

Corrosion Protection for Complex Large Equipment

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Keywords

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Introduction

Dover Castle on the south east coast of England has the longest recorded history of any in Britain. Three brick-lined casemate tunnels were excavated under the famous White Cliffs to house troops during the Napoleonic Wars. These tunnels housed Rear Admiral Ramsey's headquarters for the evacuation from Dunkirk during World War II. The tunnels are partially presented as they would have been during that period. The presentation includes large amounts of historic steel cabinet-type telecommunications equipment in the Repeater Station and Equipment Room, see Figure 1. The porous nature of the chalk, and close proximity to the sea, give rise to an extremely aggressive atmosphere inside the tunnels towards steel and copper alloys. The historic original natural ventilation system for the tunnels was supplemented, for their use as a headquarters, with the addition of sets of fans and filters at the cliff face in each casemate. Mild steel trunking, is used to distribute the air down the length of the casemate. The fans for the central casemate ran twenty four hours a day, whilst those for the two outer casemates only ran when the site is closed overnight. After a serious outbreak of mould in 2002, additional free standing fans and some background heating were introduced in vulnerable areas. The very large visitor numbers attracted to the tunnels, (in excess of 600,000 in 2013), causes large amounts of dust to be deposited on surfaces, despite chest high open wooden barriers restricting access into many of the collection spaces. An environmental assessment of the tunnels has been carried out for the collections on display. The results for metals have been reported (Thickett 2008). Immediately after the initial work, completed in 2005, it was clear a very efficient corrosion inhibitor would be required for the steel in the tunnels and practical trials began exposing steel coupons coated with a selection of recommended materials. The metal composition of the repeater units was analysed with a Bruker Tracer III/IV to help design the experiments. Analysis used the instruments built in database. The validity for historic alloys was confirmed by analysing 13 different steel samples of known type, which the instrument correctly categorised. The most common metal present in the repeater units was low carbon steel. The associated plastics present in the Repeater Station were analysed with a portable near infra red, NIR spectroscopy (ASD

LabSpec 2500 dispersive NIR instrument with fibre optic probes. Results are shown in Figure 2.



Figure 1. The Repeater Station in the Secret Wartime Tunnels at Dover Castle.

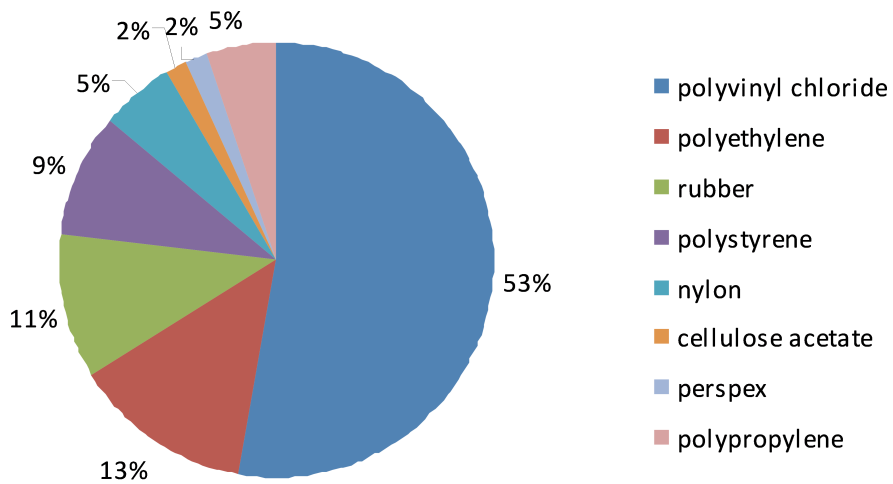


Figure 2: Numbers of types of plastic present in the Repeater Station

The ventilation system was adapted to ‘smart’ ventilation in 2010 with air being filtered and brought into the tunnels only when its absolute humidity was lower than the average of the readings inside the tunnels. Whilst this slightly lowered the overall average RH, conditions are still very aggressive in the Repeater Station.

The environmental conditions in the chalk tunnel are extremely aggressive towards steel and rapid corrosion has been observed on most objects. The relative humidity averages 82% and reaches 95% in the autumn, see Figure 3. The maritime location introduces amounts of chloride through indirect aerosol deposition. The filters on the ventilation system effectively remove sea salt aerosol (monitoring in the ducts confirmed very low particulate concentrations). However, the salt deposits on the ground above the tunnels, and percolates through the porous chalk and effloresces inside the brick linings of the tunnels. The salt is redistributed by the large visitor numbers. A strong correlation of suspended and deposited particulates with visitor activity and numbers has been reported (Thickett 2008). Chloride deposition rates were measured at four locations in the Repeater Station. Glass slides were also changed monthly. The slides were extracted with 15ml of 18.2MΩ cm water. The extracts were analysed with ion chromatography (Dionex DX600 with AS14A column, 8mM sodium carbonate, 18mM sodium bicarbonate eluent).

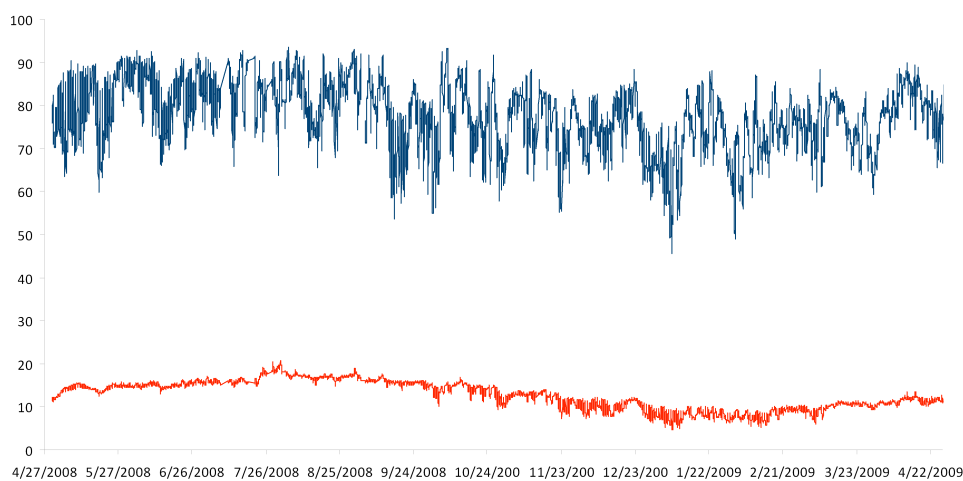


Figure 3: Temperature and Relative Humidity at front of Repeater Station.

Results are shown in Figure 4. The chloride deposition rates are not particularly high, corresponding to ISO 9223 S₀. The particulate deposition rate does not fall off with distance from the visitor route as reported from previous studies (Lloyd et al 2002). This is probably a combination of the higher visitor numbers (600,000 per annum, compared to 150,000

maximum in Lloyd et al) and the effect of the directional ventilation system. Similar effects have been observed during deposited particulate monitoring at the British Museum.

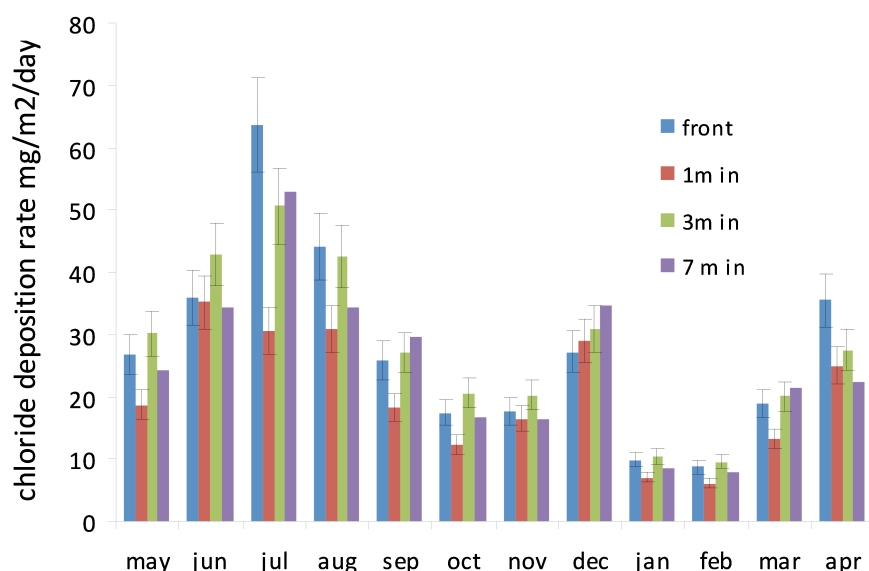


Figure 4: Chloride deposition rates as dust.

Methodology

Selection of Corrosion Inhibitors

A range of materials, reported to be in use and recommended by external conservators acting as consultants to English Heritage, were tested. The complex nature of repeater units precluded many coatings such as Paraloid B72. Renaissance wax was included in the testing as it was the preferred method used by English Heritage conservators. They needed to be transparent, readily applicable over large, complex surfaces, useable with minimum health and safety precautions and ideally with a minimum 3 year lifetime, before re-application. The repeated units are complex, with several other materials in close proximity to the metal and the materials need to have no adverse effects on these materials.

In Situ Corrosion Protection Tests

Each of the corrosion inhibitors and coatings was applied to 15 by 40mm coupons cut from 0.2mm low carbon steel sheet, according to manufacturer's instructions or common conservation practise. The steel sheet was abraded with 1200 grade silicon carbide paper and degreased in propanone, followed by drying over silica gel. The coupons were placed at two

locations within the Repeater Station; besides the public barrier and 7 m into the tunnel. These locations were used to account for the effect of visitors on redistributing dust and especially chlorides. There is also a RH gradient down the tunnel with the front (visitor end) experiencing lower RH values. The temperature and RH at each point was monitored with ACR SmartReader SR002 loggers. Glass slides were also deployed and changed quarterly. The amount of dust falling on glass was determined with automated microscopy and image analysis (Howell 2002). The slides were extracted with 15ml of 18.2M Ω cm water. The extracts were analysed with ion chromatography (Dionex DX600 with AS14A column, 8mM sodium carbonate, 18mM sodium bicarbonate eluent). The coated coupons were analysed monthly with image analysis. A Canon Powershot A75 camera was placed on a 40mm Perspex ring above the coupon and an image acquired. The images were analysed with Image J for percentage coverage. The errors on the image analysis were estimated using printed percentage coverage sheets (Dorado 1989). After one years exposure the coated coupons were removed. The coatings were removed to manufacturers' recommendations. Any residues after coating removal were analysed with multiple reflection FTIR spectroscopy (Perkin Elmer 2000 with Amplif-IR, with mirror set at 50 μ m for maximum sensitivity, taking into account the rough corroded surfaces present on some coupons). The mirror was set using an Acuity AR600-00125 laser displacement sensor. The coupons were then cathodically stripped with a Uniscan PG580 potentiostat in a solution of 7.5% sodium hydroxide, 2.5 % sodium sulfate and 7.5% sodium carbonate (ASTM G1 1999). Additional analysis was undertaken on the Renaissance Wax coating, before removal and stripping. The non corroded areas were analysed with a Nicolet Inspect IR microscope in direct reflection and Germanium ATR mode. Fifteen 0.1mm areas were analysed. The direct reflection mode, bounces the collimated IR beam off the metal surface, whereas the Germanium ATR is extremely surface sensitive, due to the high refractive index of Germanium.

The best three performing coatings were applied to two-year exposed coupons to test their performance on uncleaned steel. After a year the amount of additional corrosion was determined and compared to a second three-year corroded control coupon, exposed simultaneously, with the method described above.

Reversibility

Each material was applied to a gold coated glass microscope slide. The slides were aged in a closed glass vessel at 60°C and approximately 100% RH for 28 days. Two millilitres of 18.2M Ω cm water was added to the 50ml vessel. After aging the coatings were removed from the slides and the slides dried above dry silica gel. The slide surface was then analysed with multiple reflection FTIR spectroscopy, with the mirror set at 5 μ m for maximum sensitivity. The method was roughly calibrated for shield. The percentage solids was calculated by drying 20ml of shield as supplied and weighing on a six figure balance. Sequential dilutions were carried out to deposit different amounts of shield onto gold coated glass microscope slides. The calculated amounts were 0.1-100 μ g per cm². A linear calibration was obtained

plotting the peak height at 684cm^{-1} against the calculated amount. The detection limit was estimated at $0.01\mu\text{g per cm}^2$.

Chloride Resistance

The chloride resistance of each coating was tested by applying it to a chloride specific ion electrode and immersing the electrode in 1M sodium chloride solution. The meter was connected to an SR007 data-logger which recorded the reading every minute. The meter and electrode were calibrated with 10 to 10000ppm sodium chloride solutions. The resistance was assessed as the number of hours required to reach 100ppm chloride. This value was selected as research with carbon steels has shown this level to affect the electrochemical behaviour (Deyab and Keera 2012). The Renaissance wax was tested last, taking account of the reversibility results.

Effects on associated materials.

The materials associated with the steel components of the repeater units were found to be; copper, zinc, cadmium, polyethylene, polyvinyl chloride, glass and paper. Metal sheet was acquired along with plastic samples and Whatman number 1 filter paper, details are shown in Table 2. The best performing inhibitor, Shield, was applied to one half of approximately 20 by 10mm pieces of each material. All materials, except paper were exposed to sealed aging at 60°C and approximately 100% RH for twenty eight days (Lee 1995). Paper was aged in duplicate at 110°C following the method developed by Strlic (Strlic et al 2010). After aging, the extent of metal corrosion was assessed visually, compared to the controls and then with scanning electron microscopy with energy dispersive x-ray analysis (Joel SEM with Cambridge ISIS detector and software) and reflectance FTIR set at $10\mu\text{m}$. The plastic and glass samples had the Shield removed with white spirit or sodium hydroxide solution, were dried above silica gel and analysed with FTIR-ATR. The degree of deterioration was assessed by the methods developed by Rhyll-Svedsen (Rhyll-Svedsen 2006), Thickett (Thickett 2012), PVC (Stomberg, Straus and Achhammer 1958). The FTIR spectrum of shield has adsorptions in some of the wavenumber regions utilised for the analysis. Additionally, the ATR method is very surface sensitive and no information may be acquired beyond a depth of approximately 1micron. The exact information depth depends on the wavelength of interest and the refractive index of Shield, which is not known. The Shield film thickness was approaching this value and it was thought best to remove the shield before analysis. Shield also contaminates the ATR plate and significant cleaning is required to remove all residues from it. The controls were treated similarly to detect any effects of the cleaning. The aged paper samples were analysed in triplicate with viscometry to determine the degree of polymerisation of the cellulose (Strlic et al 2010).

FTIR spectroscopy can provide information on the deterioration of natural rubbers. The spectrum of cis-1,4-polyisoprene shows absorption bands for cis alkene bonds at 830 cm^{-1} ($\delta_{\text{C=C}}$). As degradation and oxidation proceeds, absorptions appear for carbonyl bonds at 1720 cm^{-1} ($\nu_{\text{C=O}}$) and hydroperoxides at 3435 cm^{-1} ($\nu_{\text{O-H}}$). The CH_2 and CH_3 stretching bands at 1450 cm^{-1} were used as an internal reference. Rhyll Svendsen (2006) has used the CH_3 stretching bands at 2930 cm^{-1} as an internal reference. It was decided to keep the 1450 cm^{-1} reference band to make the results comparable with previous work, where this band was used as the 2930 cm^{-1} band is susceptible to the action of mould (Thickett and Richardsen 2008).

Similar methods have been developed for polyethylene (Thickett 2012) using absorptions at 1714 cm^{-1} and 1471 cm^{-1} and polyvinyl chloride using 1720 cm^{-1} and 1430 cm^{-1} (Stomberg, Straus and Achhammer 1958)

All FTIR of aged and unaged materials was undertaken on the cleaned samples using a Amplif-IR diamond ATR on a Perkin Elmer 2000 FTIR spectrometer.

Differential Scanning Calorimetry, DSC is a standard method to determine the degree of crystallinity of polymers (Thickett 2012). Small samples, approximately 30mg were analysed with a Shimadzu DSC50 with open aluminium crucibles under $60\text{ cm}^3/\text{min}$ of nitrogen, heating rate $10^\circ\text{C}/\text{min}$ to 250°C . This method also determines the glass transition temperature of polymers, which is essential to know for accelerated aging. Aging across the T_g (at a higher temperature) alters the structure of the polymer and can introduce reactions that won't occur at room temperature.

Results

In Situ Corrosion Protection Tests

Results from the image analysis are shown in Figure 5 and from the stripping in Figure 6.

There is a clear distinction between the performance of the inhibitors. The Shield, Wax/Oil and Waxoyl perform significantly better than any of the other materials. After 12 months the Shield appears to be better than Wax/Oil and Waxoyl, but the method errors are larger than the difference. Poligen ES91009 appears to perform slightly better than Poligen CE9 and Ship to Shore, but again the errors are too large to separate these three materials. The Renaissance wax is protective for the first three months, but after this period there is actually more corrosion on the coupon than on the untreated coupon, this is statistically significant after five months. The stripping results are in close agreement after 12 months. Neither Wax/Oil and Waxoyl or the two Poligenes can be separated statistically, although the Poligen ES91009 is now statistically better than Ship to Shore. As the image analysis only assesses the surface coverage, the stripping results are a better method, determining the loss of iron from the coupons and more weight should be given to them.

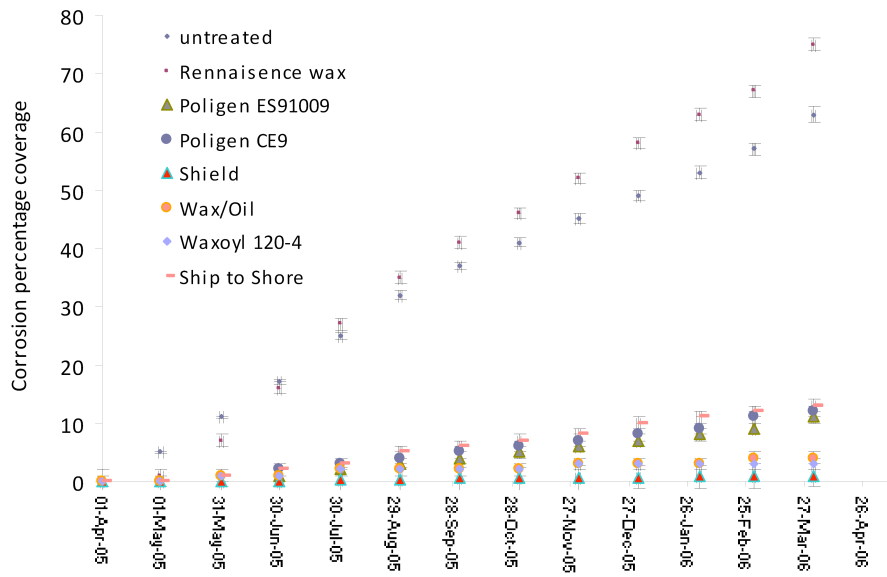


Figure 5: Percentage of surface area of treated coupons showing corrosion.

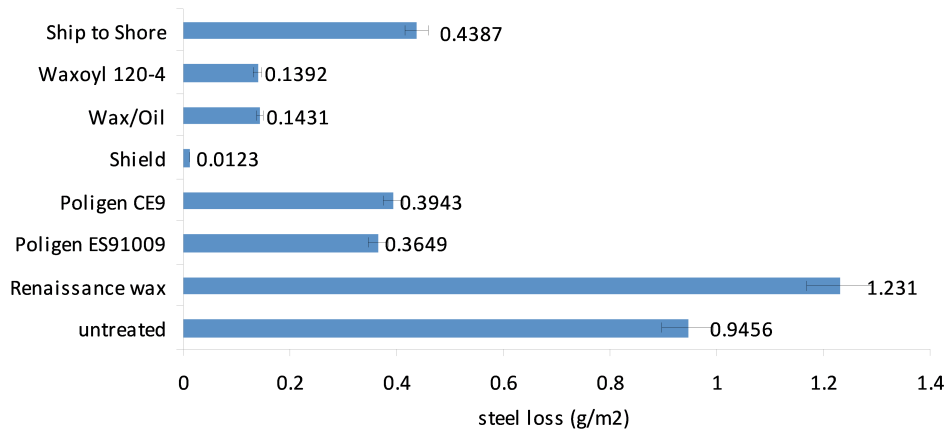


Figure 6: Metal loss from corrosion over 12 months of treated coupons

FTIR microscopy analysis indicated water trapped below the Renaissance Wax film. The direct reflection spectra showed strong absorptions at 1634cm^{-1} , which was absent in the Germanium head spectra, indicating the water was below the film.

Results from the pre-corroded tests are shown in Figure 7.

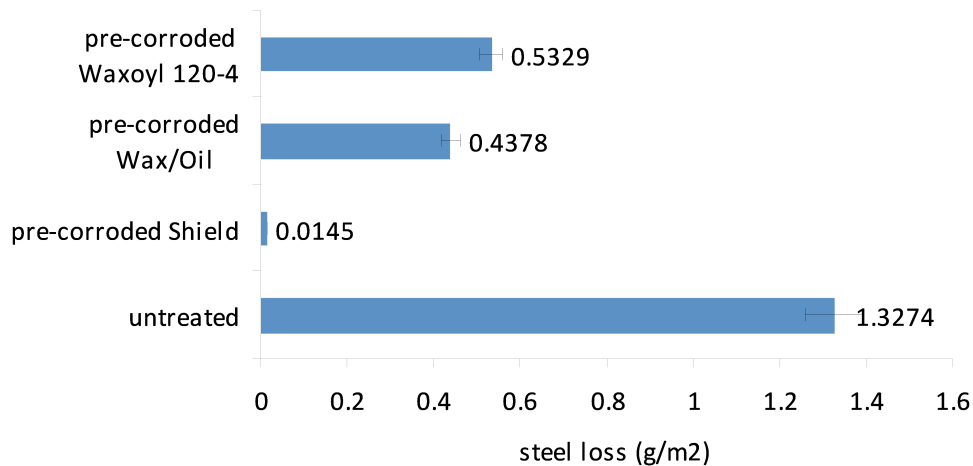


Figure 7: Metal loss from corrosion over 12 months of treated pre-corroded coupons.

The corrosion rate of the untreated steel has actually increased. Again Shield performs very well. In these test the Wax/Oil performs better than Waxoyl and this is statistically significant. The Wax/Oil appeared to have a lower viscosity, which perhaps explains the difference.

Reversibility

With the exception of Renaissance Wax, all the materials where cleaned successfully with white spirit, Table 3. A polyethylene wax residue was left with Renaissance Wax.

Chloride Resistance

The time taken to reach 100ppm reading for chloride under the inhibitor is included in Table 3. Results follow the same trend as the in situ corrosion tests. The manufacturers' information for shield states that it resists salt spray tests for 100 hours, which is consistent with the value found here. These tests were stopped after seven days. Previous time of wetness

measurements showed this rarely occurred continuously for periods longer than seven days (Thickett 2008). Renaissance wax showed rapid break-through of chloride ions.

Effects on associated materials.

The three metals tested showed no visible extra corrosion beyond that of the controls. Analysis with SEM-EDX indicated only oxygen present on the surface. Reflectance FTIR indicated cuprite present on the copper and zinc oxide on the zinc, while no spectra were obtained from the cadmium surface. No significant changes were observed in the carbonyl ratios or degree of crystallinity for the polymers. For context, for rubber a ratio figure of 0.45 has been found to mark the limit of acceptability for display (Thickett and Richardsen 2008). The value 0.23 is significantly under this figure. Although the figure has increased marginally on aging with Shield, the increase is not statistically significant. Even if there is a real increase, the magnitude is such that many decades would be required to reach the limit of acceptability. Also the DP of Whatman's number 1 filter paper did not drop below that of the control. These results indicate that the Shield after 28 days of accelerated aging had no discernible effect on the materials tested. Very slight increases in degradation rates may have occurred masked by the errors in the techniques used, but the high temperatures used for accelerated aging would mean these effects would not be apparent for many decades and the materials performs at least as well as many common conservation materials (Horie 2012).

Discussion and Conclusions

The in situ testing showed obvious discrimination between almost all the different products. Arrow Shield provided the best level of protection against corrosion and showed no discernible negative effects on materials present around the steel units. The combination of tests on clean and corroded steel coupons distinguished between the performance of Wax/oil and Waxyol. The performance of Poligen ES91009 and CE9 could not be discriminated, which reinforces the manufacturers suggestion as CE9 as a replacement for the experimental ES91009. Renaissance wax was protective for three months, but the corrosion rate under the wax was actually faster than the untreated steel after five months. This may be related to water being trapped under the wax, increasing the time of wetness. The wax was also found not to be fully reversible in white spirit, its most common solvent used in conservation.

An important aspect of the use of corrosion protection for this application is the level to which iron corrosion needs to be removed before application. The large areas of intricate metalwork would be extremely time consuming to clean. The low viscous liquid nature of some materials allows them to penetrate the corrosion products and potentially provide protection of the uncleaned metal. Tests with pre-corroded steel coupons using coupons from assessment of the corrosion rate in the tunnels were also undertaken.

The inhibitor is now used within a series of preventive conservation measures to manage the corrosion rate of this large, complex assemblage in its extremely aggressive environment. Smart ventilation was introduced into these tunnels in 2011. The tour route has been designed so the repeater station is the last main space visited and the visitor circulation space is large, reducing turbulence. Dust has been observed to decrease throughout tour routes and sharp turns were also observed to increase dust deposition (Lloyd et al 2002). There is only a single door to the repeater station, so visitors must turn, but the large area for this is thought to decrease dust. The staffing for cleaning both the tour routes and objects has been doubled.

Tables

Table 1: Inhibitor Materials Tested

Material	Composition	Solvent	Supplier
Renaissance wax	100 g Cosmoloid H80. 25 g polyethylene wax, 300 mL hydrocarbon solvent	White spirit	Preservation Equipment, Vinces Road, Diss, Norfolk, IP224HQ, UK
Poligen ES91009	Polyethylene Wax, surfactant, water	Sodium hydroxide solution	BASF Aktiengesellschaft Carl-BoschStr.38, 67056 Ludwigschafen, Germany
Poligen CE9	Polyethylene Wax, surfactant, water	Sodium hydroxide solution	As above
Shield A056	Oxidised waxes, inhibitors in hydrocarbons	White spirit	Arrow Solutions, Rawdon Road, Moira, Swadlincote, Derbyshire, DE126DA, UK
Wax/Oil	Calcium soap of oxidised wax, butyl alcohol, petroleum distillates	White spirit	Tetrosyl Limited Bevis Green, Bury, Lancashire BL9 6RE, UK
Waxoyl 120-4	Oxidised wax	White spirit	Waxoyl AG. Oberwilerstrasse 98 4015 Basel, Switzerland
Ship to Shore	Unknown, water	Sodium hydroxide solution	Ship-2-Shore, Box 48205, Victoria, BC V8Z 7H6, Canada

Table 2: Associated materials on which Shield was tested

Material	Notes	Supplier
Copper	99.9% 0.075mm foil CU000542	Goodfellows Cambridge Ltd
Zinc	99.7% 0.5mm foil ZN000311	Goodfellows Cambridge Ltd
Cadmium	99.9% 0.2mm foil CD000239	Goodfellows Cambridge Ltd
Polyethylene		Stewart Limited
Polyvinyl chloride	unplasticized	Solvay Chemicals
Natural Rubber		Morten Rhyll-Svendsen
Whatmans number 1 filter paper		Whatman Maidstone

Table 3: Residues detected after removal and chloride resistance test results

Material	Residue detected with FTIR	Identification	Time to 100ppm chloride (mins)
Renaissance wax	Y	Polyethylene wax	27
Poligen ES91009	N		2603
Poligen CE9	N		2743
Shield	N		>10080
Wax Oil	N		3254
Waxoyl	N		3376
Ship to Shore	N		2095

Effect on	Control	Shield
Copper	Slight darkening of surface	Slight darkening of surface
Zinc	Slight darkening of surface	Slight darkening of surface
Cadmium	No visible difference	No visible difference
Rubber carbonyl ratio	0.21 ± 0.02	0.24 ± 0.02
Polyethylene carbonyl ratio	0.017 ± 0.005	0.016 ± 0.005
Polyethylene degree of crystallinity	29.3 ± 0.82	29.6 ± 0.81
Polyvinyl chloride carbonyl ratio	0.006 ± 0.002	0.007 ± 0.002
Polyvinyl chloride degree of crystallinity	8.4 ± 0.92	8.0 ± 0.92
Paper (DP)	1643 ± 57	1603 ± 57

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