for paints is defined under ISO 2813 2014/ASTM D532 (Chadwick, Kentridge 2015). The Standard specifies a method of using three geometries of 20º, 60º and 85º to measure the gloss level of a coating by quantifying the reflectance of the surface. A sample mount was used to ensure the gloss measurement could be repeated in the same position every 12 months, the gloss of each sample was measured using a Rhopoint Novo-Gloss Trio 20/60/85 glossmeter and repeated after rotating the sample by 90º.

3. Results

3.1 Visible change

Neither the alkyd nor epoxy system samples show any visible change after 24 months of outdoor exposure. The lead/linseed oil system, however, exhibits distinct change including chalking, shrinkage, and cracking of the finish coat (Figure 6).

Figure 6. Lead paint sample before exposure (left) and after 24 months in outdoor exposure (right) showing chalking and cracking of the finish coat.

3.2 Electrochemical impedance spectroscopy

Representative electrical impedance spectroscopy Bode plots are presented for all coating systems and surface preparation methods at 12 and 24 months (Figure 7).

Figure 7. Typical Bode plots for the three different coating types after 12- and 24-months exposure.

3.3 Pull-off adhesion testing

The results of pull-off testing at 12 and 24 months are given in Figure 8 and Table 3. The average pull-off values, their range and the mode of failure of the system are provided. Pull-off testing was not carried out at 0 months as the curing of the coating systems could not be guaranteed to be complete.

Figure 8. Boxplot showing the pull-off values for samples coated with the three coating systems prepared to Sa2.5 and ST3 showing the range of values attained. The box represents the interquartile range, the horizontal line within the box denotes the median and the upper and lower whiskers show the maximum and minimum values.

Table 3. Average pull-off values and modes of failure for samples coated with the three coating systems at 12 months.

3.4 Colorimetry

The average colorimeter values as measured for samples of each coating system at 0 and 24 months of outdoor exposure are given in Table 4. The difference between the values at 0 and 24 months are used to produce the dE*, dL*, da* and db* values which express the change in colour over the exposure time.

Table 4. Colorimetry values expressed in the L*a*b* colour space with average values for samples at 24 months exposure compared to values for samples at 0 months exposure to produce dE*, dL*, da* and db* values as a measure of change. The threshold for visible change is dE*ab ≥ 1.5.

3.5 Gloss

The average gloss values for samples of each coating type exposed for 0, 12 and 24 months are given in Table 5.

Table 5. Gloss values (Gloss Units) at 20º, 60º and 80º for samples of each coating type exposed outdoors for 0, 12 and 24 months.

4. Discussion

4.1 Visible change

After two years of outdoor exposure there have been some measurable and observable changes to the paint coating systems applied to the wrought iron samples. One of the clearest signs that a coating may be beginning to lose its protective properties is a change in its appearance. This can serve as an early warning that the heritage metalwork may be at risk. To date, this is only noticeable on the lead painted sample coupons (Figure 6). Observable after 12 months, by 24 months the lead-based linseed oil coating exhibits dramatic change in the appearance of its finish coat. Not only has the surface lost much of its colour, but it has also chalked, shrunk, and cracked, likely due to loss of binder. Despite the lack of visible change in the alkyd and epoxy systems, the analytical techniques applied here reveal that all the coating types have begun to show signs of deterioration.

4.2 Electrical impedance spectroscopy measurements

EIS measurements taken after 12 months revealed that for both sets of metal samples painted with the alkyd and epoxy resin systems (Figure 7), the coatings were acting as capacitors, essentially non-conducting, with an electrical resistance of greater than 10^8 Ω cm^2. This is confirmed by creating an equivalent electrical circuit as a simulation. For the lead painted samples, the response was slightly different (Figure 7). Electrical resistance was lower after 12 months (~10^6 Ω cm^2) and had reduced to < 10^3 Ω cm^2 after 24 months. The performance of the coating was deteriorating, acting as both a resistor and capacitor. A small amount of current (amps, Ω) is flowing through the paint layers but the coating provides increasing resistance as the frequency (Hz) increases. For the alkyd and epoxy coatings the levels of electrical resistance had reduced slightly after 24 months.

4.3 Pull-off tests

Examining the pull-off test results (Figure 8; Table 3) reveals differences in the strength of each coating system and the influence of surface preparation level. After 12 months the alkyd (System 1) and epoxy resin (System 2) systems on surfaces blasted to Sa2.5 exhibit the greatest bond strength with overlapping value ranges (Figure 8) showing that there is no significant difference between the two. Adhesive failure between the coatings or between the topcoat and the dolly demonstrates that the adhesive bond of the primer to the substrate metal exceeds these values. For samples of alkyd and epoxy systems which were prepared to ST3, failure occurred within the remaining compact oxide layers on the metal surface. This shows that the weakest point in the protective system is within the oxides themselves.

With lead painted samples at 12 months, the failure occurred at the lowest forces. Failure at the interface between the primer and degraded finish coat layers is unsurprising given the extent of visible damage to the finish coat which includes shrinkage and cracking demonstrating poor adhesion to the undercoat.

4.4 Colour and gloss level changes

Both the colorimeter measurements and the gloss meter results showed that the paint surfaces have become altered. This is exhibited as subtle colour changes (Table 4) and a gradual reduction in the gloss level of the paint surface (Table 5).

Colour change for the alkyd (System 1) coated samples falls just above the threshold for a visible change although this was not perceived by the observers. The colorimeter values indicate that there has been a slight darkening of the topcoat which has become slightly more red and less yellow. Changes in the epoxy (System 2) coated samples do not meet the threshold for visibility but they exhibit a slight darkening and have become less red and more yellow. The biggest change is seen in the lead/linseed oil (System 3) coated samples whose change value exceeds the visible threshold by 7 times and indicates that the coating is lighter, more red and less yellow. This corresponds well to the chalking of the finish coat and the appearance of the red undercoat through the cracks in the finish coat.

Gloss Units (GU) are the measurement scale based on a highly polished black glass standard that gives a reflectance of 100GU at a specified angle. The angle of measurement is altered according to the level of gloss. The measurements taken at 60° revealed that the alkyd (System 1) coated surfaces have reduced in gloss level from a High (>70 GU) to a Medium Gloss (10 – 70GU) level even within the first 12 months. For the epoxy (System 2), the gloss level has largely remained unchanged after 24 months (Table 3). The original acrylic urethane finish coats applied gave a sheen rather than gloss finish. As the original level of gloss was low (<10GU) the most appropriate measurement values to use are at 85°. The lead painted samples showed significant changes to their gloss levels (Table 5). The initial gloss level was very low (>10GU) at a measured angle of 85°, and this has reduced to almost zero after 24 months exposure.

5. Conclusions

This paper has reported preliminary findings of a five-year study examining the real-time performance of three protective coating systems for historic wrought iron exposed outdoors. Even in the limited exposure period to date, it is possible to identify significant changes in the traditional lead coating which may continue to perform a protective function for the iron substrate but has completely failed in an aesthetic capacity. Aesthetic changes in the alkyd and epoxy systems are minor, being barely or not noticeable.

The findings reveal that preparing the surfaces to ST3 means that with the alkyd and epoxy systems, the corrosion product layers themselves are the primary weakness in the protective system. This has implications for heritage where justifying the loss of original material associated with blasting to near white metal can be challenging.

The initial results from the EIS measurements reveal that the epoxy resin coatings are the best performing with the alkyd paints also maintaining a high level of protection. The lead coatings show the greatest changes in their performance.

The next three years will see the coating performance challenged further by exterior exposure and the mode and extent of any breakdown of the coatings will be reported in future papers.

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